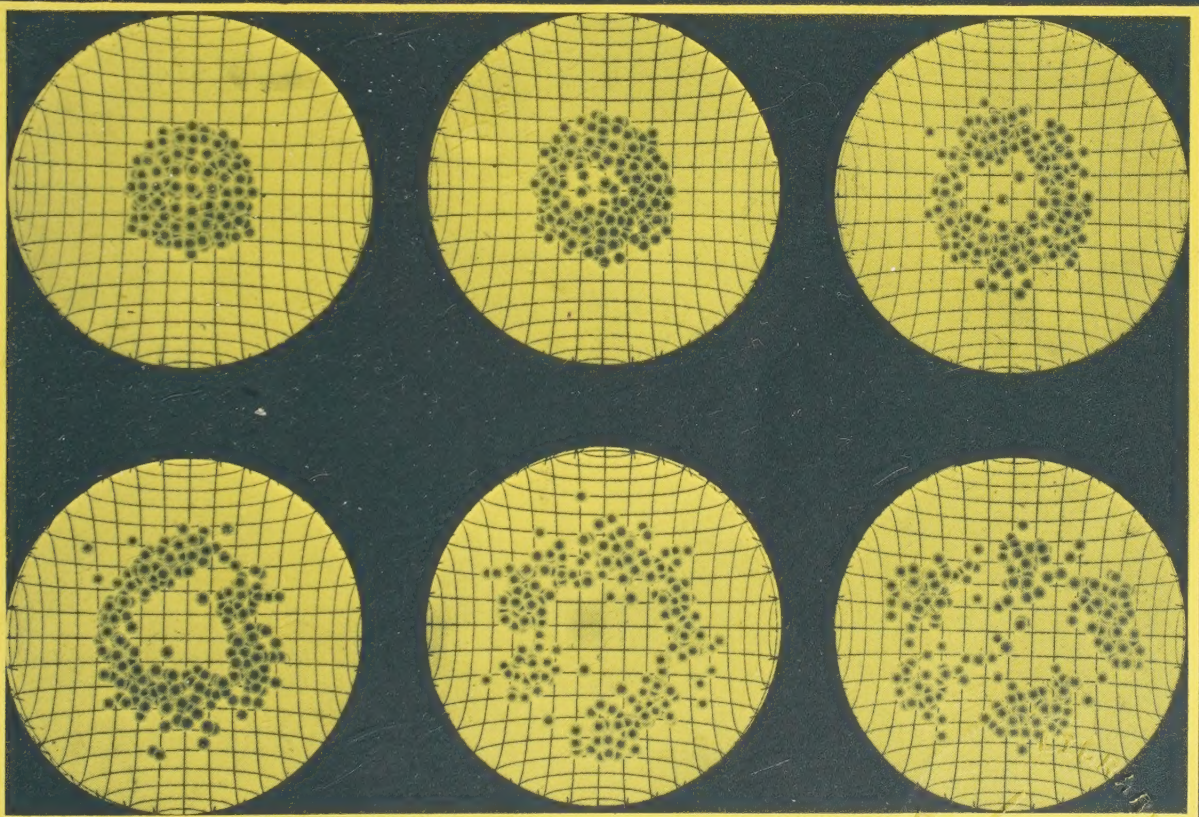


Solutions Manual to Accompany

PHYSICAL CHEMISTRY

Third Edition



Ira N. Levine

LIBRARY
CHC
CHEN



Digitized by the Internet Archive
in 2023



https://archive.org/details/isbn_0070374759

Solutions Manual
to Accompany

PHYSICAL CHEMISTRY

Third Edition

IRA N. LEVINE

Chemistry Department
Brooklyn College
City University of New York
Brooklyn, New York

McGraw-Hill Book Company

New York St. Louis San Francisco Auckland Bogotá Caracas
Colorado Springs Hamburg Lisbon London Madrid Mexico
Milan Montreal New Delhi Oklahoma City Panama Paris
San Juan São Paulo Singapore Sydney Tokyo Toronto

Solutions Manual to Accompany
PHYSICAL CHEMISTRY
Third Edition

Copyright ©1988 by McGraw-Hill, Inc. All rights reserved.
Printed in the United States of America. The contents, or
parts thereof, may be reproduced for use with

PHYSICAL CHEMISTRY
Third Edition
by Ira N. Levine

provided such reproductions bear copyright notice, but may not
be reproduced in any form for any other purpose without
permission of the publisher.

0-07-037475-9

2 3 4 5 6 7 8 9 0 W H T W H T 8 9 3 2 1 0 9 8

To the Student

The purpose of this solutions manual is to help you learn physical chemistry. This purpose will be defeated if you use this manual to avoid working homework problems. You cannot learn how to play the guitar solely by reading books titled "How to Play the Guitar" or by watching other people play the guitar. Rather, most of your time is best spent actually practicing the guitar. Likewise, you won't learn how to solve physical chemistry problems solely by reading through the solutions in this manual. Rather, most of your time is best spent actually working problems.

Do not look up the solution to a problem until you have made a substantial effort to work the problem on your own. When you work a problem, you learn a lot more than when you only read the solution. You can learn a lot by working on a problem even if you don't succeed in solving it. True learning requires active participation on your part. After you have looked up the solution to a problem you could not solve, close the solutions manual and work through the problem on your own.

Use the solutions manual as an incentive to work problems, not as a way to avoid working problems.

Ira N. Levine

Before using this manual, please read the preceding note
To the Student.

CHAPTER 1

1.1 (a) Closed, nonisolated; (b) open, nonisolated;
(c) open; nonisolated.

1.2 Three: solid AgBr, solid AgCl, and the solution.

$$\text{1.3 (a)} \quad 19.3 \frac{\text{g}}{\text{cm}^3} \frac{1 \text{ kg}}{1000 \text{ g}} \frac{(100 \text{ cm})^3}{(1 \text{ m})^3} = 19300 \text{ kg/m}^3$$

$$\text{(b)} \quad \frac{\$500}{\text{troy oz}} \frac{1 \text{ troy oz}}{480 \text{ grains}} \frac{7000 \text{ grains}}{1 \text{ pound}} \frac{1 \text{ pound}}{453.59 \text{ g}} = \$16.1/\text{g}$$

$$m = \rho V = (19.3 \text{ g/cm}^3)(10^6 \text{ cm}^3) = 1.93 \times 10^7 \text{ g}$$

$$(1.93 \times 10^7 \text{ g})(\$16.1/\text{g}) = \$3.10 \times 10^8$$

1.4 So that pressure or composition differences between systems A and B won't cause changes in the properties of A and B. Such changes can then result only from a temperature difference between A and B.

1.5 100 g of solution contains 12.0 g of HCl and 88.0 g of water. $n_{\text{HCl}} = (12.0 \text{ g})(1 \text{ mol}/36.46 \text{ g}) = 0.329 \text{ mol}$;

$$n_{\text{H}_2\text{O}} = (88.0 \text{ g})(1 \text{ mol}/18.015 \text{ g}) = 4.88_5 \text{ g. } x_{\text{HCl}} = 0.329/(0.329 + 4.88_5) = 0.0631; x_{\text{H}_2\text{O}} = 1 - x_{\text{HCl}} = 0.9369.$$

$$\text{1.6 (a)} \quad \frac{12.0 \text{ g/mol}}{6.022 \times 10^{23} \text{ atoms/mol}} = 1.99 \times 10^{-23} \text{ g/atom}$$

$$(b) \frac{18.0 \text{ g/mol}}{6.022 \times 10^{23} \text{ molecules/mol}} = 2.99 \times 10^{-23} \text{ g/molecule}$$

$$1.7 (a) P = \rho_{\text{Hg}} g h_{\text{Hg}} = \rho_{\text{H}_2\text{O}} g h_{\text{H}_2\text{O}}, \text{ so } \rho_{\text{Hg}} h_{\text{Hg}} = \rho_{\text{H}_2\text{O}} h_{\text{H}_2\text{O}}.$$

$$h_{\text{H}_2\text{O}} = \frac{(13.53 \text{ g/cm}^3)(30.0 \text{ in.})}{0.997 \text{ g/cm}^3} = 407 \text{ in.} = 33.9 \text{ ft}$$

(b) Use of $P = \rho g h$ and Eq. (2.8) gives P as

$$(13.53 \text{ g/cm}^3)(978 \text{ cm/s}^2)(30.0 \times 2.54 \text{ cm}) \frac{1 \text{ atm}}{1013250 \text{ dyn/cm}^2} \\ = 0.995 \text{ atm}$$

1.8 For m constant, n is constant, so (1.18) becomes $PV/T = nR = \text{const}$, which is (1.17).

$$1.9 (a) n = (24.0 \text{ g})(1 \text{ mol}/44.0 \text{ g}) = 0.545 \text{ mol}. P = nRT/V \\ = (0.545 \text{ mol})(82.06 \text{ cm}^3\text{-atm/mol-K})(273.1 \text{ K})/(5000 \text{ cm}^3) \\ = 2.44 \text{ atm. (b) } V = nRT/P = (1 \text{ mol})(82.06 \text{ cm}^3\text{-atm/mol-K}) \times \\ (298 \text{ K})/(1 \text{ atm}) = 24500 \text{ cm}^3. \text{ One ft}^3 = (12 \text{ in.})^3 = \\ (12 \times 2.54 \text{ cm})^3 = 28300 \text{ cm}^3. \text{ Percent error} = \\ [(28300 - 24500)/24500] \times 100\% = 16\%$$

1.10 $P = nRT/V = mRT/MV$, so $M = mRT/PV$ and

$$M = \frac{(0.0200 \text{ g})(82.06 \text{ cm}^3\text{-atm/mol-K})(298.1 \text{ K})}{(24.7/760) \text{ atm} (500 \text{ cm}^3)} = 30.1 \text{ g/mol}$$

The only hydrocarbon with molecular weight 30 is C_2H_6 .

1.11 At this T and P, N_2 is a gas that behaves nearly ideally. From $PV = nRT = (m/M)RT$, we get $m/V = PM/RT$, so

$$\rho = \frac{PM}{RT} = \frac{[(725/760) \text{ atm}](28.01 \text{ g/mol})}{(82.06 \text{ cm}^3\text{-atm/mol-K})(293 \text{ K})} = 0.00111 \text{ g/cm}^3$$

since $0.967 \text{ bar} = 0.967(750 \text{ torr}) = 725 \text{ torr}$.

1.12 Use of $P_1V_1/T_1 = P_2V_2/T_2$ gives $P_2 = (V_1/V_2)(T_2/T_1)P_1 = (V_1/2V_1)(3T_1/T_1)P_1 = 1.5P_1 = 1.5(0.600 \text{ bar}) = 0.900 \text{ bar}$.

<u>1.13</u>	PV/nT	82.025	81.948	81.880	$\text{cm}^3\text{-atm/mol-K}$
	P	1.0000	3.0000	5.0000	atm

Plotting these data and extrapolating to $P = 0$, we find

$$\lim_{P \rightarrow 0} (PV/nT) = 82.06_5 \text{ cm}^3\text{-atm/mol-K}.$$

1.14 The P/ρ values are 715.3, 706.2, and 697.1 $\text{cm}^3 \text{ atm/g}$.

A plot of P/ρ vs. P is a straight line with intercept $721.5 \text{ cm}^3 \text{ atm/g}$. We have $PV = mRT/M$, so $M = RT/(P/\rho)$, and

$$M = \frac{-(82.06 \text{ cm}^3\text{-atm/mol-K})(273.15 \text{ K})}{721.5 \text{ cm}^3 \text{ atm/g}} = 31.0_7 \text{ g/mol}$$

The only amine with molecular weight 31 is CH_3NH_2 .

1.15 Use of $n_{\text{tot}} = PV/RT$ gives

$$n_{\text{tot}} = \frac{(4.85 \times 10^6 \text{ Pa})[1600 (10^{-2} \text{ m})^3]}{(8.314 \text{ m}^3\text{-Pa/mol-K})(500 \text{ K})} = 1.867 \text{ mol}$$

The reaction is $2\text{NH}_3 \rightleftharpoons \text{N}_2 + 3\text{H}_2$. Let x moles of N_2 be formed. The numbers of moles of NH_3 , N_2 , and H_2 present at equilibrium are $1.60 - 2x$, x, and $3x$, respectively. Thus

$n_{\text{tot}}/\text{mol} = 1.60 - 2x + x + 3x = 1.867$, and $x = 0.13_3$. Then

$$n(\text{N}_2) = 0.13_3 \text{ mol}, \quad n(\text{H}_2) = 0.40_0 \text{ mol}, \quad n(\text{NH}_3) = 1.33 \text{ mol}$$

1.16 Boyle's law and Charles' law apply under different conditions (constant T, m vs. constant P, m); such equations cannot be combined.

1.17 Consider the processes

$$(P_1, V_1, T_1, m_1) \xrightarrow{a} (P_1, V_a, T_1, m_2) \xrightarrow{b} (P_2, V_2, T_2, m_2)$$

For step (a), P and T are constant, so $V_1/m_1 = V_a/m_2$. For

step (b), m is constant, so $P_1 V_a/T_1 = P_2 V_2/T_2$. Substitution for V_a in this last equation gives $P_2 V_2/T_2 =$

$$P_1 V_1 m_2/T_1 m_1 \text{ or } P_2 V_2/m_2 T_2 = P_1 V_1/m_1 T_1.$$

1.18 $P_i = x_i P.$ $n_{\text{CO}_2} = (30.0 \text{ g})(1 \text{ mol}/44.0 \text{ g}) = 0.682$

mol. $n_{\text{O}_2} = 0.625 \text{ mol.}$ $x_{\text{CO}_2} = 0.682/(0.682 + 0.625) =$

$0.522.$ $P_{\text{CO}_2} = 0.522(3450 \text{ kPa}) = 1800 \text{ kPa.}$

1.19 (a) At constant temperature, $P_2 = P_1 V_1/V_2$ for each gas. Therefore

$$P_{\text{H}_2} = \frac{(20.0 \text{ kPa})(3.00 \text{ L})}{4.00 \text{ L}}$$

$$P_{\text{CH}_4} = \frac{(10.0 \text{ kPa})(1.00 \text{ L})}{4.00 \text{ L}}$$

$$P_{\text{H}_2} = 15.0 \text{ kPa}$$

$$P_{\text{CH}_4} = 2.5 \text{ kPa}$$

$$P_{\text{tot}} = 15.0 \text{ kPa} + 2.5 \text{ kPa} = 17.5 \text{ kPa}$$

(b) $P_i = n_i RT/V$ and $P_{\text{tot}} = n_{\text{tot}} RT/V$. Hence $P_i/P_{\text{tot}} =$

$n_i/n_{\text{tot}} = x_i$. We get $x_{\text{H}_2} = 15.0 \text{ kPa}/17.5 \text{ kPa} = 0.857$ and

$x_{\text{CH}_4} = 2.5 \text{ kPa}/17.5 \text{ kPa} = 0.143.$

1.20 $P(O_2) = 751 \text{ torr} - 21 \text{ torr} = 730 \text{ torr}$. The equation

$P_1 V_1 / T_1 = P_2 V_2 / T_2$ gives $V_2 = V_1 P_1 T_2 / P_2 T_1$ and

$$V_2 = \frac{(36.5 \text{ cm}^3)(730 \text{ torr})(273 \text{ K})}{(760 \text{ torr})(296 \text{ K})} = 32.3 \text{ cm}^3$$

1.21 When a steady state is reached, the pressures in the two bulbs are equal. From $P_1 = P_2$, we get $n_1 RT_1 / V_1 = n_2 RT_2 / V_2$. Since $V_1 = V_2$, we have $n_1 T_1 = n_2 T_2$. Thus $n_1 (200 \text{ K}) = (1.00 \text{ mol} - n_1)(300 \text{ K})$; solving, we get $n_1 = 0.60 \text{ mole}$ in the 200-K bulb and $n_2 = 0.40 \text{ mole}$ in the 300-K bulb.

1.22 We have $PV = nRT = NRT/N_A$, so $N/V = PN_A/RT$ and

$$\frac{N}{V} = \frac{(6.02 \times 10^{23} \text{ mol}^{-1}) P}{(82.06 \text{ cm}^3\text{-atm/mol-K})(298 \text{ K})} = 2.46 \times 10^{19} \text{ cm}^{-3} \frac{P}{\text{atm}}$$

(a) For $P = 1 \text{ atm}$, we get $N/V = 2.5 \times 10^{19} \text{ cm}^{-3}$; (b) for $P = (1/760)10^{-6} \text{ atm}$, we get $N/V = 3.2 \times 10^{10} \text{ cm}^{-3}$; (c) for $P = (1/760)10^{-11} \text{ atm}$, $N/V = 3.2 \times 10^5 \text{ cm}^{-3}$.

1.23 Substitution in $PV = n_{\text{tot}} RT$ gives $n_{\text{tot}} = 0.01456 \text{ mol}$.

Also

$$m_{\text{tot}} = m_1 + m_2 = n_1 M_1 + n_2 M_2 = 0.1480 \text{ g} =$$

$$n_{\text{He}} (4.003 \text{ g/mol}) + (0.01456 \text{ mol} - n_{\text{He}})(20.18 \text{ g/mol})$$

$$n_{\text{He}} = 0.00902 \text{ mol}, \quad n_{\text{Ne}} = 0.00554 \text{ mol}$$

$$x_{\text{He}} = 0.00902/0.01456 = 0.619, \quad m_{\text{He}} = 0.0361 \text{ g}$$

1.24 The system pressure is less than the barometric pressure by $304.3 \text{ torr} - 202.1 \text{ torr} = 102.2 \text{ torr}$. Hence

$$P_{\text{system}} = 754.6 \text{ torr} - 102.2 \text{ torr} = 652.4 \text{ torr}.$$

1.25 The downward force of the atmosphere on the earth's surface equals the weight W of the atmosphere, so $P = W/A = mg/A$ and $m = AP/g = 4\pi r^2 P/g$, where r is the earth's radius and $P = 1 \text{ atm} = 1.01325 \times 10^6 \text{ dyn/cm}^2$. Thus

$$m = \frac{4\pi(6.37 \times 10^8 \text{ cm})^2(1.013 \times 10^6 \text{ dyn/cm}^2)}{980.7 \text{ cm/s}^2} = 5.3 \times 10^{21} \text{ g}$$

1.26 (a) Multiplication of both sides of the equation by 10^{-5} bar gives $P = 6.4 \times 10^{-5} \text{ bar}$. (b) 460 K .

1.27 Let O_2 be gas 1. We have $\rho = (m_1 + m_2)/V$. The ideal-gas law gives $PV = (n_1 + n_2)RT = (m_1/M_1 + m_2/M_2)RT$, so

$$\frac{P}{RT} = \frac{m_1/V}{M_1} + \frac{m_2/V}{M_2} = \frac{m_1/V}{M_1} + \frac{\rho - m_1/V}{M_2}$$

$$\frac{m_1}{V} = \left(\frac{PM_1M_2}{RT} - \rho M_1 \right) \frac{1}{M_2 - M_1}$$

Converting ρ to $1.185 \times 10^{-3} \text{ g/cm}^3$ and P to 1.000 atm , and substituting numerical values, one finds

$$m_1/V = 3.20 \times 10^{-4} \text{ g/cm}^3$$

$$m_2/V = \rho - m_1/V = 8.65 \times 10^{-4} \text{ g/cm}^3$$

$$\frac{n_1}{V} = \frac{3.20 \times 10^{-4} \text{ g/cm}^3}{32.00 \text{ g/mol}} = 1.00 \times 10^{-5} \text{ mol/cm}^3$$

$$\frac{n_2}{V} = \frac{8.65 \times 10^{-4} \text{ g/cm}^3}{28.01 \text{ g/mol}} = 3.09 \times 10^{-5} \text{ mol/cm}^3$$

$$x_1 = n_1/(n_1 + n_2) = (n_1/V)/(n_1/V + n_2/V) = 0.244$$

1.28 (a) Use of $P_i = x_i P$ gives $P_{N_2} = 0.78(1.00 \text{ atm}) = 0.78 \text{ atm}$, $P_{O_2} = 0.21 \text{ atm}$, $P_{Ar} = 0.0093 \text{ atm}$, $P_{CO_2} = 0.0003 \text{ atm}$. (b) $V = 3000 \text{ ft}^3$. $1 \text{ ft} = 12 \text{ in.} = 12 \times 2.54 \text{ cm} = 30.48 \text{ cm}$. $V = (3000 \text{ ft}^3)(30.48 \text{ cm})^3/\text{ft}^3 = 8.5 \times 10^7 \text{ cm}^3$. $n_{\text{tot}} = PV/RT = [(740/760) \text{ atm}](8.5 \times 10^7 \text{ cm}^3)/[(82.06 \text{ cm}^3\text{-atm/mol-K})(293 \text{ K})] = 3.4_4 \times 10^3 \text{ mol}$. $n_{N_2} = x_{N_2} n_{\text{tot}} = 0.78(3.4_4 \times 10^3 \text{ mol}) = 2.6_8 \times 10^3 \text{ mol}$. $m_{N_2} = (2680 \text{ mol})(28.0 \text{ g/mol}) = 75 \text{ kg}$. Similarly, $m_{O_2} = 23 \text{ kg}$, $m_{Ar} = 1.3 \text{ kg}$, $m_{CO_2} = 4.5 \times 10^1 \text{ g}$. We have $\rho = m_{\text{tot}}/V = (99.3 \text{ kg})/(8.5 \times 10^7 \text{ cm}^3) = 0.00117 \text{ g/cm}^3$.

1.29 $dy/dx = 2x + 1$. At $x = 1$, the slope is $2(1) + 1 = 3$.

1.30 (a) $6x^2e^{-3x} - 6x^3e^{-3x}$; (b) $-30xe^{-3x^2}$; (c) $1/x$ (not $1/2x$); (d) $1/(x+1) - x/(x+1)^2$; (e) $e^{-x}/(1 - e^{-x})$; (f) Solving for y , we get $y = 2/(1 - x)$, so $dy/dx = 2/(1 - x)^2$. (g) $d(x^2e^{3x})/dx = 2xe^{3x} + 3x^2e^{3x}$; $d^2(x^2e^{3x})/dx = 2e^{3x} + 6xe^{3x} + 6xe^{3x} + 9x^2e^{3x} = 2e^{3x} + 12xe^{3x} + 9x^2e^{3x}$; (h) $dy = 2ax \, dx + b \, dx$.

1.31 (a)

x	0.1	0.01	0.001	0.0001	0.00001
x^x	0.794	0.955	0.9931	0.9991	0.99988

This indicates (but does not prove) that the limit is 1.

(b)	x	10^{-3}	-10^{-3}	10^{-4}	-10^{-4}	10^{-5}	-10^{-5}
	$(1+x)^{1/x}$	2.717	2.720	2.7181	2.7184	2.71827	2.71828

This suggests that the limit is $e = 2.7182818\dots$

1.32 (a) Results on a calculator with 8-digit display and 11 internal digits are: $\Delta y/\Delta x = 277, 223.4, 218.88, 218.44, 218.398, 218.393, 218.4$ for $\Delta x = 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6}, 10^{-7}$, respectively. The best estimate is 218.393. (b) $dy/dx = 2xe^{x^2}$, and at $x = 2$, $dy/dx = 218.3926$. A BASIC program for part (a) is

```

5 CX = .1
10 FOR N = 1 TO 7
20 X = 2
30 CY = EXP((X + CX)^2) - EXP(X^2)
40 R = CY/CX
50 PRINT "DELTA X=";CX;
   "RATIO=";R
60 CX = CX/10
70 NEXT N
80 END

```

1.33 (a) $ax \cos(axy)$; (b) $-2byz \sin(by^2z)$; (c) $-(x^2/y^2)e^{x/y}$; (d) 0; (e) $-ae^{-a/y/y^2}(e^{-a/y} + 1)^2$.

1.34 Equation (1.30) gives $dz = 2axy^3 dx + 3ax^2y^2 dy$.

1.35 Partial differentiation of $z = x^5/y^3$ gives

$$\frac{\partial z}{\partial x} = \frac{5x^4}{y^3}, \quad \frac{\partial^2 z}{\partial x^2} = \frac{20x^3}{y^3}, \quad \frac{\partial z}{\partial y} = -\frac{3x^5}{y^4}, \quad \frac{\partial^2 z}{\partial y^2} = \frac{12x^5}{y^5}$$

$$\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial}{\partial x} \left(-\frac{3x^5}{y^4} \right) = -\frac{15x^4}{y^4}, \quad \frac{\partial^2 z}{\partial y \partial x} = \frac{\partial}{\partial y} \frac{5x^4}{y^3} = -\frac{15x^4}{y^4} = \frac{\partial^2 z}{\partial x \partial y}$$

1.36 (a) P is a function of n , T , and V , so $dP = (\partial P/\partial n)_{T,V} dn + (\partial P/\partial T)_{V,n} dT + (\partial P/\partial V)_{T,n} dV$. Partial differentiation of $P = nRT/V$ gives $(\partial P/\partial n)_{T,V} = RT/V =$

P/n (where $PV = nRT$ was used), $(\partial P/\partial T)_{V,n} = nR/V = P/T$, and $(\partial P/\partial V)_{T,n} = -nRT/V^2 = -P/V$. Substitution into the above equation for dP gives the desired result. (Note that from $P = nRT/V$, we have $\ln P = \ln n + \ln R + \ln T - \ln V$, from which $d \ln P = d \ln n + d \ln T - d \ln V$ follows at once.) (b) Approximating small changes by infinitesimal changes, we have $dn \approx \Delta n = 0$, $dT \approx \Delta T = 1.00 \text{ K}$, $dV \approx \Delta V = 50 \text{ cm}^3$. The original pressure is $P = nRT/V = 0.8206 \text{ atm}$. Then $\Delta P \approx dP \approx (0.8206 \text{ atm})[0 + (1.00 \text{ K})/(300 \text{ K}) - (50 \text{ cm}^3)/(30000 \text{ cm}^3)] = 0.00137 \text{ atm}$. (c) The accurate final pressure is $(1.0000 \text{ mol})(82.06 \text{ cm}^3\text{-atm/mol-K}) \times (301.00 \text{ K})/(30050 \text{ cm}^3) = 0.8219_7 \text{ atm}$. The accurate ΔP is $0.8219_7 \text{ atm} - 0.8206 \text{ atm} = 0.0013_7 \text{ atm}$.

1.37 $1.000 \text{ bar} = 750 \text{ torr} = (750 \text{ torr})(1 \text{ atm}/760 \text{ torr}) = 0.987 \text{ atm}$. $\bar{V} = V/n = (nRT/P)/n = RT/P = (82.06 \text{ cm}^3\text{-atm/mol-K})(293.1 \text{ K})/(0.987 \text{ atm}) = 2.44 \times 10^4 \text{ cm}^3/\text{mol}$.

1.38 (a) Division by n gives $(P + a/\bar{V}^2)(\bar{V} - b) = RT$. (b) The units of b are the same as those of \bar{V} , namely, cm^3/mol . P and a/\bar{V}^2 have the same units, so the units of a are $\text{bar} \cdot \text{cm}^6/\text{mol}^2$.

1.39 $\alpha = (1/\bar{V})(\partial \bar{V}/\partial T)_P = (1/\bar{V})(c_2 + 2c_3T - c_5P)$, where \bar{V} is given by (1.40). $\kappa = -(1/\bar{V})(\partial \bar{V}/\partial P)_T = -(1/\bar{V}) \times (-c_4 - c_5T) = (c_4 + c_5T)/(c_1 + c_2T + c_3T^2 - c_4P - c_5PT)$.

1.40 (a) $\rho = m/V = (m/n)/(V/n) = M/\bar{V}$, so $\bar{V} = M/\rho = (18.0153 \text{ g/mol})/(0.98804 \text{ g/cm}^3) = 18.233 \text{ cm}^3/\text{mol}$. (b) $\kappa = -(1/\bar{V})(\partial \bar{V}/\partial P)_T$ and $d\bar{V}/\bar{V} = -\kappa dP$ at constant T . Integrate-

tion gives $\ln(\bar{V}_2/\bar{V}_1) = -\kappa(P_2 - P_1)$ at constant T . We have $\kappa = (4.4 \times 10^{-10} \text{ Pa}^{-1})(101325 \text{ Pa}/1 \text{ atm}) = 4.4_6 \times 10^{-5} \text{ atm}^{-1}$ and $\ln[\bar{V}_2/(18.233 \text{ cm}^3/\text{mol})] = -(4.4_6 \times 10^{-5} \text{ atm}^{-1}) \times (100 \text{ atm} - 1 \text{ atm}) = -0.0044$, so $\bar{V}_2/(18.233 \text{ cm}^3/\text{mol}) = e^{-0.0044} = 0.9956$ and $\bar{V}_2 = 18.15 \text{ cm}^3/\text{mol}$.

1.41 We have $\ln \rho = \ln (m/V) = \ln m - \ln V$. Partial differentiation of this equation gives

$$\left(\frac{\partial \ln \rho}{\partial T} \right)_P = - \left(\frac{\partial \ln V}{\partial T} \right)_P = - \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = -\alpha$$

1.42 (a) At constant P , the equation $P\bar{V} = RT$ gives

$\bar{V} = aT$, where $a = R/P$ is a positive constant. The isobars on a \bar{V} - T diagram are straight lines that start at the origin and have positive slopes. (As P increases, the slope decreases.) (b) For \bar{V} constant, $P\bar{V} = RT$ gives $P = bT$, where $b = R/\bar{V}$ is constant. The isochores on a P - T diagram are straight lines that start at the origin and have positive slopes.

1.43 (a) Partial differentiation of $V = nRT(1 + aP)/P$ gives $(\partial V/\partial T)_{P,n} = nR(1 + aP)/P$. The equation of state gives $nR(1 + aP) = PV/T$, so $(\partial V/\partial T)_{P,n} = V/T$. Then $\alpha = (1/V)(\partial V/\partial T)_{P,n} = 1/T$. Partial differentiation of $V = nRT(1/P + a)$ gives $(\partial V/\partial P)_{T,n} = -nRT/P^2 = -[PV/(1 + aP)]/P^2 = -V/P(1 + aP)$, where the equation of state was used. Then $\kappa = -(1/V)(\partial V/\partial P)_T = 1/P(1 + aP)$. (b) Solving the equation of state for P , we get $P = nRT/(V - anRT)$; partial

differentiation gives $(\partial P/\partial T)_V = nR/(V - anRT) + an^2R^2T/(V - anRT)^2 = P/T + aP^2/T$, where $P = nRT/(V - anRT)$ was used. From (a), we have $\alpha/\kappa = P(1 + aP)/T = P/T + aP^2/T$, which agrees with Eq. (1.45).

1.44 For small ΔT , we have

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \approx \frac{1}{V} \left(\frac{\Delta V}{\Delta T} \right)_P$$

Since α is an intensive property, we can take any quantity of water. For 1 g, the equation $V = m/\rho$ gives

$$V = 1.002965 \text{ cm}^3 \text{ at } 25^\circ\text{C, 1 atm} \quad \text{and} \quad V = 1.003227 \text{ cm}^3 \text{ at } 26^\circ\text{C, 1 atm}$$

Hence

$$\alpha \approx \frac{1}{1.003 \text{ cm}^3} \frac{1.003227 \text{ cm}^3 - 1.002965 \text{ cm}^3}{26^\circ\text{C} - 25^\circ\text{C}} = 0.00026 \text{ K}^{-1}$$

Similarly, $\kappa = -(1/V)(\partial V/\partial P)_T \approx -(1/V)(\Delta V/\Delta P)_T$. At 25°C and 2 atm, we calculate $V = 1.002916 \text{ cm}^3$ for 1 g of water.

Thus

$$\kappa \approx - \frac{1}{1.003 \text{ cm}^3} \frac{1.002916 \text{ cm}^3 - 1.002965 \text{ cm}^3}{2 \text{ atm} - 1 \text{ atm}} = 4.9 \times 10^{-5} \text{ atm}^{-1}$$

$$\text{Eq. (1.45) gives } \left(\frac{\partial P}{\partial T} \right)_{\bar{V}} = \frac{\alpha}{\kappa} \approx \frac{2.6 \times 10^{-4} \text{ K}^{-1}}{4.9 \times 10^{-5} \text{ atm}^{-1}} = 5.3 \text{ atm/K}$$

1.45 Equation (1.45) gives $\alpha/\kappa = (\partial P/\partial T)_V \approx (\Delta P/\Delta T)_V$, so

$$\Delta P \approx \frac{\alpha}{\kappa} \Delta T = \frac{1.7 \times 10^{-4} \text{ K}^{-1}}{4.7 \times 10^{-5} \text{ atm}^{-1}} 6 \text{ K} = 22 \text{ atm}; \quad P \approx 23 \text{ atm}$$

1.46 (a) As P increases, the molecules are forced closer together; the decrease in empty space between the molecules makes it harder to compress the substance, and K is smaller. (b) Most substances expand as T increases. The increased space between molecules makes it easier to compress the substance, and K increases.

1.47 (a) $K = -(1/V)(\partial V/\partial P)_T \approx -(1/V)(\Delta V/\Delta P)_T$ and $\Delta P \approx -\Delta V/VK$ at constant T . For a 1% volume decrease, $\Delta V = -0.01V$ and we have $\Delta P \approx 0.01V/VK = 0.01/K = 0.01/(5 \times 10^{-6} \text{ atm}^{-1}) = 2000 \text{ atm}$. (b) $\Delta P \approx 0.01/K = 0.01/(1 \times 10^{-4} \text{ atm}^{-1}) = 100 \text{ atm}$.

1.48 (a) $\sum_{J=0}^4 (2J + 1) = (0 + 1) + (2 + 1) + (4 + 1) + (6 + 1) + (8 + 1) = 25$. (b) $\sum_{i=1}^S x_i V_i$. (c) $\sum_{i=1}^2 (b_{i4} + b_{i5} + b_{i6}) = b_{14} + b_{15} + b_{16} + b_{24} + b_{25} + b_{26}$.

1.49 $\sum_{i=1}^n ca_i = ca_1 + ca_2 + \dots + ca_n = c(a_1 + a_2 + \dots + a_n) = c \sum_{i=1}^n a_i$. Q.E.D. $\sum_{i=1}^n (a_i + b_i) = (a_1 + b_1) + (a_2 + b_2) + \dots + (a_n + b_n) = a_1 + a_2 + \dots + a_n + b_1 + b_2 + \dots + b_n = \sum_{i=1}^n a_i + \sum_{i=1}^n b_i$. Q.E.D. The left side of (1.51) is $\sum_{i=1}^n \sum_{j=1}^m a_i b_j = \sum_{i=1}^n (a_i b_1 + a_i b_2 + \dots + a_i b_m) = \sum_{i=1}^n a_i (b_1 + b_2 + \dots + b_m) = (\sum_{i=1}^n a_i)(b_1 + b_2 + \dots + b_m) = \sum_{i=1}^n a_i \sum_{j=1}^m b_j$, which is the right side of (1.51).

1.50 (a) $\int_3^{-2} (2V + 5V^2) dV = (V^2 + 5V^3/3)|_3^{-2} = (4 - 40/3) - (9 + 45) = -190/3$. (b) $\int_2^4 V^{-1} dV = \ln V|_2^4$

$$= \ln 4 - \ln 2 = \ln 2 = 0.693. \quad (\underline{c}) \int_1^{\infty} V^{-3} dV = -\frac{1}{2}V^{-2} \Big|_1^{\infty} = 0 - (-\frac{1}{2}) = \frac{1}{2}. \quad (\underline{d}) \text{ Let } z = x^3. \text{ Then } dz = 3x^2 dx \text{ and } \int_0^{\pi/2} x^2 \cos x^3 dx = (1/3) \int_0^{\pi^3/8} \cos z dz = (1/3) \sin z \Big|_0^{\pi^3/8} = (1/3)[\sin(\pi^3/8) - 0] = -0.2233.$$

1.51 (a) $-a^{-1} \cos ax + C$; (b) $-a^{-1} \cos ax \Big|_0^{\pi} = (1 - \cos a\pi)/a$; (c) differentiation of the answer to (b) gives $-a^{-2} + a^{-2} \cos a\pi + a^{-1}\pi \sin a\pi$.

1.52 In (b) and (c).

1.53 (a) $\int_2^3 x^2 dx \approx \sum_{i=1}^n x_i^2 \Delta x$. For $\Delta x = 0.1$ and x_i at the left end of each subinterval, $\sum_{i=1}^n x_i^2 \Delta x = 0.1[2^2 + (2.1)^2 + (2.2)^2 + \cdots + (2.9)^2] = 6.085$. For $\Delta x = 0.01$, we get 6.30835. For $\Delta x = 0.001$, we get 6.33083. The exact value is $(x^3/3) \Big|_2^3 = 27/3 - 8/3 = 6.33333\dots$. (b) $\int_0^1 e^{-x^2} dx \approx 0.01[e^{-0^2} + e^{-(0.01)^2} + e^{-(0.02)^2} + \cdots + e^{-(0.99)^2}] = 0.74998$. A BASIC program for part (a) is

```

10 N = 10          45 X = X + DX
15 FOR J = 1 TO 3   50 NEXT I
20 X = 2           55 PRINT "DELTAX="; DX; " SUM="; S
25 DX = 1/N        60 N = 10*N
30 S = 0           65 NEXT J
35 FOR I = 1 TO N   70 END
40 S = S + X*X*DX

```

1.54 (a) $\log(4.2 \times 10^{175}) = \log 4.2 + \log 10^{175} = 0.62 + 175 = 175.62$; (b) $\ln(6.0 \times 10^{-200}) = 2.3026 \times \log(6.0 \times 10^{-200}) = 2.3026 \log 6.0 + 2.3026 \log 10^{-200} = 1.79 - 460.52 = -458.73$. (c) $\log y = -138.265$; $y =$

$$10^{-138.265} = 10^{-0.265} 10^{-138} = 0.543 \times 10^{-138}. \quad (\underline{d}) \ln z = 260.433 = 2.3026 \log z; \log z = 113.10; z = 10^{0.10} 10^{113} = 1.2_6 \times 10^{113}.$$

1.55 (a) intensive; (b) extensive; (c) intensive; (d) intensive; (e) intensive; (f) intensive.

1.56 One finds that a plot of $P\bar{V}$ vs. P is approximately linear with an intercept of $P\bar{V} = 58.90 \text{ L atm/mol}$ at $P = 0$. The ideal-gas law $P\bar{V} = RT$ applies to O_2 in the limit of zero pressure, so

$$T = \lim_{P \rightarrow 0} \frac{P\bar{V}}{R} = \frac{58900 \text{ cm}^3\text{-atm/mol}}{82.06 \text{ cm}^3\text{-atm/mol-K}} = 717.8 \text{ K}$$

1.57 (a) T. (b) F. (c) F. (d) T. (e) F. (f) T. (g) T. (h) T. (i) F. (j) T.

CHAPTER 2

2.1 (a) $1 \text{ J} = 1 \text{ N m} = 1 \text{ kg m s}^{-2} \text{ m} = 1 \text{ kg m}^2 \text{ s}^{-2}$

(b) $1 \text{ Pa} = 1 \text{ N/m}^2 = 1 \text{ kg m s}^{-2} \text{ m}^{-2} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$

(c) $1 \text{ L} = 10^3 \text{ cm}^3 = 10^3 (10^{-2} \text{ m})^3 = 10^{-3} \text{ m}^3$

(d) $1 \text{ N} = 1 \text{ kg m s}^{-2}$ (e) $1 \text{ W} = 1 \text{ J/s} = 1 \text{ kg m}^2 \text{ s}^{-3}$

2.2 $1 \text{ N} = 1 \text{ kg m s}^{-2} = (10^3 \text{ g})(10^2 \text{ cm}) \text{ s}^{-2} = 10^5 \text{ dyn}$

$1 \text{ J} = 1 \text{ N m} = (10^5 \text{ dyn})(10^2 \text{ cm}) = 10^7 \text{ dyn cm} = 10^7 \text{ ergs}$

2.3 (a) $w = \int_1^2 F \, dx = \int_1^2 mg \, dx = mg \Delta x = (0.155 \text{ kg}) \times (9.81 \text{ m/s}^2)(10.0 \text{ m}) = 15.2 \text{ J}$. (b) $w = \Delta K = K_2 - K_1 = K_2 = 15.2 \text{ J}$. (c) $\frac{1}{2}mv^2 = K$ and $v = (2K/m)^{1/2} = [2(15.2 \text{ J})/(0.155 \text{ kg})]^{1/2} = 14.0 \text{ m/s}$, since $1 \text{ J} = 1 \text{ kg m}^2/\text{s}^2$.

2.4 $P = F/A = mg/A = (0.102 \text{ kg})(9.81 \text{ m/s}^2)/(1.00 \text{ m}^2) = 1.00 \text{ N/m}^2 = 1.00 \text{ Pa}$.

2.5 (a) $\text{area} = \text{length} \times \text{height} = (V_2 - V_1)P_1 = (2000 - 500)\text{cm}^3(3.00 \text{ atm}) = 4500 \text{ cm}^3 \text{ atm}$. $w_{\text{rev}} = -\text{area} = -(4500 \text{ cm}^3 \text{ atm})(8.314 \text{ J/82.06 cm}^3\text{-atm}) = -456 \text{ J}$. (b) $w_{\text{rev}} = -\int_1^2 P_1 \, dV = -P_1(V_2 - V_1) = \text{etc.}$

2.6 $w_{\text{rev}} = -\int_1^2 P \, dV = -P(V_2 - V_1) = -(275/760) \text{ atm} \times (875 - 385) \text{ cm}^3 = -177 \text{ cm}^3 \text{ atm} (8.314 \text{ J/82.06 cm}^3\text{-atm}) = -18.0 \text{ J}$.

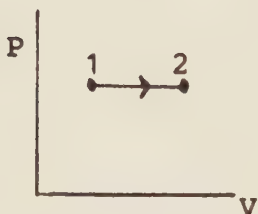
2.7 (a) The area under the curve is the sum of the areas of a rectangle and a right triangle. The rectangle's area is $(V_2 - V_1)P_2 = (2000 - 500)\text{cm}^3(1.00 \text{ atm}) = 1500 \text{ cm}^3 \text{ atm}$.

The triangle's area is $\frac{1}{2}(\text{base})(\text{alt.}) = \frac{1}{2}(V_2 - V_1)(P_1 - P_2)$
 $= \frac{1}{2}(2000 - 500)\text{cm}^3(3.00 - 1.00)\text{atm} = 1500\text{ cm}^3\text{ atm}$. Thus
 $w_{\text{rev}} = -3000\text{ cm}^3\text{ atm} (8.314\text{ J}/82.06\text{ cm}^3\text{-atm}) = -304\text{ J}$.

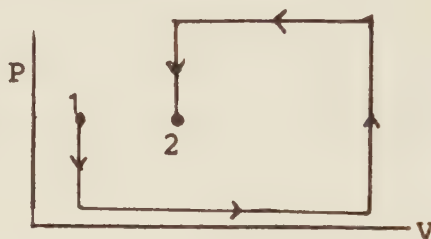
(b) Replacement of y and x with P and V in the straight-line equation gives $(P - P_1)/(V - V_1) = (P_2 - P_1)/(V_2 - V_1)$.
 $w = -\int_1^2 P dV = -\int_{V_1}^{V_2} \{P_1 + [(P_2 - P_1)/(V_2 - V_1)](V - V_1)\} dV =$
 $-P_1(V_2 - V_1) - [(P_2 - P_1)/(V_2 - V_1)][(\frac{1}{2}V_2^2 - V_1V_2) - (\frac{1}{2}V_1^2 - V_1^2)]$
 $= -P_1(V_2 - V_1) + \frac{1}{2}(P_1 - P_2)(V_2 - V_1) = \text{as in (a)}.$

2.8

(a)



(b)



2.9 Neglecting the temperature dependence of specific heat, we equate the heat gained by the water to that lost by the metal. The heat gained by the H_2O is $(24.0\text{ g}) \times (1.00\text{ cal/g-}^\circ\text{C})(10.0\text{ }^\circ\text{C}) = 240\text{ cal}$. Thus $240\text{ cal} =$
 $(45.0\text{ g})c_{\text{metal}}(70.0 - 20.0)^\circ\text{C}$ and $c_{\text{metal}} = 0.107\text{ cal/g-}^\circ\text{C}$.

2.10 He cooled the water to some temperature below 25°C and then did sufficient stirring work to raise its temperature to 40°C .

2.11 Only (c).

2.12

$$2200 \times 10^3 \frac{\text{cal}}{\text{day}} \frac{4.184\text{ J}}{1\text{ cal}} \frac{1\text{ day}}{24\text{ hr}} \frac{1\text{ hr}}{3600\text{ s}} = 107\text{ J/s} = 107\text{ W}$$

2.13 Since the process is cyclic, $\Delta U = 0$. Hence $q = -w = -145\text{ J}$.

2.14 The bulk kinetic energy acquired by the 190-ft fall is converted into internal energy, thereby warming the water by ΔT . The bulk kinetic energy equals the potential-energy decrease $mg\Delta h$. The ΔU for a temperature increase of ΔT can be set equal to the heat $q = mc_p\Delta T$ that would be needed to increase the temperature by ΔT , since the expansion work is negligible. Therefore $mg\Delta h = mc_p\Delta T$ and

$$\Delta T = \frac{g\Delta h}{c_p} = \frac{(9.80 \text{ m/s}^2)(190 \times 12 \times 2.54 \times 10^{-2} \text{ m})}{(1.00 \text{ cal/g-}^\circ\text{C})(10^3 \text{ g/kg})} \frac{1 \text{ cal}}{4.184 \text{ J}}$$

$$= 0.14 \text{ }^\circ\text{C}$$

2.15 We have $0 = \Delta U_1 + \Delta U_2 = q_1 + w_1 + q_2 + w_2 = q_1 + q_2$ (since the wall is rigid); therefore $q_2 = -q_1$.

2.16 This notation might seem to imply that q and w are state functions, which is not so. There is no such thing as the change in heat for a system. There is only an amount of heat transfer for a process.

2.17 $v = \frac{1}{2}kx^2 = \frac{1}{2}(125 \text{ N/m})(0.100 \text{ m})^2 = 0.625 \text{ J}$

$= 0.149 \text{ cal. } \Delta U = (m_1c_1 + m_2c_2)\Delta T \text{ and}$

$$\Delta T = \frac{0.149 \text{ cal}}{(1.00 \text{ cal/g-}^\circ\text{C})(112 \text{ g}) + (20 \text{ g})(0.30 \text{ cal/g-}^\circ\text{C})}$$

$\Delta T = 0.00126 \text{ }^\circ\text{C}$ and the final temperature is 18.001°C

2.18 (a) $0 = dE_{\text{syst}} + dE_{\text{surr}} = dE_{\text{syst}} + dK_{\text{surr}} + dV_{\text{surr}} +$

$dU_{\text{surr}} = dE_{\text{syst}} + dK_{\text{pist}} + mg dh + 0$, so $dE_{\text{syst}} = -mg dh$

$- dK_{\text{pist}}$. (b) $dE_{\text{syst}} = dq + dw_{\text{irrev}} = 0 + dw_{\text{irrev}}$, so

$dw_{\text{irrev}} = dE_{\text{syst}} = -mg \, dh - dK_{\text{pist}}$. But $mg \, dh = (mg/A)A \, dh$, where A is the piston's area. Since $mg/A = P_{\text{ext}}$ and $A \, dh = dV$, we have $mg \, dh = P_{\text{ext}} \, dV$ and $dw_{\text{irrev}} = -P_{\text{ext}} \, dV - dK_{\text{pist}}$. (c) $w_{\text{irrev}} = -\int_1^2 P_{\text{ext}} \, dV - \Delta K_{\text{pist}} = -P_{\text{ext}} \int_1^2 dV - 0 = -P_{\text{ext}}(V_2 - V_1) = -(0.500 \text{ bar})(4.00 \text{ dm}^3) = -2.00 \text{ dm}^3 \text{ bar}$. $1 \text{ dm}^3 = 1000 \text{ cm}^3$ and $1 \text{ bar} = 750 \text{ torr} = (750/760) \text{ atm} = 0.987 \text{ atm}$, so $w_{\text{irrev}} = -1974 \text{ cm}^3 \text{ atm} \times (8.314 \text{ J}/82.06 \text{ cm}^3\text{-atm}) = -200 \text{ J}$.

2.19 All except force, mass, and pressure.

2.20 (a) From the equation $\Delta H = q_p$. (b) It can mislead one into thinking that heat is a state function.

2.21 No. For example, in a cyclic process, ΔH is zero but q need not be zero, since q is not a state function.

2.22 $\Delta H = q_p = 0$ for the entire system. Since H is extensive, $H = H_1 + H_2$ and $\Delta H = \Delta H_1 + \Delta H_2 = q_1 + q_2$. Since $\Delta H = 0$, $q_1 + q_2 = 0$.

2.23 $\bar{C}_p = C_p/n$ and $C_p = n\bar{C}_p$. $n = (586 \text{ g})(1 \text{ mol}/16.0 \text{ g}) = 36.6 \text{ mol}$; $C_p = (36.6 \text{ mol})(94.4 \text{ J/mol-K}) = 3.46 \text{ kJ/K}$.

2.24 $\mu_{JT} = (\partial T/\partial P)_H$, $\Delta T = \int_1^2 \mu_{JT} \, dP$ and $\Delta T \approx \mu_{JT} \Delta P$ for H constant. Thus $\Delta T \approx (0.2 \text{ }^\circ\text{C/bar})(-49 \text{ bar}) = -10 \text{ }^\circ\text{C}$. The final temperature is approximately 15°C .

2.25 Equation (1.35) gives $(\partial \bar{U}/\partial \bar{V})_T = (\partial \bar{U}/\partial P)_T (\partial P/\partial \bar{V})_T$. Partial differentiation of $P = RT/\bar{V}$ gives $(\partial P/\partial \bar{V})_T =$

$-RT/\bar{V}^2 = -P^2/RT$. Hence $(\partial \bar{U}/\partial \bar{V})_T = -(\partial \bar{U}/\partial P)_T P^2/RT$. For (a):

$$\left(\frac{\partial \bar{U}}{\partial \bar{V}}\right)_T = \frac{(6.08 \text{ J/mol-atm})(1 \text{ atm})^2}{(82.06 \text{ cm}^3\text{-atm/mol-K})(301 \text{ K})} = 2.46 \times 10^{-4} \text{ J/cm}^3$$

(b) Doubling P multiplies $(\partial \bar{U}/\partial \bar{V})_T$ by 4 to give $9.84 \times 10^{-4} \text{ J/cm}^3$.

2.26 (a) Use of (1.34), (1.32), (2.64), and (2.53) gives

$$-1 = \left(\frac{\partial T}{\partial P}\right)_H \left(\frac{\partial P}{\partial H}\right)_T \left(\frac{\partial H}{\partial T}\right)_P = \frac{\mu_{JT} C_P}{(\partial H/\partial P)_T} \text{ and (2.65) follows.}$$

(b) Partial differentiation of $H = U + PV$ and use of (2.62), (1.35), (1.44), and (2.65) give

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + P \left(\frac{\partial V}{\partial P}\right)_T + V = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T - PV\kappa + V$$

$-C_P \mu_{JT} = C_V \mu_J \kappa - PV\kappa + V$ and the desired result follows.

2.27 (a) Since T is constant, $\Delta U = 0$ and $\Delta H = 0$. (U and H of a perfect gas depend on T only.) $w = -\int_1^2 P \, dV =$

$$-nRT \int_1^2 dV/V = -nRT \ln (V_2/V_1) = -(5.00 \text{ mol}) \times$$

$$(8.314 \text{ J/mol-K})(300 \text{ K}) \ln (1500/500) = -13.7 \text{ kJ. } \Delta U = q +$$

$w = 0$, so $q = -w = 13.7 \text{ kJ}$. (b) Since U and H are state functions, ΔU and ΔH are still zero. The work w is zero.

2.28 (a) $T_2 = T_1 = 300 \text{ K}$. $P_2 = nRT_2/V_2 =$

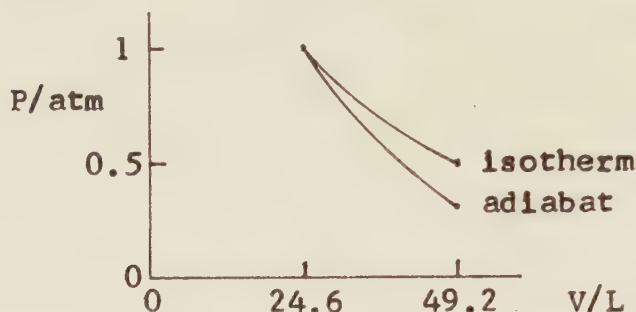
$$(1.00 \text{ mol})(82.06 \text{ cm}^3\text{-atm/mol-K})(300 \text{ K})/(49200 \text{ cm}^3) =$$

0.500 atm . (An alternative solution uses $P_2 V_2 = P_1 V_1$.)

(b) $\gamma = \bar{C}_P/\bar{C}_V = (\bar{C}_V + R)/\bar{C}_V = 2.5R/1.5R = 1.667$. $P_1 =$

$nRT_1/V_1 = 1.00 \text{ atm}$. For a reversible adiabatic process with C_V constant, Eq. (2.77) gives $P_1 V_1^\gamma = P_2 V_2^\gamma$ and $P_2 = (V_1/V_2)^\gamma P_1 = (24.6 \text{ L}/49.2 \text{ L})^{1.667} (1.00 \text{ atm}) = 0.315 \text{ atm}$. $T_2 = P_2 V_2 / nR = 189 \text{ K}$.

(c)



2.29 $q = 0$ since the process is adiabatic. $\bar{C}_V = \bar{C}_P - R = 2.5R$. $T_1 = P_1 V_1 / nR = 160 \text{ K}$.

$$T_2 = T_1 (V_1/V_2)^{R/\bar{C}_V} = (160 \text{ K}) (4.00)^{0.4} = 279 \text{ K}$$

$dU = C_V dT$ and $\Delta U = C_V \Delta T$, since C_V is constant. Thus

$$\Delta U = (0.0400 \text{ mol}) 2.5 (8.314 \text{ J/mol-K}) (119 \text{ K}) = 98.9 \text{ J}$$

$$\Delta U = q + w = w = 98.9 \text{ J}; \quad \Delta H = C_P \Delta T = 138\frac{1}{2} \text{ J}$$

(b) From $P_1 V_1^\gamma = P_2 V_2^\gamma$, we get $P_1 (nRT_1/P_1)^\gamma = P_2 (nRT_2/P_2)^\gamma$ which becomes $P_1^{1-\gamma} T_1^\gamma = P_2^{1-\gamma} T_2^\gamma$. Hence $(T_1/T_2)^\gamma = (P_2/P_1)^{1-\gamma}$ and $P_2/P_1 = (T_1/T_2)^{\gamma/(1-\gamma)}$. $\gamma = \bar{C}_P/\bar{C}_V = 3.5R/2.5R = 1.40$. $P_2/(1 \text{ atm}) = (298 \text{ K}/100 \text{ K})^{1.40/(-0.40)} = (2.98)^{-3.5} = 0.0219$, so $P_2 = 0.0219 \text{ atm} = 2.22 \text{ kPa}$.

2.30 (a) $n = 0.500 \text{ mol}$. $0.800 \text{ bar} = 0.789 \text{ atm}$. $T_1 = P_1 V_1 / nR = 384.6 \text{ K}$, $T_2 = P_2 V_2 / nR = 769.2 \text{ K}$. $dU = C_V dT$ and $\Delta U = C_V \Delta T = n\bar{C}_V \Delta T = (0.500 \text{ mol}) (1.5R) (384.6 \text{ K}) = 2.40$

$$\text{kJ. } \Delta H = C_p \Delta T = (0.500 \text{ mol})(2.5R)(384.6 \text{ K}) = 4.00 \text{ kJ.}$$

$$w = -\int_1^2 P dV = -P(V_2 - V_1) = -(0.789 \text{ atm})(20000 \text{ cm}^3) \times (8.314 \text{ J}/82.06 \text{ cm}^3\text{-atm}) = -1.60 \text{ kJ. } q = q_p = \Delta H = 4.00 \text{ kJ.}$$

$$(b) w = 0 \text{ at constant } V. T_1 = P_1 V_1 / nR = 216.5 \text{ K; } T_2 =$$

$$324.8 \text{ K. } \Delta U = C_v \Delta T = 0.675 \text{ kJ. } \Delta H = C_p \Delta T = 1.13 \text{ kJ.}$$

$$\Delta U = q + w = q, \text{ so } q = 0.675 \text{ kJ.}$$

2.31 (a) Process; (b) system property; (c) process; (d) process; (e) system property; (f) system property; (g) system property.

$$\underline{2.32} \quad C_{pr} = dq_{pr} / dT_{pr}. \quad (a) dq_{pr} > 0 \text{ and } dT_{pr} = 0, \text{ so}$$

$$C_{pr} = \infty. \quad (b) -\infty, \text{ since } dq_{pr} < 0. \quad (c) dU = 0 = dq_{pr} + dw_{pr}; dq_{pr} = -dw_{pr}; dw_{pr} < 0 \text{ and } dq_{pr} > 0. dT_{pr} = 0. \text{ Hence } C_{pr} = \infty. \quad (d) 0, \text{ since } dq_{pr} = 0.$$

$$\underline{2.33} \quad (a) \text{ Heat is required to melt the benzene, so } q > 0.$$

$\Delta H = q_p > 0$. The constant-P work is $w = -P\Delta V$; since the benzene expands on melting, $w < 0$. The volume change is slight, so $|w| \ll |q|$ and $\Delta U = q + w \approx q$; hence $\Delta U > 0$.

(b) The same as (a) except that $w > 0$ since the system contracts on melting. (c) $q = 0$ for this adiabatic process. w is negative for an expansion. We have $\Delta U = q + w =$

w , so $\Delta U < 0$. $\Delta H = \Delta U + \Delta(PV) = \Delta U + nR \Delta T$. We have $dU = C_v dT$, where $dU < 0$ and $C_v > 0$; hence $dT < 0$ and $\Delta T < 0$.

Therefore $\Delta H < 0$. (d) With T constant, we have $\Delta H = 0 = \Delta U$ for the perfect gas. w is negative for the expansion.

$$\Delta U = 0 = q + w, \text{ so } q = -w \text{ and } q \text{ is positive. } (e) q = 0,$$

$w = 0$, $\Delta U = q + w = 0$, $\Delta H = \Delta U + \Delta(PV) = \Delta U + nR\Delta T = 0$.

ΔT is zero because $\mu_J = 0$ for the perfect gas. (f) For Joule-Thomson throttling, $\Delta H = 0$. Since $\mu_{JT} = (\partial T / \partial P)_H = 0$ for a perfect gas, T is constant. Hence $\Delta U = 0$, since $dU = C_V dT = 0$. The process is adiabatic, so $q = 0$. Hence $w = \Delta U - q = 0$; this also follows from the equation $w = P_1 V_1 - P_2 V_2$ in the text, since $T_2 = T_1$. (g) $q > 0$ for heating. From $dq_P = C_P dT$, it follows that $\Delta T > 0$, since $C_P > 0$. From $dU = C_V dT$, it follows that $\Delta U > 0$, since $C_V > 0$. From $PV = nRT$, it follows that $\Delta V > 0$. Hence $w = -P\Delta V < 0$. $\Delta H = \Delta U + \Delta(PV) = \Delta U + nR\Delta T > 0$. (h) $q < 0$ and $\Delta T < 0$. Hence $\Delta U < 0$. $w = 0$ since $dw = -P dV = 0$. $\Delta H = \Delta U + nR\Delta T < 0$.

2.34 (a) $q = 0$ (since adiabatic), $w = 0$ (since constant V), $\Delta U = q + w = 0$. (b) $w = 0$ (const. V). The combustion is an exothermic process that releases heat to the surrounding bath; hence $q < 0$. $\Delta U = q + w < 0$.

2.35 The process is adiabatic, so $q = 0$. The volume change is being neglected, so $w \approx 0$. Hence $\Delta U = q + w \approx 0$. $\Delta H = \Delta U + \Delta(PV) \approx 0 + V\Delta P$, since V is constant. Thus

$$\Delta H \approx (18 \text{ cm}^3)(9.0 \text{ atm}) \frac{1.987 \text{ cal/mol-K}}{82.06 \text{ cm}^3\text{-atm/mol-K}} = 3.9 \text{ cal} = 16 \text{ J}$$

2.36 (a) $dq_P = C_P dT$; $q_P = \int_1^2 C_P dT = \int_1^2 n(a + bT) dT = n[a(T_2 - T_1) + \frac{1}{2}b(T_2^2 - T_1^2)]$. Hence

$$q = (2.00 \text{ mol})[(6.15 \text{ cal/mol-K})(100 \text{ K}) + \frac{1}{2}(0.00310 \text{ cal/mol-K}^2)(400^2 - 300^2)\text{K}^2]$$

$$q = 1447 \text{ cal}$$

$$w = -\int_1^2 P \, dV = -P\Delta V = -nR\Delta T$$

$$= -(2.00 \text{ mol})(1.987 \text{ cal/mol-K})(100 \text{ K}) = -397 \text{ cal}$$

$$\Delta U = q + w = 1447 \text{ cal} - 397 \text{ cal} = 1050 \text{ cal}$$

$$\Delta H = q_p = 1447 \text{ cal}$$

(b) $dw = -P \, dV = 0$ and $w = 0$. ΔU and ΔH are the same as in (a), since the final and initial temperatures are the same as in (a) and U and H are functions of T only for a perfect gas. Hence $\Delta H = 1447 \text{ cal}$ and $\Delta U = 1050 \text{ cal}$.

$$\Delta U = q + w = q = 1050 \text{ cal}.$$

$$\underline{2.37} \text{ (a)} \quad q = (79.7 \text{ cal/g})(18.015 \text{ g}) = 1436 \text{ cal}$$

$$w = -\int_1^2 P \, dV = -P\Delta V = -Pm(1/\rho_2 - 1/\rho_1) =$$

$$-(1 \text{ atm})(18.0 \text{ g})(1.000 \text{ cm}^3/\text{g} - 1.0905 \text{ cm}^3/\text{g}) \frac{1.987 \text{ cal}}{82.06 \text{ cm}^3 \text{ atm}}$$

$$w = 0.039 \text{ cal}; \quad \Delta U = q + w = 1436 \text{ cal}; \quad \Delta H = q_p = 1436 \text{ cal}$$

$$\text{(b)} \quad q_p = \int_1^2 C_p \, dT = C_p \Delta T =$$

$$(1.00 \text{ cal/g-}^\circ\text{C})(18.01 \text{ g})(100 \text{ }^\circ\text{C}) = 1801 \text{ cal}$$

$$w = -P\Delta V =$$

$$-(1 \text{ atm})(18.0 \text{ g})(1.044 \text{ cm}^3/\text{g} - 1.000 \text{ cm}^3/\text{g}) \frac{1.987 \text{ cal}}{82.06 \text{ cm}^3 \text{ atm}}$$

$$w = -0.019 \text{ cal}$$

$$\Delta U = q + w = 1801 \text{ cal} \quad \Delta H = q_p = 1801 \text{ cal}$$

$$\text{(c)} \quad q = (18.015 \text{ g})(539.4 \text{ cal/g}) = 9717 \text{ cal}$$

$$V_2 = \frac{(1 \text{ mol})(82.06 \text{ cm}^3\text{-atm/mol-K})(373.15 \text{ K})}{1 \text{ atm}} = 30620 \text{ cm}^3$$

$$V_1 = (18.01 \text{ g})/(0.958 \text{ g/cm}^3) = 19 \text{ cm}^3, \quad \Delta V = 30600 \text{ cm}^3$$

$$w = -P\Delta V = -(1 \text{ atm})(30600 \text{ cm}^3) \frac{1.987 \text{ cal}}{82.06 \text{ cm}^3 \text{ atm}} = -741 \text{ cal}$$

$$\Delta U = q + w = 8976 \text{ cal}, \quad \Delta H = q_p = 9717 \text{ cal}$$

2.38 For \bar{C}_V independent of T , we have $dU = C_V dT$,

$$\Delta U = C_V \Delta T = 1.5nR\Delta T; \text{ also } dH = C_P dT, \Delta H = (C_V + nR)\Delta T =$$

$$2.5nR\Delta T. \text{ (a) } \Delta T = 200 \text{ K and substitution of numerical}$$

values gives $\Delta U = 6240 \text{ J}$ and $\Delta H = 10,400 \text{ J}$. (b) Use of

$$PV = nRT \text{ gives } T_2 = 292.5 \text{ K and } T_1 = 243.7 \text{ K, so } \Delta T =$$

$$48.8 \text{ K. We find } \Delta U = 1520 \text{ J and } \Delta H = 2540 \text{ J. (c) Since}$$

$$\Delta T = 0, \text{ we have } \Delta U = 0 \text{ and } \Delta H = 0.$$

2.39 No, since q and w are not state functions.

$$\underline{2.40} \quad 1 \text{ dm}^3 = (10^{-1} \text{ m})^3 = 10^{-3} \text{ m}^3 = 10^{-3}(10^2 \text{ cm})^3 = 1000 \text{ cm}^3$$

(a)

$$w = -P\Delta V = -(1 \text{ atm})(20000 \text{ cm}^3) \frac{8.314 \text{ J/mol-K}}{82.06 \text{ cm}^3\text{-atm/mol-K}} = -2.02_6 \text{ kJ}$$

$$T_1 = P_1 V_1 / nR = 243.7 \text{ K}, \quad T_2 = P_2 V_2 / nR = 487.4 \text{ K}$$

$$q_p = C_P \Delta T = (1.00 \text{ mol})3.5 (8.314 \text{ J/mol-K}) (243.7 \text{ K})$$

$$q = 7.09 \text{ kJ}; \quad \Delta U = q + w = 5.06_4 \text{ kJ}; \quad \Delta H = q_p = 7.09 \text{ kJ}$$

(b) $w = 0$ since V is constant. $q_V = C_V \Delta T$; the process goes from 487.4 K to 243.7 K , so $\Delta T = -243.7 \text{ K}$ and

$$q = (1.00 \text{ mol})2.5 (8.314 \text{ J/mol-K}) (-243.7 \text{ K}) = -5.06_5 \text{ kJ}$$

$$\Delta U = q + w = -5.06_5 \text{ kJ}; \quad \Delta H = C_P \Delta T = -7.09 \text{ kJ}$$

(c) Since T is constant, $\Delta U = 0 = \Delta H$. $w = -\int P dV = -\int_1^2 nRT dV/V = -nRT \ln (V_2/V_1) = 1.40_4 \text{ kJ}$. $\Delta U = 0 = q + w$ and $q = -w = -1.40_4 \text{ kJ}$. For the cycle, $\Delta U = 0 = \Delta H$, $q = 7.09 \text{ kJ} - 5.06_5 \text{ kJ} - 1.40_4 \text{ kJ} = 0.62 \text{ kJ}$, $w = -2.02_6 \text{ kJ} + 0 + 1.40_4 \text{ kJ} = -0.62 \text{ kJ}$. On the P - V diagram, step (a) is a horizontal line, step (b) a vertical line, and step (c) a hyperbolic line.

2.41 (a) $V_{\text{gas}} = nRT/P = 24500 \text{ cm}^3$. Each hypothetical cube has a volume $V_{\text{cube}} = (24500 \text{ cm}^3)/(6.02 \times 10^{23}) = 4.1 \times 10^{-20} \text{ cm}^3$ and an edge length $(4.1 \times 10^{-20} \text{ cm}^3)^{1/3} = 3.4 \times 10^{-7} \text{ cm} = 34 \text{ \AA}$. (b) The distance between the uniformly distributed molecules equals the distance between the cube centers, which is $3.4 \times 10^{-7} \text{ cm}$. (c) At 40 atm and 25°C , $V_{\text{gas}} = 610 \text{ cm}^3$, $V_{\text{cube}} = 1.0 \times 10^{-21} \text{ cm}^3$ and the distance between centers is 10 \AA .

2.42 At 300 K and 1 atm, the contribution of intermolecular interactions to C_P and C_V is small and can be neglected. At room T , $C_{V,\text{vib}}$ is negligible for diatomic molecules that are not heavy. We thus consider only $C_{V,\text{tr}}$ and $C_{V,\text{rot}}$. (a) $\bar{C}_V = \bar{C}_{V,\text{tr}} = 3R/2$; $\bar{C}_P = \bar{C}_V + R = 5R/2$. (b) $\bar{C}_V = \bar{C}_{V,\text{tr}} + \bar{C}_{V,\text{rot}} = 3R/2 + R = 5R/2$; $\bar{C}_P = 7R/2$.

2.43 The contribution of intermolecular interactions to C_P of the liquid can be estimated by taking $C_{P,\text{liq}} - C_{P,\text{gas}}$, since intermolecular interactions are quite small

in the gas. Figure 2.12 shows that $C_{P,liq} - C_{P,gas}$ is positive. Therefore $C_{P,intermol} = (\partial U_{intermol} / \partial T)_P$ is positive and $U_{intermol}$ must increase as T increases at constant P . (Recall from Sec. 2.11 that $U_{intermol}$ is negative. An increase in $U_{intermol}$ means a less negative $U_{intermol}$ and corresponds to a decrease in intermolecular attractions as T increases.)

2.44 (a) Kinetic; (b) kinetic; (c) kinetic and potential; (d) kinetic and potential.

2.45 At the low temperature of 10 K, the 1-atm gas density is rather high, the average intermolecular distance is rather small, and intermolecular interactions are of significant magnitude. These interactions cause \bar{C}_P to deviate from the monatomic ideal-gas \bar{C}_P .

2.46(a) Using $q = mc\Delta T$ and $w = \text{power} \times \text{time}$, we have

$$q = (27 \text{ lb})(454 \text{ g/lb})(1 \text{ cal/g-}^\circ\text{C})(100^\circ\text{C}) = 12.3 \times 10^5 \text{ cal}$$

$$w = (746 \text{ J/s})(3600 \text{ s/hr})(2.5 \text{ hr}) = 67.1 \times 10^5 \text{ J}$$

$$12.3 \times 10^5 \text{ cal} = 67.1 \times 10^5 \text{ J} \quad \text{and} \quad 1 \text{ cal} = 5.5 \text{ J}$$

(b) Using $V = mgh$ to find the work needed to raise a one-pound weight by one foot, we have

$$1 \text{ ft-lb} = (454 \text{ g})(980 \text{ cm/s}^2)(12 \times 2.54 \text{ cm})(1 \text{ J}/10^7 \text{ ergs})$$

$$1 \text{ ft-lb} = 1.356 \text{ J} \quad \text{and} \quad 772 \text{ ft-lb} = 1047 \text{ J}$$

$$q = (454 \text{ g})(1 \text{ cal/g-}^\circ\text{C})(1^\circ\text{F})(\frac{5}{9}^\circ\text{C}/^\circ\text{F}) = 252 \text{ cal}$$

$$252 \text{ cal} = 1047 \text{ J} \quad \text{and} \quad 1 \text{ cal} = 4.15 \text{ J}$$

2.47 (a) $T = 273.15^\circ + 1.8^\circ = 274.9_5 \text{ K}$, which has 4 significant figures. Calculation of $1/T$ to 4 significant figures gives $1/T = 0.003637 \text{ K}^{-1}$. (b) Ignoring significant figures, we have $\log 4.83 = 0.68395$, $\log 4.84 = 0.68485$, $\log (4.83 \times 10^{20}) = \log 4.83 + \log 10^{20} = 20.68395$, $\log (4.84 \times 10^{20}) = 20.68485$. The numbers 4.83 and 4.84 differ by 1 in their third significant digit and their logs differ by 1 in the third significant digit after the decimal point. The logs of 4.83×10^{20} and 4.84×10^{20} differ by 1 in the third significant digit after the decimal point. The portion of the log that precedes the decimal point should not be considered (since this portion comes from the power of 10) and the log should have as many significant digits after the decimal point as there are significant digits in the number. Thus the logs should be expressed as 0.684, 0.685, 20.684, and 20.685.

2.48 (a) Solving (1.39) for P , we get $P = nRT/(V - nb) - an^2/V^2$. For a reversible isothermal process, $w = -\int_1^2 P \, dV = -\int_1^2 [nRT/(V - nb) - an^2/V^2] \, dV = -nRT \ln (V - nb) \Big|_1^2 - an^2/V \Big|_1^2 = nRT \ln [(V_1 - nb)/(V_2 - nb)] + an^2(1/V_1 - 1/V_2)$. For $a = 0 = b$, we get $w = nRT \ln (V_1/V_2)$, which is (2.74).

2.49 (a) 8.0 K. (b) 5.00 J/K.

2.50 $PV = \text{constant}$ holds only when T is constant, and T is not constant in a reversible adiabatic perfect-gas expansion.

2.51 $dq = C_p \, dT$ holds only in a constant- P process, and P is not constant in a reversible isothermal perfect-gas expansion.

2.52 Genevieve erroneously applied an equation for a reversible adiabatic process to an irreversible adiabatic process.

2.53 $dU = C_V dT$. $T = PV/nR$ and $dT = (P/nR) dV$. Since $dV > 0$, dT is positive. Hence dU is positive and U increases.

2.54 (a) Intensive; kg/m^3 . (b) Extensive; J. (c) Intensive; J/mol. (d) Extensive; J/K. (e) Intensive; J/kg-K. (f) Intensive; J/mol-K.

2.55 Insertion of the dimensions of each physical quantity in the equation gives

$$\frac{\text{energy}}{\text{temperature}} - \frac{\text{energy}}{\text{temperature}} = (\text{temp.})(\text{vol.}) \frac{(\text{press.})^n}{(\text{temp.})^m}$$

Equating the powers of temperature on each side of the equation, we get $-1 = 1 - m$ and $m = 2$. Also, $n = 1$, since the product pressure \times volume has the dimensions $(\text{force}/\text{length}^2)\text{length}^3 = \text{force} \times \text{length} = \text{energy}$.

2.56 $\gamma = \bar{C}_P/\bar{C}_V = 1.13$. Also, the gas is nearly ideal under these conditions, so $\bar{C}_P = \bar{C}_V + R$. Therefore, $\gamma = (\bar{C}_V + R)/\bar{C}_V = 1 + R/\bar{C}_V = 1.13$; $R/\bar{C}_V = 0.13$ and $\bar{C}_V = R/0.13 = 15 \text{ cal/mol-K}$; $\bar{C}_P = \bar{C}_V + R = 17 \text{ cal/mol-K}$.

2.57 (a) False; ΔH is the change in a state function. (b) False; for a perfect gas, C_V is a function of T only, but need not be independent of T . (c) False; the system must be closed. (d) False; for an isothermal process, T must remain constant throughout the process. (e) False; U must be replaced by ΔU . (f) False. For a perfect gas, U depends on T only, but this is not true for other kinds of systems. An isothermal pressure change changes the

average intermolecular distance and hence changes the contribution of intermolecular interactions to the internal energy. (g) False; see the first example in Sec. 2.8. (h) True. (i) False; for example, T drops in a reversible adiabatic perfect-gas expansion. (j) False; the entire path of the process must be specified. (k) False; for example, a real gas expanding adiabatically into vacuum can undergo a change in T . (l) True.

CHAPTER 3

3.1 (a) $e_{\text{rev}} = 1 - T_C/T_H = 1 - (273 \text{ K})/(1073 \text{ K}) = 0.746$

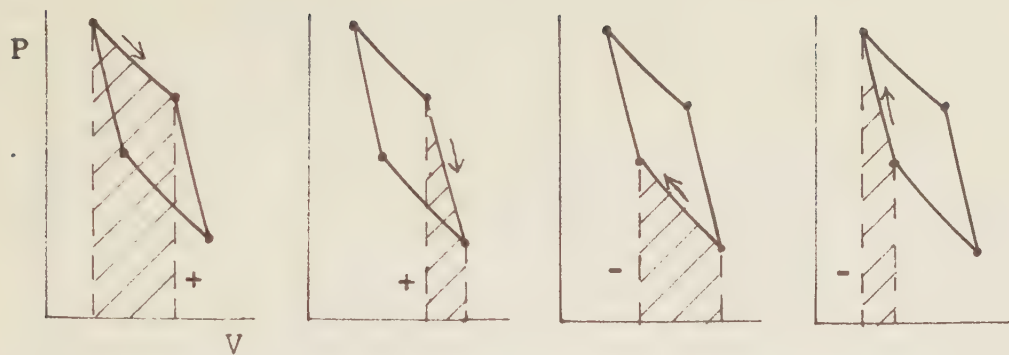
(b) $e_{\text{rev}} = -w_{\text{max}}/q_H$, $-w_{\text{max}} = 0.746(1000 \text{ J}) = 746 \text{ J}$,
 $-q_{C,\text{min}} = 1000 \text{ J} - 746 \text{ J} = 254 \text{ J}$

3.2 $e_{\text{rev}} = 1 - T_C/T_H = 0.90 = 1 - (283 \text{ K})/T_H$, $T_H = 2830 \text{ K}$

3.3 $w = -2.50 \text{ kJ}$. $e = -w/q_H = 0.45 = 2.50 \text{ kJ}/q_H$ and $q_H = 5.56 \text{ kJ}$. $\Delta U = 0 = q + w = q_C + q_H + w = q_C + 5.56 \text{ kJ} - 2.50 \text{ kJ}$ and $q_C = -3.06 \text{ kJ}$.

3.4 (a) Since a Carnot cycle is a cyclic process, the first law gives $\Delta U = q + w = 0 = q_C + q_H + w$. Since a Carnot cycle is reversible, we have $\Delta S = \oint dq_{\text{rev}}/T = 0 = q_C/T_C + q_H/T_H$, which can be rearranged to $q_C/q_H = -T_C/T_H$. Use of the two boxed equations gives $K_{\text{rev}} = q_C/w = -q_C/(q_C + q_H)$; division of numerator and denominator by q_C gives $K_{\text{rev}} = -1/(1 + q_H/q_C) = -1/(1 - T_H/T_C) = T_C/(T_H - T_C)$. Also, $\epsilon_{\text{rev}} = -q_H/w = q_H/(q_C + q_H) = 1/(q_C/q_H + 1) = 1/(-T_C/T_H + 1) = T_H/(T_H - T_C)$. (b) From (a), $\epsilon_{\text{rev}} = 1/(1 - T_C/T_H)$; the denominator is less than 1 and greater than 0, so $\epsilon_{\text{rev}} > 1$. (c) $\epsilon_{\text{rev}} = T_H/(T_H - T_C) = (293 \text{ K})/(20 \text{ K}) = 15 = |q_H|/w$, so $|q_H| = 15w = 15 \text{ J}$. (This indicates why heat pumps are attractive devices for heating homes in winter.) (d) $K_{\text{rev}} = T_C/(T_H - T_C)$, which goes to 0 as T_C goes to 0 K.

3.5



Combining the shaded areas using the marked signs, we get the area enclosed by the cycle.

3.6 For the anti-Clausius device removing heat from the cold reservoir at the same rate the heat engine deposits heat in this reservoir, we have a cyclic device that has a positive net work output; the net energy flow into the cold reservoir is zero, so the energy input for the work output must come entirely from heat extracted from the hot reservoir. The combined system is thus a cyclic device that converts heat completely into work with no other effects and therefore violates the Kelvin-Planck statement.

An anti-Kelvin-Planck device converts the heat input from the hot reservoir completely into work. We use this work output to run a heat pump and we run the heat pump at a rate that uses up all the work output of the anti-Kelvin-Planck device. The combined system is then a cyclic system that transfers heat from the cold to the hot reservoir with no net work input, thereby violating the Clausius statement. This completes the proof.

3.7 $dS = dq_{\text{rev}}/T$. (a) $dq_{\text{rev}} > 0$ so $\Delta S > 0$. (b) $dq_{\text{rev}} > 0$ so $\Delta S > 0$. (c) $dq_{\text{rev}} = 0$, so $\Delta S = 0$. (d) $dq_{\text{rev}} > 0$, so

$\Delta S > 0$. (e) This is an irreversible process in an isolated system, so $\Delta S > 0$. (f) This is an irreversible adiabatic process, so $\Delta S > 0$. This also follows from Eq. (3.29) with $dT = 0$ and $V_2 > V_1$. (g) $dq_{\text{rev}} > 0$, so $\Delta S > 0$. (h) $dq_{\text{rev}} < 0$, so $\Delta S < 0$; (a) This is an irreversible process in an isolated system, so $\Delta S > 0$.

3.8 (a) $\Delta S_{\text{vap}} = q/T = (1560 \text{ cal})/(87.3 \text{ K}) = 17.9 \text{ cal/K}$.

(b) $(5.00 \text{ g})(1 \text{ mol}/39.95 \text{ g}) = 0.125 \text{ mol}$.

$q = -(0.125 \text{ mol})(1560 \text{ cal/mol}) = -195 \text{ cal}$.

$\Delta S = q/T = (-195 \text{ cal})/(87.3 \text{ K}) = -2.24 \text{ cal/K}$.

3.9 $\Delta S = \int_1^2 dq_{\text{rev}}/T = \int_1^2 (C_P/T) dT = \int_1^2 n(a/T + b) dT =$
 $= n[a \ln (T_2/T_1) + b(T_2 - T_1)]$. Thus

$$\Delta S = 2.00 \text{ mol} \left(6.15 \frac{\text{cal}}{\text{mol K}} \ln \frac{400 \text{ K}}{300 \text{ K}} + 0.00310 \frac{\text{cal}}{\text{mol K}^2} 100 \text{ K} \right) = 4.16 \text{ cal/K}$$

3.10 For melting the ice to liquid water at 0°C , $\Delta S_a =$
 $q_{\text{rev}}/T = (18.015 \text{ g})(79.7 \text{ cal/g})/(273.15 \text{ K}) = 5.26 \text{ cal/K}$.

For heating the water from 0 to 100°C at 1 atm , $\Delta S_b =$
 $\int_1^2 C_P dT/T = C_P \ln (T_2/T_1)$

$= (18.01 \text{ g})(1.00 \text{ cal/g-K}) \ln (373.15/273.15) = 5.62 \text{ cal/K}$

For vaporization of the liquid to vapor at 100°C and 1

atm, $\Delta S_c = q_{\text{rev}}/T = 26.04 \text{ cal/K}$. For the isothermal expansion of the vapor (assumed ideal), Eq. (3.29) gives

$\Delta S_d = nR \ln (V_2/V_1) = (1.00 \text{ mol})(1.987 \text{ cal/mol-K}) \ln 2 = 1.38 \text{ cal/K}$. We have for the overall process: $\Delta S = 5.26 \text{ cal/K} + 5.62 \text{ cal/K} + 26.04 \text{ cal/K} + 1.38 \text{ cal/K} = 38.30 \text{ cal/K}$.

3.11 For an ideal gas with \bar{C}_V constant and equal to $1.5R$, Eq. (3.29) gives $\Delta S = C_V \ln (T_2/T_1) + nR \ln (V_2/V_1) = nR[1.5 \ln (T_2/T_1) + \ln (V_2/V_1)]$.

$$(a) (2.50 \text{ mol})(8.314 \text{ J/mol-K})(1.5 \ln 1.5 + \ln 0.75) = 6.66 \text{ J/K}$$

$$(b) (2.50 \text{ mol})(8.314 \text{ J/mol-K})(1.5 \ln 1.2 + \ln 1.5) = 14.1 \text{ J/K}$$

$$(c) (2.50 \text{ mol})(8.314 \text{ J/mol-K})(0 + \ln 1.474) = 8.06 \text{ J/K}$$

3.12 0, since the process is cyclic.

3.13 0, since $dq_{\text{rev}} = 0$.

3.14 From (3.29), $\Delta S = nR[2.5 \ln (T_2/T_1) + \ln (V_2/V_1)]$.

$$(a) (1.00 \text{ mol})(8.314 \text{ J/mol-K})[2.5 \ln 2 + \ln 2] = 20.2 \text{ J/K}$$

$$(b) (1.00 \text{ mol})(8.314 \text{ J/mol-K})[2.5 \ln \frac{1}{2} + 0] = -14.4 \text{ J/K}$$

$$(c) (1.00 \text{ mol})(8.314 \text{ J/mol-K})[0 + \ln \frac{1}{2}] = -5.8 \text{ J/K}$$

For the cycle, $\Delta S = 0$.

3.15 Use the reversible path in Fig. 3.7. For the first step, $\Delta S_1 = C_P \ln (T_2/T_1) =$

$$(10 \text{ g})(1.01 \text{ cal/g-K}) \ln (273.1/263.1) = 0.38 \text{ cal/K}$$

For the second step, $\Delta S_2 = q_{\text{rev}}/T =$

$$-(79.7 \text{ cal/g})(10 \text{ g})/(273.1 \text{ K}) = -2.92 \text{ cal/K}$$

For the third step, $\Delta S = C_P \ln (T_2/T_1) =$

$$(10 \text{ g})(0.50 \text{ cal/g-K}) \ln (263.1/273.1) = -0.19 \text{ cal/K}$$

For the complete process, $\Delta S = 0.38 \text{ cal/K} - 2.92 \text{ cal/K} - 0.19 \text{ cal/K} = -2.73 \text{ cal/K}$.

3.16 For the step $1 \rightarrow 2$ in Fig. 3.4b: $q > 0$, $w < 0$,

$\Delta U = 0$ (since U depends only on T for a perfect gas),

$\Delta S = q_H/T_H > 0$. For the step $2 \rightarrow 3$: $q = 0$, $w < 0$,

$\Delta U < 0$, $\Delta S = 0$ (since reversible and adiabatic). For the

step $3 \rightarrow 4$: $q < 0$, $w > 0$, $\Delta U = 0$, $\Delta S = q_C/T_C < 0$. For

the step $4 \rightarrow 1$: $q = 0$, $w > 0$, $\Delta U > 0$, $\Delta S = 0$.

3.17 (a) $m_1 c_1 |\Delta T_1| = m_2 c_2 |\Delta T_2|$

$$(200 \text{ g})(0.0313 \text{ cal/g-K})(120^\circ\text{C} - x) =$$

$$(25.0 \text{ g})(1.00 \text{ cal/g-K})(x - 10^\circ\text{C})$$

$$x = 32.0^\circ\text{C}$$

(b) $\Delta S = C_P \ln (T_2/T_1)$. For Au, ΔS is

$$(0.0313 \text{ cal/g-K})(200 \text{ g}) \ln (305.1/393.1) = -1.59 \text{ cal/K}$$

(c) For the water, ΔS is

$$(1.00 \text{ cal/g-K})(25.0 \text{ g}) \ln (305.1/283.1) = 1.87 \text{ cal/K}$$

(d) $-1.59 \text{ cal/K} + 1.87 \text{ cal/K} = 0.28 \text{ cal/K}$

3.18 $\Delta S = n_a R \ln [(n_a + n_b)/n_a] + n_b R \ln [(n_a + n_b)/n_b]$

$$n_a = 2.50 \text{ mol}, \quad n_b = 0.3125 \text{ mol}$$

$$\Delta S = (8.314 \text{ J/mol-K})[2.50 \ln (2.81/2.50)$$

$$+ 0.3125 \ln (2.81/0.3125)] = 8.14 \text{ J/K}$$

Reminder: Do not look up the solution to a problem until you have made a serious effort to solve it.

3.19 ΔS for the unmixing is the negative of ΔS in Eq.

$$(3.33), \text{ so } \Delta S = n_a R \ln x_a + n_b R \ln x_b = \\ (n_a + n_b) R (x_a \ln x_a + x_b \ln x_b). \text{ We have}$$

$$n_a + n_b = \frac{0.00100 \text{ g}}{(18.998 + 35.453) \text{ g/mol}} = 1.83_7 \times 10^{-5} \text{ mol}$$

$$\Delta S = (1.83_7 \times 10^{-5} \text{ mol})(1.987 \text{ cal/mol-K}) \\ \times (0.755 \ln 0.755 + 0.245 \ln 0.245) \\ = -2.03 \times 10^{-5} \text{ cal/K} = -8.50 \times 10^{-5} \text{ J/K}$$

3.20 To carry out the change of state reversibly, we put the part at T_2 in contact with a heat reservoir whose temperature is infinitesimally less than T_2 and wait until heat dq flows into the reservoir. Then we remove the reservoir from this part of the system and put the part at T_1 in contact with a heat reservoir whose temperature is infinitesimally greater than T_1 and wait until heat dq flows into the system part at T_1 . Since these two heat flows are reversible, we can use $dS = dq_{\text{rev}}/T$ to write the system's entropy change as $dS = dq/T_1 - dq/T_2$. (The entropy changes of the reservoirs are irrelevant to dS of the system.)

3.21 (a) q_H/T_H , 0, q_C/T_C , 0. (b) 0, 0, 0, 0, since each step is reversible.

3.22 ΔS_{univ} is 0 for a reversible process and positive for an irreversible process. Hence: (a) 0; (b) 0; (c) 0; (d) 0; (e) positive; (f) positive; (g) 0; (h) 0; (a) positive; (b) positive.

3.23 Assume that $dS = dq_{\text{rev}}/T$ is a state function such

that $\Delta S_{\text{univ}} \geq 0$ for any process. Let an anti-Clausius device exist. Such a device extracts heat $q > 0$ from a cold reservoir and deposits an equal amount of heat in the hot reservoir, with no other effects. For one cycle of such a device, $\Delta S_{\text{hot res.}} = q/T_H$, $\Delta S_{\text{cold res.}} = -q/T_C$, and $\Delta S_{\text{device}} = 0$ (since the process is cyclic). We have $\Delta S_{\text{univ}} = q/T_H - q/T_C = q(T_C - T_H)/T_C T_H < 0$, which violates the assumption that $\Delta S_{\text{univ}} \geq 0$. Hence an anti-Clausius device cannot exist. This completes the proof.

3.24 $-q_C/q_H = T_C^{1/2}/T_H^{1/2}$ and $T_C/T_H = q_C^2/q_H^2$. Thus $T/200.00^\circ\text{M} = q^2/q_{\text{tr}}^2$. But $|q|/|q_{\text{tr}}| = T/(273.16 \text{ K})$. Hence the Melvin temperature T is given by $T/200.00^\circ\text{M} = T^2/(273.16 \text{ K})^2$.

(a) For the steam point, $T = 373.13 \text{ K}$ and we find $T = 373.2^\circ\text{M}$. (b) For the ice point, $T = 273.15 \text{ K}$ and $T = 199.99^\circ\text{M}$.

3.25 $e_{\text{rev}} = 1 + q_C/q_H$ and $g = 1 - e_{\text{rev}} = -q_C/q_H$. We have $g(T_2, T_3) = -q_{2A}/q_3$ and $g(T_1, T_2) = -q_1/q_{2B} = q_1/q_{2A}$, so $g(T_2, T_3)g(T_1, T_2) = -q_1/q_3$.

3.26 (a) Substitution of $x = 3$ gives 0.002736 as the probability that $x \geq 3$. Hence $1 - 0.002736 = 0.9973$ is the probability that an observation is within 3 standard deviations from the mean. (b) Substitution of $x = 10^6$ gives the desired probability as $p = 8 \times 10^{-7} \times e^{-0.5 \times 10^{12}}$. If $e^z = 10^y$, then taking logs gives $z \log e = y$; hence

$y = -0.5 \times 10^{12} \times 0.434 = -2.2 \times 10^{11}$ and we have

$$p = 8 \times 10^{-7} \times 10^{-2.2 \times 10^{11}} \approx 10^{-2.2 \times 10^{11}}.$$

3.27 (a) The probability p of observing a deviation $\geq 10^6$ standard deviations in one observation is $10^{-2 \times 10^{11}}$.

The probability of not observing such a deviation in n trials is $(1 - 10^{-2 \times 10^{11}})^n$. For $(1 - 10^{-2 \times 10^{11}})^n = 0.5$,

the probability of not observing such a deviation is 0.5 and the probability of observing such a deviation is 0.5. We have $\ln 0.5 = n \ln (1 - 10^{-2 \times 10^{11}}) \approx -n \times 10^{-2 \times 10^{11}}$,

where Eq. (8.30) was used. We get $n = 0.7 \times 10^{2 \times 10^{11}}$.

There are 3×10^7 seconds in a year, so it takes $(0.7 \times 10^{200,000,000,000}) / (3 \times 10^7)$ years of measurements at the rate of one per second to reach the 50% probability.

(b) We want $1 - (1 - p)^n \geq 0.99$. Since $p = \frac{1}{2}$, we want $0.01 \geq 1/2^n$ or $2^n \geq 100$. The minimum value of n is 7.

3.28 (a) q cannot be calculated, since q depends on the path and the path is not specified. (b) The path-dependent quantity w cannot be calculated. (c) $dU = C_V dT = n\bar{C}_V dT$ and $\Delta U = \int_1^2 n\bar{C}_V dT = \int_1^2 n(a + bT) dT = na(T_2 - T_1) + \frac{1}{2}nb(T_2^2 - T_1^2) = (4.00 \text{ mol})(25.0 \text{ J/mol-K})(500 - 300)\text{K} + \frac{1}{2}(4.00 \text{ mol})(0.0300 \text{ J/mol-K}^2)(500^2 - 300^2)\text{K}^2 = 29.6 \text{ kJ}$.

(d) $\Delta H = \Delta U + \Delta(PV) = \Delta U + nR \Delta T = 29600 \text{ J} + (4.00 \text{ mol}) \times (8.314 \text{ J/mol-K})(200 \text{ K}) = 36.3 \text{ kJ}$. (e) From (3.29), $\Delta S = \int_1^2 (C_V/T) dT + nR \ln (V_2/V_1)$. But $C_V/T = n\bar{C}_V/T = n(a/T + b)$, so $\Delta S = n \int_1^2 (a/T + b) dT + nR \ln (V_2/V_1) =$

$$n_a \ln (T_2/T_1) + n_b(T_2 - T_1) + nR \ln[(nRT_2/P_2)/(nRT_1/P_1)] \\ = (4.00 \text{ mol})(25.0 \text{ J/mol-K}) \ln (500/300) + (4.00 \text{ mol}) \times \\ (0.0300 \text{ J/mol-K}^2)(500 - 300)\text{K} + (4.00 \text{ mol})(8.314 \text{ J/mol-K}) \times \\ \ln [(500 \text{ K})(2.00 \text{ atm})/(300 \text{ K})(3.00 \text{ atm})] = 78.6 \text{ J/K}.$$

3.29 (a) Rev; (b) irrev.; (c) irrev; (d) irrev; (e) irrev; (f) irrev; (g) rev.

3.30 (a) Since U and S are extensive, the 10 g has the higher U and the higher S . (b) The vapor; the vapor. (c) The 40°C benzene; the 40°C benzene. (d) If the system at 300 and 310 K is adiabatically enclosed, it will spontaneously go to the state at 305 K. Since S increases in a spontaneous adiabatic process, the 305-K system has the higher S . Since $q = 0$ and w is negligible for this process, the two systems have the same U .

3.31 Since $P dV + V dP = d(PV)$ and $dq_{\text{rev}}/T = dS$, (b) and (d) vanish. Also (c) and (f) vanish.

3.32 (a) C_p , k , U/T ; (b) \bar{C}_p , R .

3.33 The second law of thermodynamics is "hardly ever" violated.

3.34 Assume they do intersect. Join the adiabats with a reversible isotherm that passes above (or below) the intersection point. The closed curve so formed is a cyclic process. Let the cycle be traversed in the direction such that positive heat q flows into the system in the isothermal process, and let this heat come from a heat reservoir. The only heat transfer occurs along the isotherm, so the system undergoes a cycle in which it absorbs heat q from a reservoir and (since $\Delta U = q + w = 0$) converts

this heat entirely into work, with no other effects. Such a cycle violates the Kelvin-Planck statement of the second law and is therefore impossible. The initial assumption that two adiabats intersect is therefore false.

3.35 No. (A pilot plant using this method has been built.)

3.36 Suppose we could prepare a reservoir at $T_C = 0$ and could reduce the engine's temperature to absolute zero.

Then e_{rev} would become equal to 1. The Carnot cycle would convert the heat q_H completely into work. But this would violate the Kelvin-Planck statement of the second law.

Hence we can't achieve absolute zero. (See also Sec. 5.10 in the text.)

3.37 (a) $\Delta H = q_p = 0$. (b) Suppose the final state consisted of ice at 0°C , with no liquid present. A hypothetical path to attain this state is to warm the supercooled liquid from -10°C to 0°C and then to freeze all the liquid at 0°C . ΔH for warming the liquid is $(1.00 \text{ cal/g}\cdot\text{K})(10.0 \text{ g})(10.0 \text{ K}) = 100 \text{ cal}$ and ΔH for freezing all the liquid is $-(79.7 \text{ cal/g})(10.0 \text{ g}) = -797 \text{ cal}$.

The overall ΔH is -697 cal , which is not 0. Hence the equilibrium state is not ice at 0°C . If the equilibrium state were all ice below 0°C , ΔH would be even more negative than -697 cal , and hence this is not the equilibrium state. Therefore the equilibrium state must consist of ice and liquid water in equilibrium at 0°C . To satisfy the condition that $\Delta H = 0$, the mass m_{ice} of ice produced

must satisfy $-(79.7 \text{ cal/g})m_{\text{ice}} = -100 \text{ cal}$ and $m_{\text{ice}} = 1.25 \text{ g}$. The mass of liquid remaining is $10.0 \text{ g} - 1.25 \text{ g} = 8.75 \text{ g}$. (c) A reversible path for the process is

liq. at $-10^\circ\text{C} \xrightarrow{a} \text{liq. at } 0^\circ\text{C} \xrightarrow{b} m_{\text{ice}} + m_{\text{liq}} \text{ at } 0^\circ\text{C}$

$$\Delta S = \Delta S_a + \Delta S_b = (10.0 \text{ g})(1.00 \text{ cal/g-K}) \ln (273/263) - (79.7 \text{ cal/g})(1.25 \text{ g})/(273 \text{ K}) = 0.373 \text{ cal/K} - 0.365 \text{ cal/K} = 0.008 \text{ cal/K}, \text{ where (3.30) and (3.27) were used.}$$

3.38 (a) False. (b) False. (c) True. (d) False. (e) True.

3.39 (a) False. (For example, a nonideal gas expanding into vacuum can undergo a change in T--the Joule experiment.) (b) True. (c) False; S increases in an irreversible process in an isolated system. (d) False. For example, a Carnot cycle is reversible, has $\Delta V = 0$ and has $w \neq 0$.

CHAPTER 4

4.1 Processes a and b are reversible, isothermal, and isobaric and have $\Delta S = q_p/T$. (a) $\Delta G = \Delta H - T \Delta S = q_p - T(q_p/T) = 0$. $\Delta A = \Delta U - T \Delta S = q_p + w - T(q_p/T) = w = -\int_1^2 P dV = -P \Delta V = -(1 \text{ atm})[(36.0 \text{ g})/(1.000 \text{ g/cm}^3) - (36.0 \text{ g})/(0.958 \text{ g/cm}^3)] = (1.58 \text{ cm}^3 \text{ atm})(8.314 \text{ J}/82.06 \text{ cm}^3\text{-atm}) = 0.160 \text{ J}$. (b) As in (a), $\Delta G = 0$ and $\Delta A = w = -P \Delta V = -P(V_{\text{gas}} - V_{\text{liq}}) \approx -PV_{\text{gas}} = -nRT = -(0.50 \text{ mol}) \times (8.314 \text{ J/mol-K})(353.2 \text{ K}) = -1.47 \text{ kJ}$. (c) Since the gas is perfect, the final T is 300 K. $\Delta H = 0$ and $\Delta U = 0$, since U and H depend only on T for a perfect gas. From (3.29), $\Delta S = nR \ln (V_2/V_1) = (0.100 \text{ mol})(8.314 \text{ J/mol-K}) \ln (6.00/2.00) = 0.91_3 \text{ J/K}$. $\Delta G = \Delta H - T \Delta S = 0 - (300 \text{ K})(0.91_3 \text{ J/K}) = -274 \text{ J}$. $\Delta A = \Delta U - T \Delta S = -274 \text{ J}$.

4.2 For $dH = T dS + V dP = M dx + N dy$, we have $M = T$, $N = V$, $x = S$, $y = P$, and $(\partial M/\partial y)_x = (\partial N/\partial x)_y$ gives $(\partial T/\partial P)_S = (\partial V/\partial S)_P$. The equations in (4.45) are derived similarly from Eqs. (4.35) and (4.36).

4.3 (a) Use of $(\partial U/\partial V)_T = \alpha T/K - P$ gives

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{(3.04 \times 10^{-4} \text{ K}^{-1})(303.15 \text{ K})}{4.52 \times 10^{-5} \text{ atm}^{-1}} - 1 \text{ atm} = 2040 \text{ atm}$$

(b) Use of $\mu_{JT} = \bar{V}(\alpha T - 1)/\bar{C}_P$ gives μ_{JT} as

$$\frac{18.1 \text{ cm}^3/\text{mol}}{17.99 \text{ cal/mol-K}} [(3.04 \times 10^{-4} \text{ K}^{-1})(303.1 \text{ K}) - 1]$$

$$\times (1.987 \text{ cal})/(82.06 \text{ cm}^3\text{-atm}) = -0.0221 \text{ K/atm}$$

4.4 From (4.53), $\bar{C}_P - \bar{C}_V = T\bar{V}\alpha^2/\kappa$. We have $\bar{V} = M/\rho = (119.4 \text{ g/mol})/(1.49 \text{ g/cm}^3) = 80.1 \text{ cm}^3/\text{mol}$ and $T\bar{V}\alpha^2/\kappa = (298 \text{ K})(80.1 \text{ cm}^3/\text{mol})(1.33 \times 10^{-3} \text{ K}^{-1})^2/(9.8 \times 10^{-5} \text{ atm}^{-1}) = (431 \text{ cm}^3\text{-atm/mol-K})(8.314 \text{ J/82.06 cm}^3\text{-atm}) = 44 \text{ J/mol-K}$. Then $\bar{C}_V = (116 - 44) \text{ J/mol-K} = 72 \text{ J/mol-K}$.

4.5 Division of Eq. (4.30) by n gives $(\partial\bar{H}/\partial T)_P = \bar{C}_P$. For (b), we use (4.48) divided by n ; for (c), (4.47); for (d), (4.49)/ n ; for (e), (4.50)/ n ; for (f), (4.53)/ n ; for (g), we use $(\partial A/\partial V)_T = -P$, which follows from (4.35).

Substitution of numerical values gives: (a) $(\partial\bar{H}/\partial T)_P = \bar{C}_P = 40 \text{ cal/mol-K}$; (b) $(\partial\bar{H}/\partial P)_T = \bar{V} - T\bar{V}\alpha = 50 \text{ cm}^3/\text{mol} - (298 \text{ K})(50 \text{ cm}^3/\text{mol})(10^{-3} \text{ K}^{-1}) = 35 \text{ cm}^3/\text{mol} = (35 \text{ cm}^3/\text{mol})(1.99 \text{ cal/82 cm}^3\text{-atm}) = 0.85 \text{ cal/atm-mol}$; (c) $(\partial U/\partial V)_T = \alpha T/\kappa - P = (10^{-3} \text{ K}^{-1})(298 \text{ K})/(10^{-4} \text{ atm}^{-1}) - 1 \text{ atm} = 3000 \text{ atm} = (3000 \text{ atm})(1.99 \text{ cal})/(82 \text{ cm}^3 \text{ atm}) = 70 \text{ cal/cm}^3$; (d) $(\partial\bar{S}/\partial T)_P = \bar{C}_P/T = (40 \text{ cal/mol-K})/(298 \text{ K}) = 0.13 \text{ cal/mol-K}^2$; (e) $(\partial\bar{S}/\partial P)_T = -\alpha\bar{V} = -(10^{-3} \text{ K}^{-1})(50 \text{ cm}^3/\text{mol})(1.99 \text{ cal})/(82 \text{ cm}^3 \text{ atm}) = -0.0012 \text{ cal/mol-K-atm}$; (f) $\bar{C}_V = \bar{C}_P - T\bar{V}\alpha^2/\kappa = (40 \text{ cal/mol-K}) - (298 \text{ K})(50 \text{ cm}^3/\text{mol})(10^{-6} \text{ K}^{-2})/(10^{-4} \text{ atm}^{-1}) = 40 \text{ cal/mol-K} - (150 \text{ cm}^3\text{-atm/mol-K})(1.99 \text{ cal/82 cm}^3\text{-atm}) = 40 \text{ cal/mol-K} - 3.6 \text{ cal/mol-K} = 36 \text{ cal/mol-K}$; (g) $(\partial A/\partial V)_T = -P = -(1 \text{ atm})(1.99 \text{ cal/82 cm}^3\text{-atm}) = -0.024 \text{ cal/cm}^3$, where (1.19) and (1.21) were used.

4.6 (a) The Gibbs equation $dU = T dS - P dV$ becomes $dU_T = T dS_T - P dV_T$ at constant T . Division by dP_T gives $dU_T/dP_T = T dS_T/dP_T - P dV_T/dP_T$ or $(\partial U/\partial P)_T = T(\partial S/\partial P)_T - P(\partial V/\partial P)_T$. But the Maxwell equation (4.45) gives $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$, so $(\partial U/\partial P)_T = -T(\partial V/\partial T)_P - P(\partial V/\partial P)_T = -TV\alpha + PV\kappa$. (b) From (1.35) we have $(\partial U/\partial P)_T = (\partial U/\partial V)_T(\partial V/\partial P)_T = -(\partial U/\partial V)_T\kappa V$. Substitution of (4.47) gives the desired result.

4.7 (a) At constant P , $dU_P = T dS_P - P dV_P$. Division by dT_P gives $(\partial U/\partial T)_P = T(\partial S/\partial T)_P - P(\partial V/\partial T)_P = C_P - PV\alpha$, where (4.31) and (4.39) were used. (b) $C_P = (\partial H/\partial T)_P = [\partial(U + PV)/\partial T]_P = (\partial U/\partial T)_P + P(\partial V/\partial T)_P$, so $(\partial U/\partial T)_P = C_P - P(\partial V/\partial T)_P = C_P - PV\alpha$.

4.8 At constant T , we have $dH_T = T dS_T + V dP_T$. Division by dV_T gives $(\partial H/\partial V)_T = T(\partial S/\partial V)_T + V(\partial P/\partial V)_T = T(\partial P/\partial T)_V + V(\partial P/\partial V)_T = \alpha T/\kappa - 1/\kappa$, where (4.45), (1.42), (1.44), and (1.32) were used.

4.9 Differentiation followed by use of (4.51) gives

$$\left(\frac{\partial(GT^{-1})}{\partial T} \right)_P = -\frac{1}{T^2} G + \frac{1}{T} \left(\frac{\partial G}{\partial T} \right)_P = -\frac{H - TS}{T^2} - \frac{S}{T} = -\frac{H}{T^2}$$

4.10 From (2.62), $\mu_J = -(\partial U/\partial V)_T/C_V$. Use of (4.47) gives the desired result.

4.11 Replacement of z , x , u , y in (1.35) with S , H , T , P gives

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial H}\right)_P \left(\frac{\partial H}{\partial T}\right)_P = \frac{(\partial H/\partial T)_P}{(\partial H/\partial S)_P} = \frac{C_P}{T}$$

where $(\partial H/\partial S)_P = T$ [which follows from (4.34) with $dP = 0$] and (4.30) were used.

Reminder: Don't look up the solution to a problem until you have made a serious effort to solve it.

4.12 $\bar{V} = RT/P + bRT.$

$$\alpha = \frac{1}{\bar{V}} \left(\frac{\partial \bar{V}}{\partial T}\right)_P = \frac{1}{\bar{V}} \frac{R + bPR}{P} \quad K = - \frac{1}{\bar{V}} \left(\frac{\partial \bar{V}}{\partial P}\right)_T = \frac{RT}{\bar{V}P^2}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{\alpha T}{K} - P = (1 + bP)P - P = bP^2$$

$$\bar{C}_P - \bar{C}_V = T\bar{V}\alpha^2/K = \frac{(R + bPR)^2}{R} = R(1 + bP)^2$$

$$\mu_{JT} = \frac{V}{C_P} (\alpha T - 1) = \frac{V}{C_P} \left(\frac{RT(1 + bP)}{P\bar{V}} - 1 \right) = \frac{V}{C_P} \left(\frac{P\bar{V}}{P\bar{V}} - 1 \right) = 0$$

4.13

$$\begin{aligned} \left(\frac{\partial C_P}{\partial P}\right)_T &= \left[\frac{\partial}{\partial P} \left(\frac{\partial H}{\partial T}\right)_P \right]_T = \left[\frac{\partial}{\partial T} \left(\frac{\partial H}{\partial P}\right)_T \right]_P = \left\{ \frac{\partial}{\partial T} \left[-T \left(\frac{\partial V}{\partial T}\right)_P + V \right] \right\}_P \\ &= - \left(\frac{\partial V}{\partial T}\right)_P - T \left(\frac{\partial^2 V}{\partial T^2}\right)_P + \left(\frac{\partial V}{\partial T}\right)_P = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P \end{aligned}$$

4.14 (a) $V = V_0 + aV_0(T - 273 \text{ K}) + bV_0(T - 273 \text{ K})^2,$
 $(\partial V/\partial T)_P = aV_0 + 2bV_0(T - 273 \text{ K})$ and $(\partial^2 V/\partial T^2)_P = 2bV_0.$

$$(\partial \bar{C}_P / \partial P)_T = -T(\partial^2 \bar{V} / \partial T^2)_P = -2b\bar{V}_0 T, \text{ so}$$

$$\begin{aligned} \left(\frac{\partial \bar{C}_P}{\partial P} \right)_T &= -2(0.78 \times 10^{-8} \text{ K}^{-2})(298 \text{ K}) \frac{200.6 \text{ g/mol}}{13.595 \text{ g/cm}^3} \\ &= -6.8_6 \times 10^{-5} \text{ cm}^3 \text{ K}^{-1} \text{ mol}^{-1} \frac{1.987 \text{ cal}}{82.06 \text{ cm}^3 \text{ atm}} \\ &= -1.66 \times 10^{-6} \text{ cal/mol-K-atm} \end{aligned}$$

$$(b) \Delta \bar{C}_P \approx (\partial \bar{C}_P / \partial P)_T \Delta P =$$

$$(-1.66 \times 10^{-6} \text{ cal/mol-K-atm})(10^4 \text{ atm}) = -0.02 \text{ cal/mol-K.}$$

$$\bar{C}_P = 6.66 \text{ cal/mol-K} - 0.02 \text{ cal/mol-K} = 6.64 \text{ cal/mol-K.}$$

4.15 (a) $C_P - C_V = TV\alpha^2/\kappa$. As in Prob. 1.39, $\alpha = (1/\bar{V}) \times$

$(c_2 + 2c_3T - c_5P)$ and $\kappa = (c_4 + c_5T)/\bar{V}$. So $C_P - C_V =$

$nT(c_2 + 2c_3T - c_5P)^2/(c_4 + c_5T)$, since $V/\bar{V} = n$. (b)

$(\partial U/\partial V)_T = \alpha T/\kappa - P = T(c_2 + 2c_3 - c_5P)/(c_4 + c_5T) - P.$

(c) $(\partial S/\partial P)_T = -\alpha V = -n(c_2 + 2c_3T - c_5P)$. (d) $\mu_{JT} =$

$(\bar{V}/\bar{C}_P)(\alpha T - 1) = (T/\bar{C}_P)(c_2 + 2c_3T - c_5P) - \bar{V}/\bar{C}_P.$ (e)

$(\partial S/\partial T)_P = C_P/T$. (f) $(\partial G/\partial P)_T = V.$

4.16 (a) $(\partial V/\partial T)_S = 1/(\partial T/\partial V)_S = -1/(\partial P/\partial S)_V = -(\partial S/\partial P)_V$

$= -(\partial S/\partial T)_V(\partial T/\partial P)_V = -(C_V/T)/(\partial P/\partial T)_V = -C_V\kappa/\alpha T$, where

(1.45) was used. Hence $\alpha_S = -C_V\kappa/TV\alpha$. (b) For a perfect gas, $\alpha = 1/T$ and $\kappa = 1/P$ [Eqs. (1.46) and (1.47)], so α_S

$= -C_V/PV = -C_V/nRT = -\bar{C}_V/RT = V^{-1}(\partial V/\partial T)_S$, so $dV/V =$

$-(\bar{C}_V/RT) dT$ at constant \bar{S} and $\ln(V_2/V_1) = (\bar{C}_V/R) \times \bar{C}_V/R$

$\ln(T_1/T_2) = \ln(T_1/T_2)^{\bar{C}_V/R}$; hence $V_2/V_1 = (T_1/T_2)^{\bar{C}_V/R}$

or $T_2/T_1 = (V_1/V_2)^{R/\bar{C}_V}$. (c) $(\partial V/\partial P)_S = (\partial V/\partial T)_S(\partial T/\partial P)_S$.

From (a), $(\partial V/\partial T)_S = -C_V\kappa/\alpha T$. From (4.44), $(\partial T/\partial P)_S =$

$$\begin{aligned}
 (\partial V/\partial S)_P &= [(\partial S/\partial V)_P]^{-1} = [(\partial S/\partial T)_P(\partial T/\partial V)_P]^{-1} = \\
 (C_P/T)^{-1}(\partial V/\partial T)_P &= (T/C_P)\alpha_V = \alpha_TV/C_P. \text{ So } (\partial V/\partial P)_S = \\
 (-C_V\kappa/\alpha T)(\alpha_TV/C_P) &= -C_V\kappa V/C_P; \kappa_S = -V^{-1}(\partial V/\partial P)_S = C_V\kappa/C_P.
 \end{aligned}$$

4.17 For a gas not at high pressure, $\bar{C}_P - \bar{C}_V \approx R = 2 \text{ cal/mol-K}$. The \bar{C}_P and \bar{C}_V data after Eq. (4.54) show that $\bar{C}_P - \bar{C}_V$ for solids is usually less than 2 cal/mol-K and for liquids is usually greater than 2 cal/mol-K. Therefore $\bar{C}_P - \bar{C}_V$ is largest for liquids and smallest for solids.

4.18 $(\partial H/\partial P)_T = V - T(\partial V/\partial T)_P$. For an ideal gas, $V = nRT/P$ and $(\partial V/\partial T)_P = nR/P$, so $(\partial H/\partial P)_T = nRT/P - T(nR/P) = 0$.

4.19 (a) As noted preceding Eq. (4.57),

$$\begin{aligned}
 \bar{U}_{\text{intermol}}(T, V') &= \bar{U}(T, V') - \bar{U}(T, \infty) = \int_{\infty}^{V'} (\partial \bar{U}/\partial \bar{V})_T dV = \\
 \int_{\infty}^{V'} (a/\bar{V}^2) dV &= -a/\bar{V} \Big|_{\infty}^{V'} = -a/\bar{V}'. \quad (\text{b}) \text{ At } 25^\circ\text{C and } 1 \text{ atm,} \\
 \bar{V} = RT/P &= 24500 \text{ cm}^3/\text{mol and } \bar{U}_{\text{intermol}} = -a/\bar{V} = \\
 -(10^6 \text{ to } 10^7)(\text{cm}^6\text{-atm/mol}^2)/ & (24500 \text{ cm}^3/\text{mol}) = \\
 (-40 \text{ to } -400)(\text{cm}^3\text{-atm/mol})(1.99 \text{ cal/} & 82 \text{ cm}^3\text{-atm}) = \\
 -1 \text{ to } -10 \text{ cal/mol, where (1.19) and (1.21) were used.} \\
 \text{At } 25^\circ\text{C and } 40 \text{ atm, } \bar{V} \approx RT/P &= 610 \text{ cm}^3/\text{mol and } \bar{U}_{\text{intermol}} \\
 \approx -40 \text{ to } -400 \text{ cal/mol.}
 \end{aligned}$$

4.20 (a) The c and d values are given after Eq. (4.57). We have $c/\bar{V} = (3.22 \times 10^6 \text{ J cm}^3/\text{mol}^2)/(114 \text{ cm}^3/\text{mol}) = 2.82 \times 10^4 \text{ J/mol}$ and $d/9\bar{V}^9 = (4.88 \times 10^{21} \text{ J cm}^{27}/\text{mol}^{10})/$

$9(114 \text{ cm}^3/\text{mol})^9 = 167 \text{ J/mol}$. The repulsive term $d/9\bar{V}^9$ is only 0.6% as large as the absolute value of the attractive term and is quite negligible. (b) At $\bar{V} = 104 \text{ cm}^3/\text{mol}$, we find $c/\bar{V} = 3.10 \times 10^4 \text{ J/mol}$ and $d/9\bar{V}^9 = 381 \text{ J/mol}$, so the repulsive term is 1.2% as large as the absolute value of the attractive term. (c) At $94 \text{ cm}^3/\text{mol}$, we get $c/\bar{V} = 3.43 \times 10^4 \text{ J/mol}$ and $d/9\bar{V}^9 = 946 \text{ J/mol}$, and the repulsive term is 2.8% as large as the absolute value of the attractive term.

4.21 (a) $\Delta \bar{U}_{\text{vap}} \approx -\bar{U}_{\text{intermol}}$. We have $\bar{U}_{\text{intermol}} = -(3.22 \times 10^6 \text{ J cm}^3/\text{mol}^2)/(106.6 \text{ cm}^3/\text{mol}) + (4.88 \times 10^{21} \text{ J cm}^{27} \text{ mol}^{-10})/9(106.6 \text{ cm}^3/\text{mol})^9 = -3.02 \times 10^4 \text{ J/mol} + 305 \text{ J/mol} = -2.99 \times 10^4 \text{ J/mol}$ and $\Delta \bar{U}_{\text{vap}} \approx 29.9 \text{ kJ/mol}$. (b) $\Delta \bar{U}_{\text{vap}} = \Delta \bar{H}_{\text{vap}} - \Delta(P\bar{V})_{\text{vap}}$. $\bar{V}_{\text{gas}} - \bar{V}_{\text{liq}} = RT/P - 107 \text{ cm}^3/\text{mol} = 25200 \text{ cm}^3/\text{mol}$. $\Delta \bar{U}_{\text{vap}} = (6400 \text{ cal/mol})(4.184 \text{ J/cal}) - (1 \text{ atm})(25200 \text{ cm}^3/\text{mol}) \times (8.314 \text{ J})/(82.06 \text{ cm}^3 \text{ atm}) = 24.2 \text{ kJ/mol}$.

4.22 (a) We use the van der Waals expression $-a/\bar{V}$ from Prob. 4.19a to approximate $\bar{U}_{\text{intermol}}$ in both liquid and gaseous Ar. We have $a = (1.34 \times 10^6 \text{ cm}^6 \text{ atm mol}^{-2}) \times (8.314 \text{ J}/82.06 \text{ cm}^3 \text{ atm}) = 1.36 \times 10^5 \text{ J cm}^3 \text{ mol}^{-2}$. The molar translational kinetic energy is $\bar{U}_{\text{tr}} = \frac{3}{2}RT = 1.5(8.314 \text{ J/mol-K})T = (12.5 \text{ J/mol-K})T$. The molar electronic energy is a constant (except at very high T). Addition of \bar{U}_{tr} , $\bar{U}_{\text{intermol}}$, and \bar{U}_{el} gives the desired

result. (b) For the liquid, $\bar{V}_{\text{liq}} = M/\rho = (39.95 \text{ g/mol})/(1.38 \text{ g/cm}^3) = 28.9 \text{ cm}^3/\text{mol}$. For the gas, $\bar{V}_{\text{gas}} = RT/P = 7160 \text{ cm}^3/\text{mol}$. We have $\bar{U}_{\text{intermol,liq}} \approx -a/\bar{V}_{\text{liq}} = -(1.36 \times 10^5 \text{ J cm}^3 \text{ mol}^{-2})/(28.9 \text{ cm}^3/\text{mol}) = -4710 \text{ J/mol}$ and $\bar{U}_{\text{intermol,gas}} \approx -a/\bar{V}_{\text{gas}} = -19 \text{ J/mol}$. For both the liquid and the gas, $\bar{U}_{\text{tr}} = 3RT/2 = 1090 \text{ J/mol}$. (c) $\Delta \bar{U}_{\text{vap}} = \bar{U}_{\text{intermol,gas}} - \bar{U}_{\text{intermol,liq}} \approx -19 \text{ J/mol} + 4710 \text{ J/mol} = 4700 \text{ J/mol}$, which isn't too far from the true value.

4.23 Each process is isothermal, so $\Delta A = \Delta U - T \Delta S$ and $\Delta G = \Delta H - T \Delta S$. (For q , w , ΔU and ΔH , see the answers to Prob. 2.33.) (a) $\Delta U = q + w$ and $\Delta S = q/T$, so $\Delta A = w$. Since $w < 0$, we have $\Delta A < 0$. Since $\Delta H = q$, $\Delta G = q - q = 0$. (b) The same as (a), except that $w > 0$ and $\Delta A > 0$. (d) $\Delta U = 0 = \Delta H$. $\Delta A = -T \Delta S = -T(q/T) = -q = w < 0$. Also, $\Delta G = -T \Delta S < 0$. (e) $\Delta U = 0 = \Delta H$. For this irreversible adiabatic process, ΔS is positive and $\Delta A = -T \Delta S$ is negative. Also, $\Delta G = -T \Delta S$ is negative. (f) The same as (e).

4.24 Since T is constant, we have $\Delta A = \Delta U - T \Delta S$ and $\Delta G = \Delta H - T \Delta S$. From Prob. 2.38c, $\Delta H = 0$ and $\Delta U = 0$. From Prob. 3.11c, $\Delta S = 8.06 \text{ J/K}$. So $\Delta A = 0 - (400 \text{ K})(8.06 \text{ J/K}) = -3220 \text{ J}$ and $\Delta G = -3220 \text{ J}$.

4.25 Each is zero, since the process is cyclic.

4.26 (a) $\Delta G = \Delta H - T \Delta S = \Delta H - T(\Delta H/T) = 0$, as it must be for a reversible (equilibrium) process at constant T and

P. (b) From Prob. 3.15, $\Delta S = -2.73 \text{ cal/K}$. For the reversible path in Fig. 3.7, ΔH for each step is:

$$\Delta H_1 = (1.01 \text{ cal/g-K})(10.0 \text{ g})(10 \text{ K}) = 101 \text{ cal},$$

$$\Delta H_2 = -(79.7 \text{ cal/g})(10.0 \text{ g}) = -797 \text{ cal},$$

$$\Delta H_3 = -(0.50 \text{ cal/g-K})(10.0 \text{ g})(10 \text{ K}) = -50 \text{ cal}.$$

The overall process therefore has $\Delta H = -746 \text{ cal}$. For the isothermal process at -10°C , we have $\Delta G = \Delta H - T\Delta S = -746 \text{ cal} - (263.15 \text{ K})(-2.73 \text{ cal/K}) = -28 \text{ cal}$.

4.27 Since T is constant and U and H of ideal gases depend on T only, $\Delta U = 0$ and $\Delta H = 0$. From (3.33), $\Delta S = -0.200 \text{ mol R} \ln 0.400 - 0.300 \text{ mol R} \ln 0.600 = 2.80 \text{ J/K}$.
 $\Delta A = \Delta U - T \Delta S = -T \Delta S = -(300 \text{ K})(2.80 \text{ J/K}) = -840 \text{ J}$.
 $\Delta G = \Delta H - T \Delta S = -T \Delta S = -840 \text{ J}$.

4.28 Let the path be

$$(27^\circ\text{C}, 1 \text{ atm}) \xrightarrow{a} (100^\circ\text{C}, 1 \text{ atm}) \xrightarrow{b} (100^\circ\text{C}, 50 \text{ atm})$$

where step (a) is isobaric and step (b) is isothermal.

For a liquid, V varies rather slowly with T and P .

(a) Use of (4.63) with C_p , α , and V assumed constant gives

$$\Delta H_a = C_p(T_2 - T_1) = (18.0 \text{ cal/K})(73 \text{ K}) = 1310 \text{ cal} = 5.50 \text{ kJ}$$

$$\Delta H_b = (V - TV\alpha)(P_2 - P_1) =$$

$$\begin{aligned} & [18.1 \text{ cm}^3 - (373 \text{ K})(18.1 \text{ cm}^3)(3.04 \times 10^{-4} \text{ K}^{-1})](49 \text{ atm}) \\ & \times \frac{1.987 \text{ cal}}{82.06 \text{ cm}^3 \text{ atm}} = 19 \text{ cal} = 0.080 \text{ kJ} \end{aligned}$$

$$\Delta H = \Delta H_a + \Delta H_b = 1.33 \text{ kcal} = 5.58 \text{ kJ}$$

(b) $\Delta U = \Delta H - \Delta(PV)$. Since V changes only slightly,
 $\Delta(PV) \approx V \Delta P = (18.1 \text{ cm}^3)(49 \text{ atm}) = 887 \text{ cm}^3 \text{ atm} =$
 $(887 \text{ cm}^3 \text{ atm})(1.987 \text{ cal}/82.06 \text{ cm}^3\text{-atm}) = 21 \text{ cal} = 90 \text{ J}.$
 $\Delta U = 1330 \text{ cal} - 21 \text{ cal} = 1.31 \text{ kcal} = 5.49 \text{ kJ}.$

(c) Use of (4.60) [or (4.61) and (4.62)] with C_p , α , and V assumed constant gives $\Delta S_a = C_p \ln(T_2/T_1) =$
 $(18.0 \text{ cal/K}) \ln(373/300) = 3.92 \text{ cal/K} = 16.4 \text{ J/K};$

$$\Delta S_b = -\alpha V(P_2 - P_1) =$$

$$-(3.04 \times 10^{-4} \text{ K}^{-1})(18.1 \text{ cm}^3)(49 \text{ atm}) \frac{1.987 \text{ cal}}{82.06 \text{ cm}^3 \text{ atm}}$$

$$= -0.0065 \text{ cal/K} = -0.027 \text{ J/K}$$

$$\Delta S = \Delta S_a + \Delta S_b = 3.91 \text{ cal/K} = 16.4 \text{ J/K}$$

4.29 $dG = -S dT + V dP = V dP$ at constant T .

$\Delta G = V \Delta P$ at constant T and V .

$$\Delta G = \frac{30.0 \text{ g}}{0.997 \text{ g/cm}^3} 99.0 \text{ atm} \frac{1.987 \text{ cal}}{82.06 \text{ cm}^3 \text{ atm}} = 72.1 \text{ cal}$$

$$= 302 \text{ J}$$

4.30 $\bar{V} = RT/P + bRT + cRTP$. $\alpha = (1/\bar{V})(\partial \bar{V}/\partial T)_P =$
 $(1/\bar{V})(R/P + bR + cRP)$. Use the path

$$(P_1, T_1) \xrightarrow{a} (P_1, T_2) \xrightarrow{b} (P_2, T_2)$$

where step (a) is isobaric and step (b) is isothermal.

$$\bar{V} - T\bar{V}\alpha = RT/P + bRT + cRTP - (RT/P + bRT + cRTP) = 0.$$

Equation (4.63) gives $\Delta \bar{H}_a = \int_{T_1}^{T_2} \bar{C}_P dT = \bar{C}_P(T_2 - T_1)$ and

$\Delta \bar{H}_b = 0$. Then $\Delta \bar{H} = \Delta \bar{H}_a + \Delta \bar{H}_b = \bar{C}_P(T_2 - T_1)$, where \bar{C}_P is assumed constant. From (4.60) with \bar{C}_P constant:

$$\Delta \bar{S}_a = \bar{C}_P \ln (T_2/T_1)$$

$$\Delta \bar{S}_b = -\int_1^2 (R/P + bR + cRP) dP$$

$$= R \ln (P_1/P_2) + bR(P_1 - P_2) + \frac{1}{2}cR(P_1^2 - P_2^2)$$

$$\Delta \bar{S} = \Delta \bar{S}_a + \Delta \bar{S}_b = \text{etc.}$$

4.31 From Prob. 4.16c, $(\partial V/\partial P)_S = -V\kappa_S$ and $\Delta V_S \approx -V\kappa_S \Delta P_S$
 $= -V\kappa(C_V/C_P) \Delta P_S$. From (4.54) and preceding data:

$$\begin{aligned} \Delta V_S &\approx -(18.1 \text{ cm}^3)(4.52 \times 10^{-5}/\text{atm})(17.72/17.99)(9.00 \text{ atm}) \\ &= -7.25 \times 10^{-3} \text{ cm}^3 \end{aligned}$$

$$\text{We have } V_{\text{final}} = 18.1 \text{ cm}^3 - 0.007 \text{ cm}^3 = 18.1 \text{ cm}^3.$$

From Prob. 4.16a, $(\partial V/\partial T)_S = \alpha_S V$ and $\Delta V_S \approx \alpha_S V \Delta T_S$, so
 $\Delta T_S \approx \Delta V_S / \alpha_S V = -\Delta V_S (\alpha T / C_V \kappa)$.

$$\begin{aligned} \Delta T_S &\approx 0.00725 \text{ cm}^3 \frac{(3.04 \times 10^{-4} \text{ K}^{-1})(303.15 \text{ K})}{(17.72 \text{ cal/K})(4.52 \times 10^{-5}/\text{atm})} \\ &\times \frac{1.987 \text{ cal}}{82.06 \text{ cm}^3 \text{ atm}} = 0.0202 \text{ K}, \quad T_{\text{final}} = 30.02^\circ\text{C} \end{aligned}$$

We have $dU = (\partial U/\partial T)_V dT + (\partial U/\partial V)_T dV = C_V dT +$
 $(\partial U/\partial V)_T dV$ and $\Delta U \approx C_V \Delta T + (\partial U/\partial V)_T \Delta V$. Equation
 (4.47) gives $(\partial U/\partial V)_T = \alpha T / \kappa - P$. We neglect the T and P
 variation of α and κ . Also, since $\alpha T / \kappa \gg P$, we can use an
 average P with little error. Thus we take $(\partial U/\partial V)_T$ as

$$\begin{aligned} &\left[\frac{(3.04 \times 10^{-4} \text{ K}^{-1})(303 \text{ K})}{4.52 \times 10^{-5} \text{ atm}^{-1}} - 5.5 \text{ atm} \right] \frac{1.987 \text{ cal}}{82.06 \text{ cm}^3 \text{ atm}} \\ &(\partial U/\partial V)_T = 49.2 \text{ cal/cm}^3 \end{aligned}$$

$$\Delta U \approx (17.72 \text{ cal/K})(0.0202 \text{ K}) + (49.2 \text{ cal/cm}^3)(-0.00725 \text{ cm}^3)$$

$$\Delta U \approx 0.001 \text{ cal}, \quad \Delta U = q + w = w = 0.001 \text{ cal}$$

4.32 We have $dU = (\partial U/\partial T)_V dT + (\partial U/\partial V)_T dV = C_V dT + (\partial U/\partial V)_T dV$. Integrating and using a path similar to that in Fig. 4.5 but with V as the vertical axis, we get $\Delta U = \int_{T_1}^{T_2} C_V dT + \int_{V_1}^{V_2} (\partial U/\partial V)_T dV$. Using $(\partial U/\partial V)_T = a/\bar{V}^2 = an^2/V^2$ for a van der Waals gas, we have $\Delta U = \int_{T_1}^{T_2} C_V dT - an^2/V_2 + an^2/V_1$. If C_V is approximately constant over the temperature interval, then $\Delta U \approx C_V(T_2 - T_1) + an^2(1/V_1 - 1/V_2)$ for a van der Waals gas.

4.33 Set $dS = 0$, $dP = 0$, and $dn_{j \neq 1} = 0$ in Eq. (4.76). Then set $dT = 0$, $dV = 0$, and $dn_{j \neq 1} = 0$ in (4.77).

4.34 For a closed system, $dU = dq + dw$. For a mechanically reversible process in a closed system with P-V work only, $dw = -P dV$ and $dU = dq - P dV$. Equating this expression for dU to that in (4.74), we get $dq = T dS + \sum_i \mu_i dn_i$ under the conditions stated in (4.73).

4.35 Use of (4.88) gives the following results.

(a) $\mu_{\text{H}_2\text{O}(\text{solid})} = \mu_{\text{H}_2\text{O}(\text{liquid})}$; (b) $\mu_{\text{sucrose}(\text{solid})} = \mu_{\text{sucrose}(\text{in solution})}$; (c) $\mu_{\text{ether}(\text{in water phase})} = \mu_{\text{ether}(\text{in ether phase})}$ and $\mu_{\text{water}(\text{in ether phase})} = \mu_{\text{water}(\text{in water phase})}$.

4.36 The more-stable phase at the given T and P has the lower μ . (a) $\text{H}_2\text{O}(\text{g})$; (b) neither; the two phases are in equilibrium and have equal μ 's; (c) $\text{H}_2\text{O}(\text{l})$; (d) $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$; substance i flows out of the phase with the higher μ_i ; (e) neither; (f) $\text{C}_6\text{H}_{12}\text{O}_6(\text{aq})$; (g) $\text{H}_2\text{O}(\text{g})$, since $\mu = \bar{G}$ for a pure substance.

4.37 $\mu_{\text{H}_2\text{O}(\text{s})} = \mu_{\text{H}_2\text{O}(\text{l})} = \bar{G}_{\text{H}_2\text{O}(\text{s})} = \bar{G}_{\text{H}_2\text{O}(\text{l})}$, since $\mu = \bar{G}$ for a pure substance. Multiplication by n gives $G_{\text{H}_2\text{O}(\text{s})} = G_{\text{H}_2\text{O}(\text{l})}$ or $\Delta G = G_{\text{H}_2\text{O}(\text{l})} - G_{\text{H}_2\text{O}(\text{s})} = 0$.

4.38 $\nu_{\text{C}_3\text{H}_8} = -1, \nu_{\text{O}_2} = -5, \nu_{\text{CO}_2} = 3, \nu_{\text{H}_2\text{O}} = 4$.

4.39 $\mu_{\text{N}_2} + 3\mu_{\text{H}_2} = 2\mu_{\text{NH}_3}$, where (4.98) was used.

4.40 $\xi = \Delta n_{\text{O}_3} / \nu_{\text{O}_3} = (7.10 \text{ mol} - 6.20 \text{ mol}) / (-2) = -0.45 \text{ mol}$.

4.41 (a) Heat is needed to vaporize the liquid, so q is positive. Hence $\Delta H = q_p > 0$. For this reversible isothermal process, $\Delta S = q/T > 0$. Since the process is reversible, $\Delta S_{\text{univ}} = 0$. Also, $\Delta G = \Delta H - T\Delta S = q - q = 0$, as it must be for a reversible process at constant T and P.

(b) q is positive. $\Delta U = q + w = q > 0$. For this irreversible isothermal process, Eq. (4.8) gives $dS > dq/T$ and $\Delta S > q/T$. Since q is positive, ΔS is positive. Since the process is irreversible, ΔS_{univ} is positive. Finally, $\Delta A = \Delta U - T\Delta S$. Since $\Delta U = q$ and $T\Delta S > q$, we have $\Delta A < 0$. [This also follows from (4.22) with $w_{\text{by}} = 0$.]

4.42 (a) All are zero, since the process is cyclic. (b)

The process is adiabatic, so $q = 0$. Since V is constant, $w = 0$. The system is closed. Hence $\Delta U = q + w = 0$. There is no reason for any of the others to be zero. (c) $q = 0$, but $w \neq 0$. Hence $\Delta U \neq 0$. Equation (2.63) gives $\Delta H = 0$. There is no reason for any of the others to be zero. (d) $\Delta G = 0$ for this reversible constant- T -and- P process. None of the others is zero.

4.43 From (4.47), $(\partial U/\partial V)_T = \alpha T/K - P$. Both K and T are always positive. For liquid water between 0°C and 4°C at 1 atm, α is negative and hence $(\partial U/\partial V)_T$ is negative.

4.44 (a) ν_i , stoichiometric coefficient; (b) μ_i , chemical potential; (c) x_i , extent of reaction; (d) α , thermal expansivity; (e) κ , isothermal compressibility; (f) ρ , density.

4.45 (a) Closed system at rest in the absence of external fields. (b) Closed system (at rest in the absence of external fields), reversible process, P - V work only.

(c) System (at rest in the absence of fields) in mechanical and thermal equilibrium, P - V work only.

4.46 (a) J ; (b) $\text{J mol}^{-1} \text{K}^{-1}$; (c) J/K ; (d) J/mol .

4.47 (a) The chemical potential of substance i is the same in every phase in which i is present, and this condition holds for each substance. (b) $\sum_i \nu_i \mu_i = 0$. (c) $dG = 0$ is a valid equilibrium condition only for systems held at constant T and P .

4.48 $G = H - TS$. At constant T and P , $dG = dH - T dS = dq_p - T dS$. Solving for dS , we get $dS = dq_p/T - dG/T$.

4.49 (a) False; the equation holds only for ideal gases. (b) True. (c) False; the system must be held at constant T and P . (d) False; the system must be held at constant T and P . (e) True; $w_{by} = -w = q - \Delta U$ and if q is positive then $w_{by} > -\Delta U$. (f) True. (g) False; there is no law of conservation of free energy. (h) False; ΔS_{univ} is positive for an irreversible process, but ΔS of the system can be positive, negative, or zero. (i) True. (j) False. (k) True. (l) False. (m) False. (n) False; the system must be isolated or adiabatically enclosed.

CHAPTER 5

$$\underline{5.1} \quad \Delta H_T^\circ = 2\bar{H}_{T, H_2O(1)}^\circ + 2\bar{H}_{T, SO_2(g)}^\circ - 2\bar{H}_{T, H_2S(g)}^\circ - 3\bar{H}_{T, O_2(g)}^\circ$$

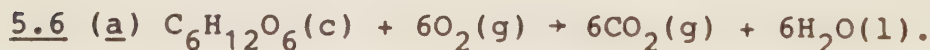
5.2 (a) The stoichiometric coefficients are doubled, so Eq. (5.2) gives $2(-319 \text{ kJ/mol}) = -638 \text{ kJ/mol}$.

(b) $4(-319 \text{ kJ/mol}) = -1276 \text{ kJ/mol}$. (c) $-1(-319 \text{ kJ/mol}) = 319 \text{ kJ/mol}$.



5.4 The 25°C reference form is the form most stable at 25°C and 1 bar. The elements that are liquid at 25°C and 1 bar are Hg and Br_2 . Those that are gaseous at 25°C and 1 bar are He, Ne, Ar, Kr, Xe, Rn, H_2 , F_2 , Cl_2 , N_2 , O_2 .

$$\begin{aligned} \underline{5.5} \quad (\underline{a}) \quad & [2(-285.830) + 2(-296.830) - 2(-20.63) - 3(0)] \\ & \text{kJ/mol} = -1124.06 \text{ kJ/mol}. \quad (\underline{b}) \quad [2(-241.818) + 2(-296.830) \\ & - 2(-20.63) - 3(0)] \text{ kJ/mol} = -1036.04 \text{ kJ/mol}. \quad (\underline{c}) \\ & [-187.78 + 4(0) - 2(294.1) - 2(90.25)] \text{ kJ/mol} = -956.5 \\ & \text{kJ/mol}. \end{aligned}$$



$$\begin{aligned} \Delta H_{C, 298}^\circ / (\text{kJ/mol}) &= 6(-393.509) + 6(-285.830) - (-1274.4) \\ &- 6(0) = -2801.6. \quad \Delta H^\circ = \Delta U^\circ + (\Delta n_g / \text{mol})RT = \Delta U^\circ + (6 - 6)RT \\ &= \Delta U^\circ = -2801.6 \text{ kJ/mol}. \quad (\underline{b}) \quad (0.7805 \text{ g})(1 \text{ mol}/180.158 \text{ g}) = \\ &0.004332 \text{ mol}. \text{ The heat flowing out of the bomb is} \\ &(2801.6 \text{ kJ/mol})(0.004332 \text{ mol}) = 12.13_7 \text{ kJ}. \text{ The water mass} \\ &\text{is } (2500 \text{ cm}^3)(0.9973 \text{ g/cm}^3) = 2493 \text{ g}. \text{ The heat capacity} \\ &\text{of the steel bomb plus surrounding water is } (14050 \text{ g}) \times \end{aligned}$$

$(0.450 \text{ J/g-}^\circ\text{C}) + (2493 \text{ g})(4.180 \text{ J/g-}^\circ\text{C}) = 1.67_4 \times 10^4 \text{ J/}^\circ\text{C}$. So $12137 \text{ J} = (1.67_4 \times 10^4 \text{ J/}^\circ\text{C})\Delta t$ and $\Delta t = 0.725^\circ\text{C}$.
 $t_{\text{final}} = 24.030^\circ\text{C} + 0.725^\circ\text{C} = 24.755^\circ\text{C}$.

5.7 Initially, $n_{\text{O}_2} = PV/RT = (30 \text{ atm})(380 \text{ cm}^3)/R(297.2 \text{ K}) = 0.47 \text{ mol}$. At the end, $n_{\text{O}_2} = 0.47 \text{ mol} - 6(0.004332 \text{ mol}) = 0.44 \text{ mol}$, $n_{\text{H}_2\text{O}(l)} = 0.026 \text{ mol}$, $n_{\text{CO}_2} = 0.026 \text{ mol}$. The heat capacity C_{sys} of the system is gotten by adding the heat capacity C_{con} of the bomb contents to the heat capacity of the steel bomb and surrounding water. The gases are heated at constant V , so we use \bar{C}_V of the gases. Appendix data gives $C_{\text{con}} = (0.44 \text{ mol})(29.36 - 8.31)(\text{J/mol-K}) + (0.026 \text{ mol})(37.11 - 8.31)(\text{J/mol-K}) + (0.026 \text{ mol})(75.29 \text{ J/mol-K}) = 12.0 \text{ J/K}$. $C_{\text{sys}} = 12.0 \text{ J/K} + 1.67_4 \times 10^4 \text{ J/K} = 1.67_5 \times 10^4 \text{ J/K}$. We get $\Delta t = 0.725^\circ\text{C}$ and $t_{\text{final}} = 24.755^\circ\text{C}$.

5.8 (a) For the benzoic acid run, $\Delta U_r = (-26.434 \text{ kJ/g}) \times (0.5742 \text{ g}) + (0.0121 \text{ g})(-6.28 \text{ kJ/g}) = -15.25_4 \text{ kJ}$ and (5.7) gives $-15.25_4 \text{ kJ} = -C_{K+P}(1.270 \text{ K})$ and $C_{K+P} = 12.01 \text{ kJ/K}$. (b) For the naphthalene run, (5.7) gives $\Delta U_r = -(12.01 \text{ kJ/K})(2.035 \text{ K}) = -24.44 \text{ kJ}$. The contributions of the combustion wire and the naphthalene to ΔU_r are $(0.0142 \text{ g})(-6.28 \text{ kJ/g}) + (0.6018 \text{ g})\Delta U_{\text{C,naph}}$, where $\Delta U_{\text{C,naph}}$ is per gram of naphthalene. Then $-24.44 \text{ kJ} = -0.089 \text{ kJ} + (0.6018 \text{ g})\Delta U_{\text{C,naph}}$ and $\Delta U_{\text{C,naph}} = -40.46 \text{ kJ/g}$. $\Delta U_c^\circ \approx \Delta \bar{U}_{\text{C,naph}} = (-40.46 \text{ kJ/g})(128.17 \text{ g/mol}) = -5186 \text{ kJ/mol}$. The combustion reaction $\text{C}_{10}\text{H}_8(\text{s}) + 12\text{O}_2(\text{g}) \rightarrow$

$10\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})$ has $\Delta n_{\text{g}}/\text{mol} = 10 - 12 = -2$ and $\Delta H_{\text{C}}^{\circ} = \Delta U_{\text{C}}^{\circ} - 2RT = -5186 \text{ kJ/mol} - 2(8.314 \times 10^{-3} \text{ kJ/mol-K})(298 \text{ K}) = -5191 \text{ kJ/mol}$.

5.9 $U_{\text{el}} = VIt = (8.412 \text{ V})(0.01262 \text{ A})(812 \text{ s}) = 86.2 \text{ J}$

$$\Delta U_{\text{reaction}, 298} = -U_{\text{el}} = -86.2 \text{ J}$$

If we neglect the difference between U of the standard states and U of the states in the calorimeter, then ΔU_{298}° is $\Delta U_{\text{reaction}, 298}$ per mole, where "per mole" means for $\Delta \xi = 1 \text{ mol}$. The reaction as written involves a coefficient of 3 for B, so $\Delta \xi = 1 \text{ mol}$ corresponds to $\Delta n(\text{B}) = 3 \text{ mol}$. We have $n(\text{B}) = (1.450 \text{ g})/(168.1 \text{ g/mol}) = 0.008626 \text{ mol}$, and

$$\Delta U_{298}^{\circ} \approx 3 \frac{-86.2 \text{ J}}{0.008626 \text{ mol}} = -29.98 \text{ kJ/mol}$$

Then $\Delta n_{\text{g}}/\text{mol} = 6 - 2 = 4$ and $\Delta H_{298}^{\circ} = \Delta U_{298}^{\circ} + \Delta n_{\text{g}} RT/\text{mol}$
 $\approx -29.98 \text{ kJ/mol} + 4(0.0083145 \text{ kJ/mol-K})(298.15 \text{ K})$
 $= -20.06 \text{ kJ/mol}$.

5.10 (a) With \bar{V}_{liq} neglected, $\Delta H_{298}^{\circ} - \Delta U_{298}^{\circ} = (\Delta n_{\text{g}}/\text{mol})RT$
 $= (-1.5)(8.3145 \text{ J/mol-K})(298.15 \text{ K}) = -3718.5 \text{ J/mol}$. (b)

$\Delta H_{298}^{\circ} - \Delta U_{298}^{\circ} = P \Delta V^{\circ} = P \bar{V}_{\text{H}_2\text{O}(\text{l})}^{\circ} + P \Delta V_{\text{gas}}^{\circ} = (1 \text{ atm}) \times$
 $(18 \text{ cm}^3/\text{mol})(8.3 \text{ J/82 cm}^3\text{-atm}) + (\Delta n_{\text{g}}/\text{mol})RT = 1.8 \text{ J/mol}$
 $- 3718.5 \text{ J/mol} = -3716.7 \text{ J/mol}$.

5.11 $(\text{CH}_3)_2\text{CO}(\text{l}) + 4\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$. For this reaction, Equation (5.5) gives: $\Delta H_{298}^{\circ} =$

$\Sigma_1 \nu_1 \Delta H_{f,298,1}^\circ = 3\Delta H_{f,298,\text{CO}_2(\text{g})}^\circ + 3\Delta H_{f,298,\text{H}_2\text{O}(\text{l})}^\circ - \Delta H_{f,298,(\text{CH}_3)_2\text{CO}(\text{l})}^\circ - 4\Delta H_{f,298,\text{O}_2(\text{g})}^\circ$. Use of Appendix data for CO_2 and H_2O gives $-1790 \text{ kJ/mol} = 3(-393.509 \text{ kJ/mol}) + 3(-285.830 \text{ kJ/mol}) - 4(0) - \Delta H_{f,298,(\text{CH}_3)_2\text{CO}(\text{l})}^\circ$ and $\Delta H_{f,298,(\text{CH}_3)_2\text{CO}(\text{l})}^\circ = -248 \text{ kJ/mol}$. The formation reaction is $3\text{C}(\text{graphite}) + 3\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow (\text{CH}_3)_2\text{CO}(\text{l})$ and has $\Delta n_g/\text{mol} = -3.5$. Neglecting the volumes of condensed phases, we have $\Delta U_{f,298}^\circ = \Delta H_{f,298}^\circ - \Delta(PV)_{f,298}^\circ = \Delta H_{f,298}^\circ - RT \Delta n_g/\text{mol} = -248 \text{ kJ/mol} - (0.008314 \text{ kJ/mol-K})(298.1 \text{ K})(-3.5) = -239 \text{ kJ/mol}$.

5.12 $\text{NH}_2\text{CH}(\text{CH}_3)\text{COOH}(\text{s}) + \frac{15}{4}\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + \frac{7}{2}\text{H}_2\text{O}(\text{l}) + \frac{1}{2}\text{N}_2(\text{g})$. For this reaction, Equation (5.5) gives $\Delta H_{298}^\circ = 3\Delta H_{f,298,\text{CO}_2(\text{g})}^\circ + 3.5\Delta H_{f,298,\text{H}_2\text{O}(\text{l})}^\circ + \frac{1}{2}\Delta H_{f,298,\text{N}_2(\text{g})}^\circ - 3.75\Delta H_{f,298,\text{O}_2(\text{g})}^\circ - \Delta H_{f,298,\text{alanine}(\text{s})}^\circ$. Use of Appendix data for CO_2 and H_2O gives $-1623 \text{ kJ/mol} = 3(-393.51 \text{ kJ/mol}) + 3.5(-285.83 \text{ kJ/mol}) + 0 - 0 - \Delta H_{f,298,\text{alanine}(\text{s})}^\circ$ and $\Delta H_{f,298,\text{alanine}(\text{s})}^\circ = -558 \text{ kJ/mol}$. The formation reaction is $\frac{1}{2}\text{N}_2(\text{g}) + \frac{7}{2}\text{H}_2(\text{g}) + 3\text{C}(\text{graphite}) + \text{O}_2(\text{g}) \rightarrow \text{NH}_2\text{CH}(\text{CH}_3)\text{COOH}(\text{s})$ and has $\Delta n_g/\text{mol} = -5$. Then $\Delta U_{f,298}^\circ = \Delta H_{f,298}^\circ - RT \Delta n_g/\text{mol} = -558000 \text{ J/mol} - (8.314 \text{ J/mol-K})(298.1 \text{ K})(-5) = -546 \text{ kJ/mol}$.

5.13 Let the reactions be numbered (1), (2), (3), (4).

Taking $-(2) + (4) - \frac{1}{2}(3)$, we get the desired formation reaction $\text{Fe(s)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{FeO(s)}$. Hence $\Delta H_{f,298}^\circ(\text{FeO}) = [-37 - 94 + \frac{1}{2}(135)] \text{ kcal/mol} = -63\frac{1}{2} \text{ kcal/mol}$. Taking $-(1) + 3(4) - \frac{3}{2}(3)$, we get $2\text{Fe} + \frac{3}{2}\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3$, so $\Delta H_{f,298}^\circ(\text{Fe}_2\text{O}_3) = [-117 + 3(-94) - \frac{3}{2}(-135)] \text{ kcal/mol} = -196\frac{1}{2} \text{ kcal/mol}$.

5.14 For reaction (1), $\Delta H_{298}^\circ = \sum_i \nu_i \Delta H_{f,298,i}^\circ = -1560 \text{ kJ/mol} = 2(-393\frac{1}{2} \text{ kJ/mol}) + 3(-286 \text{ kJ/mol}) - \Delta H_{f,298}^\circ(\text{C}_2\text{H}_6(\text{g})) - \frac{7}{2}(0)$, where the data of reactions (2) and (3) were used to give $\Delta H_{f,298}^\circ$ of $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$, and where ΔH_f° of the stable-form element $\text{O}_2(\text{g})$ is zero. Solving, we find $\Delta H_{f,298}^\circ(\text{C}_2\text{H}_6(\text{g})) = -85 \text{ kJ/mol}$.

5.15(a) $\bar{V} = RT/P + b$. Eq. (5.16) gives

$$\bar{H}_{\text{id}}(T, P) - \bar{H}_{\text{re}}(T, P) = \int_0^P [T(\partial \bar{V} / \partial T)_P - \bar{V}] dP' = \int_0^P [RT/P' - (RT/P' + b)] dP' = \int_0^P -b dP' = -bP$$

(b)

$$-bP = -(45 \text{ cm}^3/\text{mol})(1 \text{ atm}) \frac{8.314 \text{ J}}{82.06 \text{ cm}^3 \text{ atm}} = -4.6 \text{ J/mol}$$

5.16 (a) From Eq. (5.17), $\bar{H}_{298}^\circ = 0$. (b) $(\partial \bar{H} / \partial T)_P = C_P$ and with the T dependence of C_P neglected, $\Delta \bar{H} \approx \bar{C}_P \Delta T$; hence $\bar{H}_{308}^\circ = \bar{H}_{298}^\circ + (28.824 \text{ J/mol-K})(10 \text{ K}) = 288.2 \text{ J/mol}$. (c) From Sec. 5.4, $\bar{H}_{\text{H}_2\text{O}(1)}^\circ = \Delta H_{f,\text{H}_2\text{O}(1)}^\circ + \bar{H}_{\text{H}_2(\text{g})}^\circ + \frac{1}{2}\bar{H}_{\text{O}_2(\text{g})}^\circ = -285.83 \text{ kJ/mol}$ at 25°C . (d) Use of $\Delta \bar{H} \approx \bar{C}_P \Delta T$ gives for $\text{H}_2\text{O}(\text{l})$, $\bar{H}_{308}^\circ = \bar{H}_{298}^\circ + \bar{C}_P(10 \text{ K}) = -285830 \text{ J/mol} + (75.291 \text{ J/mol-K})(10 \text{ K}) = -285.08 \text{ kJ/mol}$.

5.17 Eq. (5.19) with ΔC_P° assumed constant gives

$$\Delta H_{T_2}^\circ - \Delta H_{T_1}^\circ = \Delta C_P^\circ (T_2 - T_1). \quad (\text{See the Prob. 5.5 solution for } \Delta H_{298}^\circ.)$$

$$\begin{aligned} \text{(a)} \quad \Delta C_P^\circ / (\text{J/mol-K}) &= 2(75.291) + 2(39.87) - 2(34.23) \\ &\quad - 3(29.355) = 73.80 \end{aligned}$$

$$\begin{aligned} \Delta H_{370}^\circ &= -1124.06 \text{ kJ/mol} + (0.07380 \text{ kJ/mol-K})(72 \text{ K}) \\ &= -1118.75 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad \Delta C_P^\circ / (\text{J/mol-K}) &= 2(33.577) + 2(39.87) - 2(34.23) \\ &\quad - 3(29.355) = -9.63 \end{aligned}$$

$$\Delta H_{370}^\circ = -1036.04 \text{ kJ/mol} + (-0.00963 \text{ kJ/mol-K})(72 \text{ K})$$

$$\Delta H_{370}^\circ = -1036.73 \text{ kJ/mol}$$

$$\text{(c)} \quad \Delta C_P^\circ = 58.55 \text{ J/mol-K}, \quad \Delta H_{370}^\circ = -952.3 \text{ kJ/mol}$$

5.18 The formation reaction is $\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{HCl}(\text{g})$.

As in the Sec. 5.5 example, $\Delta H_{T_2}^\circ - \Delta H_{T_1}^\circ = \Delta d(T_2 - T_1) + \frac{1}{2}\Delta e(T_2^2 - T_1^2) - \Delta f(T_2^{-1} - T_1^{-1})$. We have $\Delta d/(\text{cal/mol-K}) =$

$$6.34 - \frac{1}{2}(8.82) - \frac{1}{2}(6.52) = -1.33; \quad \Delta e/(\text{cal/mol-K}^2) =$$

$$0.00110 - \frac{1}{2}(0.00006) - \frac{1}{2}(0.00078) = 0.00068;$$

$$\Delta f/(\text{cal K/mol}) = 0.54 \times 10^5. \quad \text{From the Appendix, } \Delta H_{f,298}^\circ =$$

$$(-92307 \text{ J/mol})(1 \text{ cal}/4.184 \text{ J}) = -22062 \text{ cal/mol. Then}$$

$$\Delta H_{f,1000}^\circ/(\text{cal/mol}) = -22062 - 1.33(1000 - 298.15) +$$

$$\frac{1}{2}(0.00068)(1000^2 - 298.15^2) - 0.54 \times 10^5(1000^{-1} - 298.15^{-1})$$

$$= -22559 \text{ and } \Delta H_{f,1000}^\circ = -22559 \text{ cal/mol} = -94.385 \text{ kJ/mol.}$$

5.19 (a) Integration of $(\partial S/\partial T)_P = C_P/T$ at constant P

$$\text{gives } \bar{S}_T^\circ = \int_0^T (\bar{C}_P^\circ/T') dT', \text{ since } \bar{S}_0^\circ = 0 \text{ [Eq. (5.28)]}.$$

Use of the low-T relation (5.31) gives $\bar{S}_T^\circ = \int_0^T aT'^2 dT' = aT^3/3$. (b) 10 K is cold enough to use the Debye equation (5.31): $\bar{C}_P^\circ = aT^3$. Substitution in this equation gives $0.200 \text{ cal/mol-K} = a(10.0 \text{ K})^3$ and $a = 0.000200 \text{ cal/mol-K}^4$. At 6.0 K, $\bar{C}_P^\circ = aT^3 = (0.000200 \text{ cal/mol-K}^4)(6.0 \text{ K})^3 = 0.043 \text{ cal/mol-K}$. Use of the result of part (a) gives $\bar{S}_{6 \text{ K}}^\circ = aT^3/3 = \bar{C}_P^\circ/3 = 0.014 \text{ cal/mol-K}$.

5.20 (a) We use (5.29) and $\int_u^w f(x) dx = \int_u^v f(x) dx + \int_v^w f(x) dx$. The reasoning of Prob. 5.19a and Eq. (5.31) give $\bar{S}_{10 \text{ K}}^\circ = a(10 \text{ K})^3/3 = \bar{C}_{P,10 \text{ K}}^\circ/3 = [c(10 \text{ K})^3 + d(10 \text{ K})^4]/3$. Then $\bar{S}_{300 \text{ K}}^\circ = 333c \text{ K}^3 + 3333d \text{ K}^4 + \int_{10 \text{ K}}^{20 \text{ K}} (cT^2 + dT^3) dT + \int_{20 \text{ K}}^{200 \text{ K}} (e/T + f + gT + hT^2) dT + (1450 \text{ cal/mol})/(200 \text{ K}) + \int_{200 \text{ K}}^{300 \text{ K}} (i/T + j + kT + lT^2) dT = (2666 \text{ K}^3)c + (40833 \text{ K}^4)d + 2.3026e + (180 \text{ K})f + (19800 \text{ K}^2)g + (2664000 \text{ K}^3)h + 7.25 \text{ cal/mol-K} + 0.4055i + (100 \text{ K})j + (25000 \text{ K}^2)k + (6333333 \text{ K}^3)l$. (b) From $(\partial \bar{H}/\partial T)_P = \bar{C}_P$, we have $\bar{H}_{T'}^\circ - \bar{H}_0^\circ = \int_0^{T'} \bar{C}_P^\circ dT$ for the solid at T' . Use of the Debye T^3 law (5.31) gives $\bar{H}_{10 \text{ K}}^\circ - \bar{H}_0^\circ = \int_0^{10 \text{ K}} \bar{C}_P^\circ dT = \int_0^{10 \text{ K}} aT^3 dT = \frac{1}{4}(10 \text{ K})^4 a$. But, as noted in part (a), $a = \bar{C}_{P,10 \text{ K}}^\circ/(10 \text{ K})^3$, so $\bar{H}_{10 \text{ K}}^\circ - \bar{H}_0^\circ = \frac{1}{4}(10 \text{ K})\bar{C}_{P,10 \text{ K}}^\circ = (2.5 \text{ K})[c(10 \text{ K})^3 + d(10 \text{ K})^4]$. Also, $\bar{H}_{200 \text{ K}}^\circ - \bar{H}_{10 \text{ K}}^\circ = \int_{10 \text{ K}}^{20 \text{ K}} \bar{C}_P^\circ(s) dT + \int_{20 \text{ K}}^{200 \text{ K}} \bar{C}_P^\circ(s) dT$, $\Delta \bar{H}_{\text{fus}}^\circ = 1450 \text{ cal/mol}$, and $\bar{H}_{300}^\circ - \bar{H}_{200}^\circ = \int_{200 \text{ K}}^{300 \text{ K}} \bar{C}_P^\circ(l) dT$. Substitution of the expressions for \bar{C}_P° and integration gives $\bar{H}_{300}^\circ - \bar{H}_0^\circ = (40000 \text{ K}^4)c + (645000 \text{ K}^5)d + (180 \text{ K})e$

$$+ (19800 \text{ K}^2)f + (2664000 \text{ K}^3)g + (3.9996 \times 10^8 \text{ K}^4)h + 1450 \text{ cal/mol} + (100 \text{ K})i + (25000 \text{ K}^2)j + (6333333 \text{ K}^3)k + (1.625 \times 10^9 \text{ K}^4)l.$$

5.21 (a) The first trapezoid has its parallel sides at a and $a + w$ and its area is $\frac{1}{2}(f_0 + f_1)w$. The second trapezoid's area is $\frac{1}{2}(f_1 + f_2)w$; the third has area $\frac{1}{2}(f_2 + f_3)w$; ...; the last has area $\frac{1}{2}(f_{n-1} + f_n)w$. Addition of these areas gives $\frac{1}{2}(f_0 + 2f_1 + 2f_2 + \cdots + 2f_{n-1} + f_n)w$, which is the desired result. (b) With $n = 10$, the trapezoidal rule gives $\int_1^2 x^{-1} dx \approx 0.1[\frac{1}{2}(1)^{-1} + (1.1)^{-1} + (1.2)^{-1} + \cdots + (1.9)^{-1} + \frac{1}{2}(2)^{-1}] = 0.693771$. With $n = 20$ the trapezoidal rule gives $0.05[\frac{1}{2}(1)^{-1} + (1.05)^{-1} + (1.1)^{-1} + \cdots + (1.95)^{-1} + \frac{1}{2}/2] = 0.693303$. The $n = 10$ Simpson's rule estimate is $\frac{1}{3}(0.1)[1^{-1} + 4/1.1 + 2/1.2 + 4/1.3 + 2/1.4 + 4/1.5 + 2/1.6 + 4/1.7 + 2/1.8 + 4/1.9 + 1/2] = 0.693150$. The exact value is $\int_1^2 x^{-1} dx = \ln(2/1) = 0.693147$.

5.22 (a) $\int_{15 \text{ K}}^{60 \text{ K}} (\bar{C}_P/T) dT \approx 5[\frac{1}{2}(0.83)/15 + 1.66/20 + 2.74/25 + \cdots + 8.02/55 + \frac{1}{2}(8.62)/60] \text{ cal/mol-K} = 5.70_7 \text{ cal/mol-K}$. Next, $\int_{60 \text{ K}}^{190 \text{ K}} (\bar{C}_P/T) dT \approx 10[\frac{1}{2}(8.62)/60 + 9.57/70 + \cdots + 15.42/180 + \frac{1}{2}(16.02)/190] \text{ cal/mol-K} = 13.76_7 \text{ cal/mol-K}$. Finally, $\int_{190 \text{ K}}^{197.64 \text{ K}} (\bar{C}_P/T) dT \approx 7.64[\frac{1}{2}(16.02)/190 + \frac{1}{2}(16.50)/197.64] \text{ cal/mol-K} = 0.64_1 \text{ cal/mol-K}$. Addition of the three contributions gives $\int_{15 \text{ K}}^{197.64 \text{ K}} (\bar{C}_P/T) dT \approx 20.11_5 \text{ cal/mol-K}$. (b)

$\int_{15\text{ K}}^{55\text{ K}} (\bar{C}_P/T) dT \approx \frac{1}{3}(5)[0.83/15 + 4(1.66)/20 + 2(2.74)/25 + 4(3.79)/30 + 2(4.85)/35 + 4(5.78)/40 + 2(6.61)/45 + 4(7.36)/50 + 8.02/55] \text{ cal/mol-K} = 4.99_2 \text{ cal/mol-K.}$ Next, $\int_{55\text{ K}}^{60\text{ K}} (\bar{C}_P/T) dT \approx 5[\frac{1}{2}(8.02)/55 + \frac{1}{2}(8.62)/60] \text{ cal/mol-K} = 0.72_4 \text{ cal/mol-K.}$ Next, $\int_{60\text{ K}}^{180\text{ K}} (\bar{C}_P/T) dT \approx \frac{1}{3}(10)[8.62/60 + 15.42/180 + 4(9.57/70 + 10.93/90 + 11.97/110 + 12.83/130 + 13.82/150 + 14.85/170) + 2(10.32/80 + 11.49/100 + 12.40/120 + 13.31/140 + 14.33/160)] \text{ cal/mol-K} = 12.91_2 \text{ cal/mol-K.}$ Next, $\int_{180\text{ K}}^{190\text{ K}} (\bar{C}_P/T) dT \approx 10[\frac{1}{2}(15.42)/180 + \frac{1}{2}(16.02)/190] \text{ cal/mol-K} = 0.85_0 \text{ cal/mol-K.}$ Finally, $\int_{190\text{ K}}^{197.64\text{ K}} (\bar{C}_P/T) dT \approx \dots = 0.64_1 \text{ cal/mol-K.}$ Addition of the contributions gives $20.11_9 \text{ cal/mol-K.}$ (c) The trapezoidal rule gives $\int_{197.64\text{ K}}^{200\text{ K}} (\bar{C}_P/T) dT \approx 0.24_9 \text{ cal/mol-K;}$ $\int_{200\text{ K}}^{260\text{ K}} (\bar{C}_P/T) dT \approx 5.46_9 \text{ cal/mol-K;}$ $\int_{260\text{ K}}^{263.1\text{ K}} (\bar{C}_P/T) dT \approx 0.24_5 \text{ cal/mol-K.}$ Addition gives $\int_{197.64\text{ K}}^{263.1\text{ K}} (\bar{C}_P/T) dT \approx 5.96_3 \text{ cal/mol-K.}$ For the gas, $\int_{263.1\text{ K}}^{280\text{ K}} (\bar{C}_P/T) dT \approx 0.60_3 \text{ cal/mol-K}$ and $\int_{280\text{ K}}^{298.15\text{ K}} (\bar{C}_P/T) dT \approx 0.613 \text{ cal/mol-K.}$ Addition gives $\int_{263.1\text{ K}}^{298.15\text{ K}} (\bar{C}_P/T) dT \approx 1.21_6 \text{ cal/mol-K.}$

5.23 Not being a masochist, I didn't do this one. If you do work it correctly, the answer will be very close to the value 20.12 cal/mol-K found in Prob. 5.22b.

5.24 (a) The Appendix gives $\bar{S}_{298}^\circ = 69.91 \text{ J/mol-K.}$

(b) Equation (4.61) with the T dependence of \bar{C}_P° neglected

gives $\bar{S}_{348}^{\circ} \approx \bar{S}_{298}^{\circ} + \bar{C}_P^{\circ} \ln (T_2/T_1)$, so

$$\bar{S}_{348}^{\circ} \approx 69.91 \text{ J/mol-K} + (75.291 \text{ J/mol-K}) \times \ln (348.1/298.1) = 81.58 \text{ J/mol-K.}$$

(c) Equation (4.62) with the pressure dependence of α and \bar{V} neglected gives $\bar{S}_{298, 100 \text{ bar}} \approx \bar{S}_{298}^{\circ} - \alpha \bar{V} \Delta P$, so

$$\begin{aligned} \bar{S}_{298, 100 \text{ bar}} &\approx 69.91 \frac{\text{J}}{\text{mol K}} - (0.000304 \text{ K}^{-1})(18.1 \text{ cm}^3/\text{mol}) \\ &\quad \times (99 \text{ bar}) \frac{8.314 \text{ J}}{83.14 \text{ cm}^3 \text{ bar}} \\ &= 69.86 \text{ J/mol-K} \end{aligned}$$

(d) Use the path in Fig. 4.5. The calculations of parts (b) and (c) of this problem give $\Delta S = \Delta S_a + \Delta S_b =$
 $11.67 \text{ J/mol-K} - 0.05 \text{ J/mol-K} = 11.62 \text{ J/mol-K.}$ Hence

$$\bar{S}(348 \text{ K}, 100 \text{ bar}) = [69.91 + 11.62] \text{ J/mol-K} = 81.53 \text{ J/mol-K.}$$

5.25 (a) $[2(69.91) + 2(248.22) - 2(205.79) - 3(205.138)]$
 $\text{J/mol-K} = -390.73 \text{ J/mol-K.}$ (b) $[2(188.825) + \text{as in (a)}]$
 $\text{J/mol-K} = -152.90 \text{ J/mol-K.}$ (c) $[109.6 + 4(191.61) -$
 $2(238.97) - 2(210.761)] \text{ J/mol-K} = -23.4 \text{ J/mol-K.}$

5.26 With the temperature dependence of $\Delta \bar{C}_P^{\circ}$ neglected, Eq. (5.37) gives $\Delta S_{T_2}^{\circ} = \Delta S_{298}^{\circ} + \Delta \bar{C}_P^{\circ} \ln (T_2/298 \text{ K})$. The $\Delta \bar{C}_P^{\circ}$'s are calculated in the Prob. 5.17 solution and the ΔS_{298}° 's are calculated in Prob. 5.25. (a) $\Delta S_{370}^{\circ} =$
 $-390.73 \text{ J/mol-K} + (73.80 \text{ J/mol-K}) \ln (370/298) =$
 -374.76 J/mol-K. (b) $\Delta S_{370}^{\circ} = -152.90 \text{ J/mol-K} +$
 $(-9.63 \text{ J/mol-K}) \ln (370/298) = -154.98 \text{ J/mol-K.}$
 (c) $\Delta S_{370}^{\circ} = -23.4 \text{ J/mol-K} + (58.55 \text{ J/mol-K}) \ln (370/298)$
 $= -10.7 \text{ J/mol-K.}$

5.27 Differentiation of (5.36) gives $d\Delta S^\circ/dT =$

$$\sum_i \nu_i d\bar{S}_i^\circ/dT = \sum_i \nu_i \bar{C}_{P,i}^\circ/T = \Delta C_P^\circ/T. \text{ Integration gives}$$

$$\Delta S_{T_2}^\circ - \Delta S_{T_1}^\circ = \int_{T_1}^{T_2} (\Delta C_P^\circ/T) dT.$$

5.28 $\bar{V} = RT/P + RTf(T)$ and $(\partial \bar{V}/\partial T)_P = R/P + Rf + RTf'$.

Substitution in (5.30) gives $\bar{S}_{id}(T, P) - \bar{S}_{re}(T, P) =$

$$\int_0^P [Rf(T) + RTf'(T)] dP = RP[f(T) + Tf'(T)].$$

5.29 $\Delta G_{f,298}^\circ = \Delta H_{f,298}^\circ - T \Delta S_{f,298}^\circ$. The formation reaction is $C(\text{graphite}) + \frac{1}{2}O_2(g) + N_2(g) + 2H_2(g) \rightarrow CO(NH_2)_2(c)$. Appendix data gives for this reaction, $\Delta S^\circ = \sum_i \nu_i \bar{S}_i^\circ = 104.60 \text{ J/mol-K} - 5.740 \text{ J/mol-K} - \frac{1}{2}(205.138 \text{ J/mol-K}) - 191.61 \text{ J/mol-K} - 2(130.684 \text{ J/mol-K}) = -456.69 \text{ J/mol-K} = \Delta S_{f,298,urea}^\circ$. Then $\Delta G_{f,298}^\circ = -333.51 \text{ kJ/mol} - (298.15 \text{ K})(-0.45669 \text{ kJ/mol-K}) = -197.35 \text{ kJ/mol}$.

5.30 (a) $\Delta G_a^\circ = \Delta H_a^\circ - T \Delta S_a^\circ = -1124.06 \text{ kJ/mol} - (298.15 \text{ K})(-0.39073 \text{ kJ/mol-K}) = -1007.56 \text{ kJ/mol}$. $\Delta G_b^\circ = -1036.04 \text{ kJ/mol} - (298.15 \text{ K})(-0.15290 \text{ kJ/mol-K}) = -990.45 \text{ kJ/mol}$. $\Delta G_c^\circ = -956.5 \text{ kJ/mol} - (298.15 \text{ K})(-0.0234 \text{ kJ/mol-K}) = -949.5 \text{ kJ/mol}$. (b) $\Delta G_a^\circ/(\text{kJ/mol}) = 2(-237.129) + 2(-300.194) - 2(-33.56) - 3(0) = -1007.53$. $\Delta G_b^\circ/(\text{kJ/mol}) = 2(-228.572) + 2(-300.194) - 2(-33.56) - 3(0) = -990.41$. $\Delta G_c^\circ/(\text{kJ/mol}) = -120.35 + 4(0) - 2(328.1) - 2(86.55) = -949.6$.

5.31 (a) $\Delta G_{370}^\circ = \Delta H_{370}^\circ - T \Delta S_{370}^\circ = -1118.75 \text{ kJ/mol} - (370 \text{ K})(-0.37476 \text{ kJ/mol-K}) = -980.09 \text{ kJ/mol}$. (b) $\Delta G_{370}^\circ = -1036.73 \text{ kJ/mol} - (370 \text{ K})(-0.15498 \text{ kJ/mol-K}) = -979.39 \text{ kJ/mol}$. (c) $\Delta G_{370}^\circ = -948.3 \text{ kJ/mol}$.

5.32 (a) $\bar{G}_{298}^\circ = \bar{H}_{298}^\circ - T\bar{S}_{298}^\circ = 0 - (298.15 \text{ K})(205.138$

J/mol-K) = -61.16 kJ/mol. (b) Using the result of Prob.

$$5.16c, \text{ we get } \bar{G}_{298}^{\circ} = \bar{H}_{298}^{\circ} - T\bar{S}_{298}^{\circ} = -285830 \text{ J/mol} - (298.15 \text{ K})(69.91 \text{ J/mol-K}) = -306.67 \text{ kJ/mol}.$$

5.33 The Stull-Westrum-Sinke reference gives $\Delta G_{f,1000}^{\circ}$ values for CH_4 , C_2H_6 , and H_2 as 4.58, 26.13, and 0 kcal/mol, respectively. Hence, $\Delta G_{1000}^{\circ} = [0 + 26.13 - 2(4.58)] \text{ kcal/mol} = 16.97 \text{ kcal/mol}$. Landolt-Börnstein data give 70.7 kJ/mol.

$$5.34 \quad \Delta H_{298}^{\circ} = 2(-46.11 \text{ kJ/mol}) - 0 - 3(0) = -92.22 \text{ kJ/mol}.$$

$$\Delta H_{2000}^{\circ} = \Delta H_{298}^{\circ} + \sum_i \nu_i (\bar{H}_{2000}^{\circ} - \bar{H}_{298}^{\circ}) = -92.22 \text{ kJ/mol} + 2(98.18 \text{ kJ/mol}) - 56.14 \text{ kJ/mol} - 3(52.93 \text{ kJ/mol}) = -110.79 \text{ kJ/mol}.$$

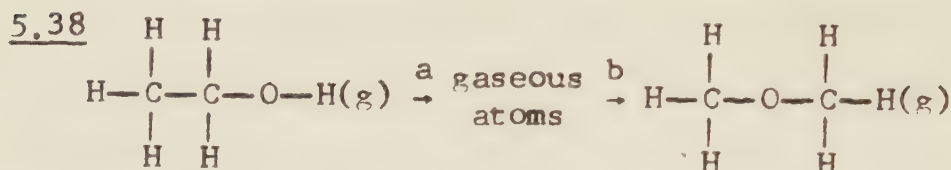
5.35 The reaction is $\frac{1}{2}\text{N}_2(\text{g}) + \frac{3}{2}\text{H}_2(\text{g}) \rightarrow \text{NH}_3(\text{g})$. The Appendix gives $\Delta H_{f,298}^{\circ} = -46.11 \text{ kJ/mol}$. Use of (5.43) gives $\Delta G_{f,2000}^{\circ} = -46110 \text{ J/mol} + (2000 \text{ K})[-242.08 - \frac{1}{2}(-223.74) - \frac{3}{2}(-161.94)](\text{J/mol-K}) = 179.29 \text{ kJ/mol}$.

$$5.36 \quad \Delta H_{298}^{\circ} + T \sum_i \nu_i [(\bar{G}_T - \bar{H}_{298}^{\circ})/T]_i = \Delta H_{298}^{\circ} + T \sum_i \nu_i \bar{G}_{i,T}^{\circ}/T - T \sum_i \nu_i \bar{H}_{i,298}^{\circ}/T = \Delta H_{298}^{\circ} + \Delta G_T^{\circ} - \Delta H_{298}^{\circ} = \Delta G_T^{\circ}.$$

5.37 (a) $\Delta G_T^{\text{bar}} - \Delta G_T^{\text{atm}} = \Delta H_T^{\text{bar}} - T \Delta S_T^{\text{bar}} - (\Delta H_T^{\text{atm}} - T \Delta S_T^{\text{atm}}) = -T(\Delta S_T^{\text{bar}} - \Delta S_T^{\text{atm}})$, since the difference between 1-bar and 1-atm enthalpies of a solid or liquid is negligible and H° of a gas is independent of P . Since the effect of a slight change in P on S of a solid or liquid is negligible, we have $\Delta S_T^{\text{bar}} - \Delta S_T^{\text{atm}} = \Delta S_{g,T}^{\text{bar}} - \Delta S_{g,T}^{\text{atm}} = \sum_{\text{gases}} \nu_i (\bar{S}_{T,i}^{\text{bar}} - \bar{S}_{T,i}^{\text{atm}}) = (0.1094 \text{ J/mol-K}) \sum_{\text{gases}} \nu_i = (0.1094 \text{ J/mol-K}) \times$

$$\Delta n_g/\text{mol} \text{ and } \Delta G_T^{\text{bar}} - \Delta G_T^{\text{atm}} = -T(0.1094 \text{ J/mol-K})\Delta n_g/\text{mol}.$$

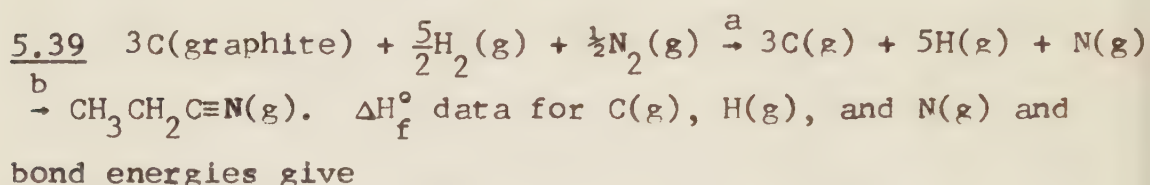
$$\text{(b) } \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}). \quad \Delta G_{f,298}^{\text{bar}} - \Delta G_{f,298}^{\text{atm}} = \\ -(298 \text{ K})(0.1094 \text{ J/mol-K})(-1.5) = 48.9 \text{ J/mol}.$$



$$\Delta H_a / (\text{kJ/mol}) = 5(415) + 344 + 350 + 463 = 3232$$

$$\Delta H_b / (\text{kJ/mol}) = -[6(415) + 2(350)] = -3190$$

$$\Delta H = \Delta H_a + \Delta H_b = 42 \text{ kJ/mol}$$



$$\Delta H_a / (\text{kJ/mol}) = 3(716.682) + 5(217.965) + 472.704 = 3712.6$$

$$\Delta H_b / (\text{kJ/mol}) = -[5(415) + 2(344) + 890] = -3653$$

$$\Delta H = \Delta H_a + \Delta H_b = 60 \text{ kJ/mol}$$

5.40 In the Benson-Buss bond-contribution method, the carbonyl group is treated as a unit and no explicit contribution is made for the C=O bond. The effect of this bond is absorbed into the contributions for bonds to the carbonyl carbon. The bond contribution to \bar{S}_{298}° for the F-CO bond is 31.6 cal/mol-K, so the total bond contribution is $2(31.6 \text{ cal/mol-K}) = 63.2 \text{ cal/mol-K}$ for $\text{COF}_2(\text{g})$. In addition, the quantity $R \ln \sigma$ must be subtracted to allow for molecular symmetry. For COF_2 , the symmetry number σ is 2, since there are two indistinguishable orientations of the molecule (obtained by 180° rotation about

the CO bond). The symmetry correction is $-R \ln 2 = -1.38$ cal/mol-K and the predicted \bar{S}_{298}° is 61.8 cal/mol-K.

5.41 ΔH_{298}° of vaporization refers to a change from liquid at 1 bar and 25°C to vapor at 1 bar and 25°C. A path to accomplish this is the following 25°C isothermal path:

liq(1 bar) $\xrightarrow{1}$ liq(23.8 torr) $\xrightarrow{2}$ gas(23.8 torr) $\xrightarrow{3}$ gas(1 bar)

$\Delta H^{\circ} = \Delta \bar{H}_1 + \Delta \bar{H}_2 + \Delta \bar{H}_3$. As noted in Sec. 4.5, a modest change in pressure from 1 bar to 24 torr will have only a very slight effect on H and S of a liquid, so we can take $\Delta \bar{H}_1 = 0$. Also, since the vapor is assumed to behave ideally, its H depends only on T, and $\Delta \bar{H}_3 = 0$. Thus $\Delta H^{\circ} = \Delta \bar{H}_2 = 10.5$ kcal/mol. For comparison, Appendix data give $\Delta H^{\circ} = (-241.818 + 285.830)$ kJ/mol = 10.519 kcal/mol.

Next, $\Delta S^{\circ} = \Delta \bar{S}_1 + \Delta \bar{S}_2 + \Delta \bar{S}_3$. To a high degree of accuracy $\Delta \bar{S}_1 = 0$. Equations (3.27) and (3.29) and Boyle's law give $\Delta \bar{S}_2 + \Delta \bar{S}_3 = \Delta \bar{H}_2/T + R \ln (P_1/P_2) = (10500 \text{ cal/mol})/(298.1 \text{ K}) + (1.987 \text{ cal/mol-K}) \ln (23.8/750) = 28.3_6 \text{ cal mol}^{-1} \text{ K}^{-1} = \Delta S^{\circ}$. The Appendix data give $\Delta S^{\circ} =$

$(188.825 - 69.91) \text{ J/mol-K} = 28.42 \text{ cal/mol-K}$. Finally,

$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} = 10.5 \text{ kcal/mol} -$

$(298.1 \text{ K})(0.0283_6 \text{ kcal/mol-K}) = 2.0_4 \text{ kcal/mol}$. The Appen-

dix gives $\Delta G^{\circ} = 2.045 \text{ kcal/mol}$.

5.42 We use the 25°C path (where M is methanol)

$M(l, 1 \text{ bar}) \xrightarrow{1} M(l, 125 \text{ torr}) \xrightarrow{2} M(g, 125 \text{ torr}) \xrightarrow{3} M(g, 1 \text{ bar}) \xrightarrow{4} M(\text{ideal gas}, 1 \text{ bar})$. For this path, $\Delta H =$

$\bar{H}_{M(g)}^\circ - \bar{H}_{M(l)}^\circ = \bar{H}_{M(g)}^\circ - H_{el}^\circ - (\bar{H}_{M(l)}^\circ - H_{el}^\circ) = \Delta H_{f,M(g)}^\circ - \Delta H_{f,M(l)}^\circ$, where H_{el}° is the standard-state enthalpy of the elements needed to form methanol. Since a moderate change in P has little effect on thermodynamic properties of a liquid, we have $\Delta H_1 \approx 0$ (and $\Delta S_1 \approx 0$). $\Delta H_2 = 37.9 \text{ kJ/mol}$. $\Delta H_3 \approx 0$ and $\Delta H_4 \approx 0$, where we neglected nonideality of the gas. Then $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 = 37.9 \text{ kJ/mol}$ and $\Delta H_{f,M(g)}^\circ = -238.7 \text{ kJ/mol} + 37.9 \text{ kJ/mol} = -200.8 \text{ kJ/mol}$. We have $\Delta S_1 \approx 0$, $\Delta S_2 = \Delta H_2/T = (37900 \text{ J/mol})/(298 \text{ K}) = 127.1 \text{ J/mol-K}$, $\Delta S_3 \approx R \ln (V_2/V_1) = R \ln (P_1/P_2) = (8.314 \text{ J/mol-K}) \ln (125/750) = -14.90 \text{ J/mol-K}$ [where (3.29) was used], and $\Delta S_4 \approx 0$, where the gas is approximated as ideal. Then $\Delta S = (127.1 - 14.9) \text{ J/mol-K} = 112.2 \text{ J/mol-K}$. So $\bar{S}_{M(g)}^\circ = 126.8 \text{ J/mol-K} + 112.2 \text{ J/mol-K} = 239 \text{ J/mol-K}$.

5.43 (a) Pa; (b) J; (c) J/mol-K; (d) J; (e) m^3/mol ; (f) K.

5.44 If ΔH° is independent of T , then $d \Delta H^\circ/dT = 0$ and (5.18) gives $\Delta C_P^\circ = 0$. Then (5.37) gives $\Delta S_{T_2}^\circ = \Delta S_{T_1}^\circ$. Q.E.D.

5.45 Equation (4.45) gives $(\partial V/\partial T)_P = -(\partial S/\partial P)_T$. The third law gives $\lim_{T \rightarrow 0} \Delta S = 0$ for an isothermal pressure change in an equilibrium system. Hence $(\partial S/\partial P)_T \rightarrow 0$ as $T \rightarrow 0$, and $\alpha = (1/V)(\partial V/\partial T)_P \rightarrow 0$ as $T \rightarrow 0$.

5.46 (a) Nonzero. (b) Nonzero. $\Delta H_{f,298}^\circ$ refers to formation of the substance from elements in their stable forms at 298 K. The 298 K stable form of chlorine is $\text{Cl}_2(\text{g})$,

not Cl(g) , and ΔH_{298}° for $\frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{Cl(g)}$ is not zero.

(c) Zero, since $\text{Cl}_2(\text{g})$ is the stable form of an element.

(d) Nonzero. (Entropies are zero at 0 K.) (e) Zero.

(f) Zero, since 350 K formation of $\text{N}_2(\text{g})$ from its stable-form element(s) is a process in which nothing happens.

(g) Zero. (h) Zero, since heat-capacities go to zero as T goes to zero, as shown by the Debye equation (5.31).

(i) Nonzero.

5.47 The 25°C reaction (step c) is $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) + \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$ and has $\Delta H = [-393.509 + 2(-285.83) - (-74.81) - 2(0)] \text{ kJ} = -890.4 \text{ kJ}$ for burning 1 mole of CH_4 . We have $\Delta H_a = \Delta H_c + \Delta H_b = 0 = -890 \text{ kJ} + \Delta H_b$ and $\Delta H_b = 890 \text{ kJ}$. From the Appendix, the heat needed to vaporize 2 mol of H_2O is $2(-241.8 + 285.8) \text{ kJ} = 88 \text{ kJ}$. In step b, the products are being heated from 25°C to the flame temperature T . The heat required to do this is $88000 \text{ J} + (1 \text{ mol})(54.3 \text{ J/mol-K})(T - 298 \text{ K}) + (2 \text{ mol}) \times (41.2 \text{ J/mol-K})(T - 298 \text{ K}) + 2(3.76 \text{ mol})(32.7 \text{ J/mol-K}) \times (T - 298 \text{ K}) = 890000 \text{ J}$. So $T - 298 \text{ K} = 2096 \text{ K}$; $T \approx 2400 \text{ K}$.

5.48 (a) $n\text{-C}_4\text{H}_{10}(\text{g})$, since larger molecules have larger entropies. (b) $\text{H}_2\text{O}(\text{g})$, since gases have higher entropies than the corresponding liquids. (c) $\text{H}_2(\text{g})$, which has larger molecules than H(g) . (d) $\text{C}_{10}\text{H}_8(\text{g})$.

5.49 (a) $\Delta H^\circ = q_p$ is positive, since heat is needed to vaporize the liquid. For $\text{liq.} \rightarrow \text{gas}$, $\Delta S^\circ > 0$. (b) ΔH° is positive since energy is needed to break the bond.

ΔS° is positive, since the number of moles of gas is increasing. (c) q is negative when the vapor condenses, so ΔH° is negative. For gas \rightarrow solid, $\Delta S^\circ < 0$. (d) $(\text{COOH})_2(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$. We can expect the reaction to be exothermic, as is generally true for combustion reactions. Hence, $\Delta H^\circ < 0$. Also, $\Delta S^\circ > 0$, since the number of moles of gases is increasing. (e) $\Delta S^\circ < 0$, since the number of moles of gases is decreasing. All species are gases, and the Table 20.1 bond energies yield $\Delta H^\circ \approx (2711 - 2834) \text{ kJ/mol} = -123 \text{ kJ/mol}$, so $\Delta H^\circ < 0$.

5.50 To find \bar{S}_{298}° from Eq. (5.29), we need \bar{C}_p° measurements for the solid from a very low temperature up to the melting point, measurements of $\Delta \bar{H}_{\text{fus}}^\circ$ and the melting point, and \bar{C}_p° data for the liquid from the melting point to 298 K. In addition, if there are any solid-solid phase transitions, we need $\Delta \bar{H}^\circ$ and the temperature of each such transition. To determine $\Delta H_{\text{f},298}^\circ$ we need ΔH_{298}° of combustion of the hydrocarbon (see, for example, Prob. 5.11). $\Delta G_{\text{f}}^\circ$ is found from $\Delta H_{\text{f}}^\circ - T \Delta S_{\text{f}}^\circ$, as in Prob. 5.29.

CHAPTER 6

6.1 For a pure substance, $G = n\bar{G} = n\mu$ and $\Delta G = n \Delta\mu$. For an isothermal process in an ideal gas, $\Delta\mu = \mu^\circ(T) + RT \ln (P_2/P^\circ) - [\mu^\circ(T) + RT \ln (P_1/P^\circ)] = RT \ln (P_2/P_1)$ and $\Delta G = nRT \ln (P_2/P_1) = (3.00 \text{ mol})(8.314 \text{ J/mol-K}) \times (400 \text{ K}) \ln (0.5P_1/P_1) = -6.92 \text{ kJ}$.

6.2 $a[\mu_A^\circ + RT \ln(P_A/P^\circ)] = b[\mu_B^\circ + RT \ln(P_B/P^\circ)] + c[\mu_C^\circ + RT \ln(P_C/P^\circ)]$ and $b\mu_B^\circ + c\mu_C^\circ - a\mu_A^\circ = -RT[b \ln(P_B/P^\circ) + c \ln(P_C/P^\circ) - a \ln(P_A/P^\circ)] = -RT[\ln(P_B/P^\circ)^b + \ln(P_C/P^\circ)^c + \ln(P_A/P^\circ)^{-a}] = -RT \ln [(P_B/P^\circ)^b (P_C/P^\circ)^c (P_A/P^\circ)^{-a}]$. The left side is $\sum_i \nu_i \mu_i^\circ = \Delta G^\circ$ and the right side is $-RT \ln \prod_i (P_i/P^\circ)^{\nu_i} = -RT \ln K_P^\circ$. This completes the proof.

6.3 (a) $P_i = x_i P$. $P_{\text{SO}_3} = (0.440)(1767 \text{ torr}) = 777 \text{ torr}$; $P_{\text{SO}_2} = (0.310)(1767 \text{ torr}) = 548 \text{ torr}$; $P_{\text{O}_2} = 442 \text{ torr}$. $K_P^\circ = \prod_i (P_i/P^\circ)^{\nu_i} = (P_{\text{SO}_3}/P^\circ)^2 / (P_{\text{SO}_2}/P^\circ)^2 (P_{\text{O}_2}/P^\circ) = (777/750)^2 / (548/750)^2 (442/750) = 3.41$. $\Delta G^\circ = -RT \ln K_P^\circ = -(8.314 \text{ J/mol-K})(1000 \text{ K}) \ln 3.41 = -10.2 \text{ kJ/mol}$. (b) $K_P^\circ = (P_{\text{SO}_3}^2 / P_{\text{SO}_2}^2 P_{\text{O}_2}) P^\circ = K_P P^\circ$ and $K_P = K_P^\circ / P^\circ = 3.41 / (1 \text{ bar}) = 3.41 \text{ bar}^{-1}$.

6.4 $A + B \rightleftharpoons 2C + 3D$. If 10.0 mmol of C is formed, then 5.0 mmol of A and 5.0 mmol of B must have reacted and $(3/2)(10.0 \text{ mmol}) = 15.0 \text{ mmol}$ of D is formed. At equilibrium, $n_A = 10.0 \text{ mmol}$, $n_B = 13.0 \text{ mmol}$, $n_C = 10.0 \text{ mmol}$, $n_D =$

$$15.0 \text{ mmol}; n_{\text{tot}} = 48.0 \text{ mmol}. x_A = n_A/n_{\text{tot}} = 0.208, x_B = 0.271, x_C = 0.208, x_D = 0.312_5. P_A = x_A P = (0.208) \times (1085 \text{ torr}) = 226 \text{ torr}, P_B = 294 \text{ torr}, P_C = 226 \text{ torr}, P_D = 339 \text{ torr}. K_P^\circ = (P_C/P^\circ)^2 (P_D/P^\circ)^3 / (P_A/P^\circ) (P_B/P^\circ) = (226/750)^2 (339/750)^3 / (226/750) (294/750) = 0.0710. \Delta G^\circ = -RT \ln K_P^\circ = -(8.314 \text{ J/mol-K})(600 \text{ K}) \ln 0.0710 = 13.2 \text{ kJ/mol}.$$

6.5 $n_{\text{tot}} = PV/RT = [(231.2/760) \text{ atm}](1055 \text{ cm}^3) / (82.06 \text{ cm}^3\text{-atm/mol-K})(323.7 \text{ K}) = 0.01208 \text{ mol}.$ Let $x \text{ mol}$ of Br_2 react to reach equilibrium. At equilibrium, $n_{\text{NO}}/\text{mol} = 0.01031 - 2x$, $n_{\text{Br}_2} = 0.00440 - x$, $n_{\text{NOBr}} = 2x$, $n_{\text{tot}} = 0.01471 - x = 0.01208$; $x = 0.00263$. So $n_{\text{NO}} = 0.00505$, $n_{\text{Br}_2} = 0.00177$, $n_{\text{NOBr}} = 0.00526$; $x_{\text{NO}} = n_{\text{NO}}/n_{\text{tot}} = 0.418$, $x_{\text{Br}_2} = 0.146_5$, $x_{\text{NOBr}} = 0.435$. $P_{\text{NO}} = x_{\text{NO}} P = (0.418)(231.2 \text{ torr}) = 96.6 \text{ torr}$, $P_{\text{Br}_2} = 33.9 \text{ torr}$, $P_{\text{NOBr}} = 100.6 \text{ torr}$, $P^\circ = 750 \text{ torr}$. $K_P^\circ = (P_{\text{NOBr}}/P^\circ)^2 / (P_{\text{NO}}/P^\circ)^2 (P_{\text{Br}_2}/P^\circ) = 24.0$. $\Delta G^\circ = -RT \ln K_P^\circ = -(8.314 \text{ J/mol-K})(323.7 \text{ K}) \ln 24.0 = -8.55 \text{ kJ/mol}.$

6.6 $(P_{\text{N}}/P^\circ)^2 / (P_{\text{N}_2}/P^\circ) = (0.12)^2 / (720)(750) = 2.7 \times 10^{-8}$, which is less than K_P° . The system is not at equilibrium; $P_{\text{N(g)}}$ and hence $n_{\text{N(g)}}$ must increase to reach equilibrium.

6.7 Consider the reaction $aA + bB \rightleftharpoons cC + dD$. Use of

$$P_i = x_i P \text{ gives}$$

$$K_P^\circ = \frac{(P_C/P^\circ)^c (P_D/P^\circ)^d}{(P_A/P^\circ)^a (P_B/P^\circ)^b} = \frac{x_C^c x_D^d}{x_A^a x_B^b} P^{c+d-a-b} (P^\circ)^{a+b-c-d} = K_x (P/P^\circ)^{\Delta n/\text{mol}}$$

6.8 $\Delta G^\circ = -RT \ln K_p^\circ = -(8.314 \text{ J/mol-K})(298.1 \text{ K}) \ln 0.144 = 4.80 \text{ kJ/mol}$. If ΔH° is assumed constant over the range 25°C to 35°C , then Eq. (6.39) applies and $\ln(0.321/0.144) = [\Delta H^\circ / (8.314 \text{ J/mol-K})][(298.1 \text{ K})^{-1} - (308.1 \text{ K})^{-1}]$; $\Delta H^\circ = 61.2 \text{ kJ/mol}$. $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = 4800 \text{ J/mol} = 61200 \text{ J/mol} - (298.1 \text{ K})\Delta S^\circ$ and $\Delta S^\circ = 189 \text{ J/mol-K}$.

6.9 We plot $\ln K_p^\circ$ versus $1/T$. The data are

$\ln K_p^\circ$	-1.406	0.688	1.601	2.235
T^{-1}/K^{-1}	0.00206 ₂	0.00187 ₃	0.00179 ₉	0.00174 ₂

The plot is very nearly linear, with slope -11400 K , and $-\Delta H^\circ/R = -11400 \text{ K}$, $\Delta H^\circ = (11400 \text{ K})(8.314 \text{ J/mol-K}) = 94.8 \text{ kJ/mol} = 22.6 \text{ kcal/mol}$ in this range of T . Then $\Delta G_{534}^\circ = -RT \ln K_p^\circ = -(8.314 \text{ J/mol-K})(534 \text{ K}) \ln 1.99 = -3.05_5 \text{ kJ/mol} = -730 \text{ cal/mol}$. From $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$, $\Delta S_{534}^\circ = (\Delta H^\circ - \Delta G^\circ)/T = (94800 + 3055) (\text{J/mol}) / (534 \text{ K}) = 183 \text{ J/mol-K} = 43.7 \text{ cal/mol-K}$. (b) $\Delta H^\circ = 22.6 \text{ kcal/mol} = 94.8 \text{ kJ/mol}$, as in (a). (The near linearity of the plot shows that ΔH° is essentially constant over this range of T .) $\Delta G_{574}^\circ = -RT \ln K_p^\circ = -10.7 \text{ kJ/mol} = -2.55 \text{ kcal/mol}$. $\Delta S_{574}^\circ = (\Delta H_{574}^\circ - \Delta G_{574}^\circ)/T = 183 \text{ J/mol-K} = 43.8 \text{ cal/mol-K}$.

6.10 Substitute (6.28) into (6.14).

6.11 When T_2 in the ΔH° expression at the end of Sec. 5.5 is replaced by T and this expression is inserted into (6.37), the right side of (6.37) becomes

$(1000 \text{ J/mol})R^{-1} \int_{T_1}^{T_2} [-571.528/T^2 + 0.00151K^{-1}/T + 2.85 \times 10^{-6} K^{-2} + (1448 \text{ K})/T^3] dT$. Also, $-RT \ln K_{P,298}^{\circ} = \Delta G_{298}^{\circ} = [2(-394.359) - 2(-137.168) - 0] \text{ kJ/mol} = -514382 \text{ J/mol}$ and $\ln K_{P,298}^{\circ} = 207.50$. Taking $T_1 = 298.15$ and evaluating the preceding integral, we find that Eq. (6.37) gives (where $K = \text{kelvin}$) $\ln K_P^{\circ}(T_2) = 207.50 - 229.67 + 68739(K/T_2) + 0.1816 \ln (T_2/298.15 \text{ K}) + 3.43 \times 10^{-4}(T_2/K) - 87080(K^2/T_2^2)$. (b) Substitution of $T_2/K = 1000$ gives $\ln K_{P,1000}^{\circ} = 47.04$ and $K_{P,1000}^{\circ} = 3 \times 10^{20}$.

6.12 Equation (5.19) gives

$$\begin{aligned}
 \Delta H_T^{\circ} &= \Delta H_{T_1}^{\circ} + \int_{T_1}^T [2e - a + (2f - b)T' + (2g - c)T'^2] dT' \\
 &= \Delta H_{T_1}^{\circ} + (2e - a)(T - T_1) + (f - \frac{1}{2}b)(T^2 - T_1^2) \\
 &\quad + \frac{1}{3}(2g - c)(T^3 - T_1^3)
 \end{aligned}$$

Substitution in (6.37) and integration gives

$$\begin{aligned}
 \ln K_P^{\circ}(T_2) &= \ln K_P^{\circ}(T_1) + \frac{1}{R} [\Delta H_{T_1}^{\circ} + (a - 2e)T_1 + (\frac{1}{2}b - f)T_1^2 \\
 &\quad + \frac{1}{3}(c - 2g)T_1^3] (T_1^{-1} - T_2^{-1}) \\
 &\quad + (2e - a) \ln \frac{T_2}{T_1} + (f - \frac{1}{2}b)(T_2 - T_1) \\
 &\quad + \frac{1}{6}(2g - c)(T_2^2 - T_1^2)
 \end{aligned}$$

6.13 From (6.25), $\ln K_c^{\circ} = \ln K_P^{\circ} - (\Delta n/\text{mol}) \ln T + \text{const.}$

Differentiation and use of (6.36) and (5.10) give

$$\frac{d \ln K_c^{\circ}}{dT} = \frac{d \ln K_P^{\circ}}{dT} - \frac{\Delta n/\text{mol}}{T} = \frac{\Delta H^{\circ}}{RT^2} - \frac{\Delta n RT/\text{mol}}{RT^2} = \frac{\Delta U^{\circ}}{RT^2}$$

6.14 From (6.27), $\ln K_x = \ln K_p^\circ - (\Delta n/\text{mol}) \ln (P/\text{bar})$.

Differentiation with respect to T and use of (6.36) gives

$(\partial \ln K_x / \partial T)_P = d \ln K_p^\circ / dT = \Delta H^\circ / RT^2$. Partial differentiation with respect to P gives (since K_p° is independent of P): $(\partial \ln K_x / \partial P)_T = -(\Delta n/\text{mol})/P$.

6.15 The Appendix $\Delta G_{f,298}^\circ$ values give for this reaction

$\Delta G_{298}^\circ = 4730 \text{ J/mol}$. From $\Delta G^\circ = -RT \ln K_p^\circ$, we find $K_p^\circ = 0.148$ at 25°C . The reaction has the form $A \rightleftharpoons 2B$, and $K_p^\circ = (P_B/P^\circ)^2 / (P_A/P^\circ) = P_B^2 / P_A P^\circ = (x_B P)^2 / x_A P P^\circ = [x_B^2 / (1 - x_B)] P / P^\circ$. Then $x_B^2 / (1 - x_B) = 0.148(0.987/0.500) = 0.292$ and the quadratic formula gives $x_B = 0.414 = x_{\text{NO}_2}$; also, $x_{\text{N}_2\text{O}_4} = 0.586$.

6.16 Since $P_i = n_i RT/V$, the partial pressures are proportional to the moles. Let zV/RT moles of CO react. The

equilibrium partial pressures are then $P_{\text{CO}} = 342 \text{ torr} - z$,

$P_{\text{Cl}_2} = 351.4 \text{ torr} - z$, $P_{\text{COCl}_2} = z$. Thus $439.5 \text{ torr} =$

$342.0 \text{ torr} - z + 351.4 \text{ torr} - z + z$ and $z = 253.9 \text{ torr}$.

$K_p^\circ = (253.9/750)/(88.1/750)(97.5/750) = 22.2$.

6.17 $\Delta G^\circ / (\text{kJ/mol}) = -394.359 + (-879) - 2(-619.2) = -35$.

$\ln K_p^\circ = -\Delta G^\circ / RT = (35000 \text{ J/mol}) / (8.314 \text{ J/mol-K})(298 \text{ K})$

$\ln K_p^\circ = 14.1$, $K_p^\circ = 1.3 \times 10^6$

Let $2z$ moles of COF_2 react. The equilibrium amounts are

$n(\text{COF}_2) = 1 - 2z$, $n(\text{CO}_2) = 1 + z$, $n(\text{CF}_4) = z$. Because K_p°

is so large, we have $2z \approx 1$ and $z \approx \frac{1}{2}$. Hence, $n(\text{CO}_2) =$

1.50 mol, $n(\text{CF}_4) = 0.50$ mol, and

$$1.3 \times 10^6 = \frac{(1.5/n_{\text{tot}})^P (0.5/n_{\text{tot}})^P}{[n(\text{COF}_2)/n_{\text{tot}}]^2 P^2}, \quad n(\text{COF}_2) = 7 \times 10^{-4} \text{ mol}$$

6.18 $\ln K_P^\circ = -\Delta G^\circ/RT = -1.258$. $K_P^\circ = 0.284$. (a) Let z moles of A react. The equilibrium amounts are $n_A = 1 - z$, $n_B = 1 - z$, $n_C = 2z$, $n_D = 2z$, and $n_{\text{tot}} = 2 + 2z$. Use of $P_i = x_i P$ gives

$$0.284 = \frac{\left(\frac{z}{1+z}\right)^2 \left(\frac{P}{P^\circ}\right)^2 \left(\frac{z}{1+z}\right)^2 \left(\frac{P}{P^\circ}\right)^2}{\left(\frac{1-z}{2(1+z)}\right)^2 \left(\frac{P}{P^\circ}\right)^2} = \frac{4z^4}{(1-z^2)^2} \left(\frac{1200}{750}\right)^2$$

$$0.533 = \frac{2z^2}{1-z^2} \frac{1200}{750}, \quad 2.333 z^2 = 0.333_1, \quad z = 0.378$$

Both times we took the positive square root, since z and $1 - z^2$ are positive. $n_A = 0.622$ mol = n_B , $n_C = 0.756$ mol = n_D . (b) The equilibrium amounts are $n_A = 1 - z$, $n_B = 2 - z$, $n_C = 2z = n_D$. We have

$$0.284 = \frac{[2z/(3+2z)]^4 (P/P^\circ)^2}{[(1-z)/(3+2z)][(2-z)/(3+2z)]}$$

$$0.00693_1 - z^4/(1-z)(2-z)(3+2z)^2 = 0$$

z lies between 0 and 1, and trial and error gives the desired root as $z = 0.530$. Hence $n_A = 0.470$, $n_B = 1.470$, $n_C = 1.060 = n_D$.

6.19 $\Delta G^\circ = -RT \ln K_P^\circ$, $\Delta G_{\text{wrong}}^\circ = -RT \ln K_{P,\text{wrong}}^\circ$.

$\Delta G^\circ - \Delta G_{\text{wrong}}^\circ = 2500 \text{ J/mol} = -RT \ln (K_P^\circ / K_{P,\text{wrong}}^\circ)$. We get
 $\ln (K_P^\circ / K_{P,\text{wrong}}^\circ) = -1.00$ and $K_{P,\text{wrong}}^\circ / K_P^\circ = 2.7$. The
 error is a factor of 2.7.

6.20 $x_A = (1.000 \text{ mol} / 6.000 \text{ mol}) = 0.1667$, $x_B = 0.5000$,
 $x_C = 0.3333$. $P_A = x_A P = 0.1667(1.000 \text{ bar}) = 0.1667 \text{ bar}$,
 $P_B = 0.5000 \text{ bar}$, $P_C = 0.3333 \text{ bar}$.

$$K_P^\circ = 0.3333 / (0.1667 \times 0.5000) = 4.000$$

Let z moles of A react to reach the new equilibrium position at $P = 2.000 \text{ bar}$. For this equilibrium, $n_A = 1 - z$,
 $n_B = 3 - z$, $n_C = 2 + z$ and $x_A = (1 - z) / (6 - z)$,
 $x_B = (3 - z) / (6 - z)$, $x_C = (2 + z) / (6 - z)$.
 $P_A = x_A P = [(1 - z) / (6 - z)](2 \text{ bar})$, $P_B = \text{etc.}$

$$K_P^\circ = 4.00 = \frac{[(2 + z) / (6 - z)]^2}{[(1 - z) / (6 - z)]^2 [(3 - z) / (6 - z)]^2}$$

$$9z^2 - 36z + 12 = 0, \quad z = 0.367 \text{ and } 3.63$$

We have $n_A = 1 - z$, so z cannot exceed 1. Therefore $z = 0.367$.
 $n_A = 0.633 \text{ mol}$, $n_B = 2.633 \text{ mol}$, $n_C = 2.367 \text{ mol}$.

6.21 $\Delta G_{298}^\circ / (\text{kJ/mol}) = -267.8 + 0 - (-305.0) = 37.2$.

$$\Delta G^\circ = -RT \ln K_P^\circ. \quad 37200 \text{ J/mol} = -(8.314 \text{ J/mol-K}) \times$$

$$(298 \text{ K}) \ln K_{P,298}^\circ. \quad K_{P,298}^\circ = 3.0 \times 10^{-7}. \quad \Delta H_{298}^\circ / (\text{kJ/mol})$$

$$= -287.0 + 0 - (-374.9) = 87.9. \text{ Equation (6.39) gives}$$

$$\ln K_{P,500}^\circ \approx \ln (3.0 \times 10^{-7}) +$$

$$[(87900 \text{ J/mol}) / (8.314 \text{ J/mol-K})][(298 \text{ K})^{-1} - (500 \text{ K})^{-1}] =$$

$$-0.699. \quad K_{P,500}^\circ = 0.50.$$

The mole fractions are $x_{\text{PCl}_3} = x_{\text{Cl}_2} = x$ and $x_{\text{PCl}_5} = 1 - x_{\text{PCl}_3} - x_{\text{Cl}_2} = 1 - 2x$. We have $K_{P,500}^\circ = 0.50 = (x_P/P^\circ)^2 / [(1 - 2x)P/P^\circ] = x^2 / (1 - 2x)$, since $P = P^\circ = 1$ bar. $x^2 = 0.50 - 1.00x$, and the quadratic formula gives $x = 0.36_6 = x_{\text{PCl}_3} = x_{\text{Cl}_2}$; $x_{\text{PCl}_5} = 1 - 2x = 0.26_8$.

6.22 (a) $\text{I}_2(\text{g}) \rightleftharpoons 2\text{I}(\text{g})$. Let n^* be the number of I_2 moles before dissociation, and let z moles of I_2 dissociate to give $2z$ moles of I , leaving $n^* - z$ moles of I_2 . The total number of moles at equilibrium is $n^* - z + 2z = n^* + z$.

Then $x_{\text{I}} = 2z/(n^* + z)$ and $x_{\text{I}_2} = (n^* - z)/(n^* + z)$. We have $n^* = P^*V/RT$ and $n^* + z = PV/RT$, so $z = PV/RT - n^* =$

$(P - P^*)V/RT$. Use of these expressions for z , $n^* + z$ and n^* gives $x_{\text{I}} = [2(P - P^*)V/RT]/(PV/RT) = 2(P - P^*)/P$ and

$x_{\text{I}_2} = [P^*V/RT - (P - P^*)V/RT]/(PV/RT) = (2P^* - P)/P$.

(b) $K_P^\circ = (x_{\text{I}}P/P^\circ)^2 / (x_{\text{I}_2}P/P^\circ) = [2(P - P^*)/P^\circ]^2 /$

$[(2P^* - P)/P^\circ] = 4(P - P^*)^2 / (2P^* - P)P^\circ$. (c) We use the

result of (b) to calculate the following K_P° values:

$K_{P,973}^\circ = 4(0.0624 - 0.0576)^2 / [2(0.0576) - 0.0624]0.987 = 0.00177$; $K_{P,1073}^\circ = 0.0112$; $K_{P,1173}^\circ = 0.0493$; $K_{P,1274}^\circ = 0.172_5$. We plot $\ln K_P^\circ$ vs. $1/T$. The data are

$\ln K_P^\circ$	-6.34	-4.49	-3.01	-1.75 ₇
$10^4/T$	10.28	9.32	8.52 ₅	7.85 K^{-1}

One finds a straight line with slope $-1.88_5 \times 10^4 \text{ K}$.

From Eq. (6.40), $\Delta H^\circ = (1.88_5 \times 10^4 \text{ K})(8.314 \text{ J/mol-K}) = 157 \text{ kJ/mol} = 37.5 \text{ kcal/mol}$.

$$\begin{aligned}
 \underline{6.23} \quad K_P^{\text{bar}}/K_P^{\text{atm}} &= [\prod_i (P_i/\text{bar})^{v_i}]/[\prod_i (P_i/\text{atm})^{v_i}] = \\
 \prod_i (P_i/\text{bar})^{v_i}/(P_i/\text{atm})^{v_i} &= \prod_i (\text{atm}/\text{bar})^{v_i}. \text{ For } aA + bB \rightleftharpoons \\
 cC + dD, \prod_i (\text{atm}/\text{bar})^{v_i} &= (\text{atm}/\text{bar})^{c+d-a-b} = \\
 (\text{atm}/\text{bar})^{\Delta n/\text{mol}} &= (760 \text{ torr}/750.062 \text{ torr})^{\Delta n/\text{mol}} = \\
 (1.01325)^{\Delta n/\text{mol}}.
 \end{aligned}$$

$$\begin{aligned}
 \underline{6.24} \quad \text{At equilibrium, } n_{N_2}/\text{mol} &= 1 - x, n_{H_2}/\text{mol} = 3 - 3x, \\
 n_{NH_3}/\text{mol} &= 2x; n_{\text{tot}}/\text{mol} = 4 - 2x. P_{N_2} = x_{N_2} P = \\
 (n_{N_2}/n_{\text{tot}})P &= [(1 - x)/(4 - 2x)]P, P_{H_2} = \\
 [3(1 - x)/(4 - 2x)]P, P_{NH_3} &= [2x/(4 - 2x)]P. K_P^\circ = \\
 (P_{NH_3}/P^\circ)^2/(P_{N_2}/P^\circ)(P_{H_2}/P^\circ)^3 &= \\
 (P^\circ)^2 P^{-2} (4 - 2x)^2 (2x)^2 / (1 - x) 3^3 (1 - x)^3 &= \\
 (P^\circ/P)^2 (16/27) (2 - x)^2 x^2 / (1 - x)^4 &= K_P^\circ. x \text{ must be between} \\
 0 \text{ and } 1. \text{ Taking the positive square root of each side} \\
 \text{gives } (P^\circ/P)(4/27)^{\frac{1}{2}}(2 - x)x/(1 - x)^2 &= K_P^{\circ\frac{1}{2}} \text{ or} \\
 4(2x - x^2)/(1 - x)^2 &= (27K_P^\circ)^{\frac{1}{2}}(P/P^\circ) = s. \text{ Hence } 8x - 4x^2 = \\
 s - 2sx + x^2 s \text{ and } (4 + s)x^2 - (2s + 8)x + s &= 0 \text{ or} \\
 x^2 - 2x + s/(s + 4) &= 0. \text{ The quadratic formula gives} \\
 x = \{2 \pm [4 - 4s/(s + 4)]^{\frac{1}{2}}\}/2 &= 1 \pm [1 - s/(s + 4)]^{\frac{1}{2}}. \text{ Since} \\
 x \text{ is less than } 1, \text{ we take the minus sign: } x &= \\
 1 - [1 - s/(s + 4)]^{\frac{1}{2}}.
 \end{aligned}$$

6.25 (a) $d \ln K_P^\circ/dT = \Delta H^\circ/RT^2$. Appendix data give $\Delta H^\circ = 87.9 \text{ kJ/mol} > 0$, so K_P° decreases as T decreases and the equilibrium shifts to the left. (b) As V decreases at constant T , the pressure increases and the equilibrium shifts to the side with fewer moles of gas, i.e., it

shifts to the left. (c) This removal decreases P_{PCl_5} , so to restore equilibrium, the reaction must shift to the left. (d) Constant T and V addition of He does not affect the partial pressures of PCl_5 , PCl_3 , or Cl_2 , and there is no shift. (e) To keep P constant as He(g) is added, V must be increased. Since $P_i = n_i RT/V$, this volume increase will decrease each partial pressure P_i by the same percentage. Since the reaction has more moles of products than of reactants, the numerator of the reaction quotient Q_p will decrease more than the denominator. Therefore the equilibrium will shift to the right to make Q_p again equal to K_p .

6.26 From Prob. 6.13, $d \ln K_c^\circ / dT = \Delta U^\circ / RT^2$; if ΔU° is positive, then K_c° increases as T increases. Since $c_i = n_i/V$ and V is held fixed, the mole numbers n_i undergo changes proportional to the changes in the concentrations, and the equilibrium shifts to the right if $\Delta U^\circ > 0$.

6.27 (a) $\ln Q_x = \ln [\prod_i (x_i)^{v_i}] = \sum_i \ln (x_i)^{v_i} = \sum_i v_i \ln x_i = \sum_i v_i \ln (n_i/n_{\text{tot}}) = \sum_i v_i \ln n_i - (\sum_i v_i) \ln (n_1 + n_2 + \dots)$. We have $\partial \ln Q_x / \partial n_j = v_j/n_j - \Delta n / (n_1 + n_2 + \dots) \text{mol} = (v_j - x_j \Delta n / \text{mol}) / n_j$. b) Case I: suppose substance j is a reactant. Then v_j is negative. To get a shift to the left, we want $\partial Q_x / \partial n_j > 0$, so that addition of j will make $Q_x > K_x$. We thus want $v_j - x_j \Delta n / \text{mol} > 0$ and $v_j > x_j \Delta n / \text{mol}$. Since v_j is negative, Δn must be negative. Division of

the inequality by the negative quantity Δn reverses its direction to give $v_j/(\Delta n/\text{mol}) < x_j$. The fact that Δn is negative means that the total moles of reactants exceeds the total moles of products, in agreement with condition (1). Case II: suppose substance j is a product. Then v_j is positive. We want $\partial Q_x/\partial n_j < 0$, so that addition of j will make $Q_x < K_x$ and shift the equilibrium to the right. We thus want $v_j - x_j \Delta n/\text{mol} < 0$ or $v_j < x_j \Delta n/\text{mol}$. v_j is positive, so Δn must be positive and division by Δn gives $x_j > v_j/(\Delta n/\text{mol})$. The fact that Δn is positive means that the product total moles exceed the reactant total moles. (c) The left side of the reaction has the greater sum of the coefficients, so constant-T-and-P addition of NH_3 will never produce more NH_3 . For N_2 , condition (2) is $x_{\text{N}_2} > (-1)/(-2) = \frac{1}{2}$, so for $x_{\text{N}_2} > 0.5$, addition of N_2 at constant T and P produces more N_2 . For H_2 , condition (2) is $x_{\text{H}_2} > (-3)/(-2) = 1.5$, which can never be satisfied.

6.28 The reaction rate at lower temperatures is too slow to make the reaction economically practical.

6.29 $\Delta G^\circ = -RT \ln K_P^\circ = -2.303RT \log K_P^\circ = -2.303 \times$

$$(8.314 \text{ J/mol-K})(500 \text{ K})[7.55 - (4830 \text{ K})/(500 \text{ K})] = 20.2 \text{ kJ/mol.}$$

$$d \ln K_P^\circ/dT = \Delta H^\circ/RT^2. \quad \Delta H^\circ = RT^2 d \ln K_P^\circ/dT =$$

$$2.303RT^2 d \log K_P^\circ/dT = 2.303RT^2(4830 \text{ K})/T^2 = 2.303 \times$$

$$(8.314 \text{ J/mol-K})(4830 \text{ K}) = 92.5 \text{ kJ/mol.} \quad \Delta S^\circ =$$

$$(\Delta H^\circ - \Delta G^\circ)/T = (72.3 \text{ kJ/mol})/(500 \text{ K}) = 144.6 \text{ J/mol-K.}$$

$$C_P = (\partial H / \partial T)_P. \quad \Delta C_P^\circ = (\partial \Delta H^\circ / \partial T)_P = 0.$$

6.30 ΔG° refers to a change from pure, separated reactants, each in its standard state, to pure, separated products, each in its standard state. ΔG° is not the change in G that occurs in the actual reaction mixture. The reacting system does not contain substances in their standard states.

6.31 K_P° is a function of T only. Therefore only (d) will will change K_P° .

6.32 (a) $\Delta H^\circ = \sum_i \nu_i \bar{H}_i^\circ$. The enthalpies of ideal gases depend on T only and are unaffected by pressure changes or by mixing with other ideal gases. Therefore, the observed ΔH per mole of reaction does equal ΔH° for the reaction. (b) Entropies of ideal gases depend strongly on P and the gases in the reaction mixture are not at 1 bar partial pressures. Therefore, the entropies in the mixture do not equal the standard-state entropies and ΔS per mole of reaction differs substantially from ΔS° . (c) Since $\Delta \bar{S} \neq \Delta S^\circ$, it follows that $\Delta \bar{G} \neq \Delta G^\circ$.

6.33 Let the superscripts 750 and 1000 denote standard states based on 750 torr and on 1000 torr, respectively.

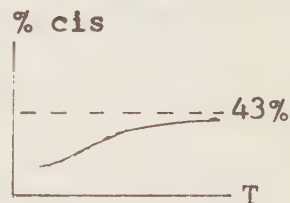
$$K_P^{\circ,1000} / K_P^{\circ,750} = [(P_{\text{NO}_2} / P^{\circ,1000})^2 / (P_{\text{N}_2\text{O}_4} / P^{\circ,1000})] \div [(P_{\text{NO}_2} / P^{\circ,750})^2 / (P_{\text{N}_2\text{O}_4} / P^{\circ,750})] = (P^{\circ,1000})^{-1} \div (P^{\circ,750})^{-1}$$

= 750/1000. (The gases are unaware of what choice of standard state has been made, so the equilibrium partial-pressure ratio $P_{\text{NO}_2}^2/P_{\text{N}_2\text{O}_4}$ is independent of the standard-state choice and cancels.) The Appendix ΔG_f° data give $\Delta G_f^{\circ,750} = 4.73 \text{ kJ/mol}$ and use of $\Delta G_f^{\circ,750} = -RT \ln K_P^{\circ,750}$ gives $K_P^{\circ,750} = 0.14_8$. Then $K_P^{\circ,1000} = (750/1000)0.14_8 = 0.11_1$.

6.34 (a) Since $\Delta H^\circ < 0$, the relation $d \ln K_P^\circ/dT = \Delta H^\circ/RT^2$ shows that K_P° decreases as T increases; thus the equilibrium amount of the cis isomer increases as T increases.

(b) We have $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \approx -T \Delta S^\circ$ in the high- T limit. Since $\Delta S^\circ > 0$, we have $\Delta G^\circ < 0$ at high T and $K_P^\circ > 1$ at high T . Thus the high- T limit has more trans isomer than cis isomer. (c) Even though the percentage of cis

isomer continually increases as T increases, it is still possible to have more trans than cis at high T . In the graph at the right, the % cis continually increases with T but always remains below its asymptotic



$T = \infty$ limit of 43%. (d) $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$, where ΔS° and ΔH° are constant. In this equation, the coefficient $-\Delta S^\circ$ of T is negative, so ΔG° decreases as T increases. As noted in (a), K_P° decreases as T increases. We have $\Delta G^\circ/T = -R \ln K_P^\circ$, and since K_P° is decreasing as T increases, $\Delta G^\circ/T$ is increasing as T increases, which is the opposite behavior as shown by ΔG° . (If this seems puzzling, note that ΔG° is negative.) (e) Yes. For the reverse reaction, trans \rightarrow cis, the results of (d) show that ΔG° increases and K_P° increases as T increases. (The behavior of K_P° is determined not by ΔG° but by $\Delta G^\circ/T$.)

6.35 $0 = (\partial/\partial m) \sum_i (y_i - mx_i - b)^2 = \sum_i 2(-x_i)(y_i - mx_i - b) = -2\sum_i x_i y_i + 2m \sum_i x_i^2 + 2b \sum_i x_i$; $b = (\sum_i x_i y_i - m \sum_i x_i^2) / \sum_i x_i$. $0 = (\partial/\partial b) \sum_i (y_i - mx_i - b)^2 = -\sum_i (y_i - mx_i - b) = -\sum_i y_i + m \sum_i x_i + nb$, since $\sum_{i=1}^n b = nb$; thus $b = (\sum_i y_i - m \sum_i x_i) / n$. Equating the two boxed expressions for b and solving the resulting equation for m, we find $m = (n \sum_i x_i y_i - \sum_i x_i \sum_i y_i) / [n \sum_i x_i^2 - (\sum_i x_i)^2]$. Substituting this expression for m into $b = (\sum_i y_i - m \sum_i x_i) / n$ and using a common denominator for the terms on the right, we obtain the equation given in the text.

6.36 (a) $n_1 - n_{1,0} = \Delta n_1 = v_1 \xi$, so $n_{1,eq} = n_{1,0} + v_1 \xi$. $n_{N_2} = 1 \text{ mol} - \xi$, $n_{H_2} = 3 \text{ mol} - 3\xi$, $n_{NH_3} = 2\xi$. (b) $G = \sum_i n_i \bar{G}_i^*(T, P_i) = \sum_i n_i \mu_i^*(T, P_i) = \sum_i n_i [\mu_i^\circ(T) + RT \ln(P_i/P^\circ)]$, where the sum goes over N_2 , H_2 , and NH_3 , the n_i 's are given in (a), and the P_i 's are: $P_{H_2} = [(3 \text{ mol} - 3\xi)/(4 \text{ mol} - 2\xi)]P$, $P_{NH_3} = [2\xi/(4 \text{ mol} - 2\xi)]P$, $P_{N_2} = (n_{N_2}/n_{tot})P = [(1 \text{ mol} - \xi)/(4 \text{ mol} - 2\xi)]P$. $H = \sum_i n_i \bar{H}_i^*(T, P_i)$. Since H of an ideal gas is independent of P, $\bar{H}_i^* = \bar{H}_i^\circ$ and $H = \sum_i n_i \bar{H}_i^\circ(T)$, where the n_i 's are given in (a). (c) A BASIC program is given on the next page.

Results at $\xi = 0, 0.2, 0.3, 0.4, 0.6, 0.8, 1.0$ are:

$G/(\text{kJ/mol}) = -284.73, -288.45, -289.06, -289.20, -288.17, -286.07, -277.21$; $H/(\text{kJ/mol}) = 23.55, 3.60, -6.37, -16.34, -36.29, -56.23, -76.18$; $TS/(\text{kJ/mol}) = 308.28, 292.05, 282.69, 272.86, 251.88, 228.83, 201.03$.

```

10 HN = 5.91
12 HH = 5.88
14 HA = -38.09
16 G1 = -97.46
18 G2 = -66.99
20 G3 = -144.37
22 T = 500
24 R = 8.314E-3
26 P0 = 1
28 P = 4
30 FOR X = 0 TO 1 STEP 0.1
32 NN = 1 - X
34 NH = 3 - 3*X
36 NA = 2*X
38 PN = ((1-X)/(4-2*X))*P
40 PH = ((3-3*X)/(4-2*X))*P
42 PA = (2*X/(4-2*X))*P
44 IF PA = 0 THEN PA = 1E-7
46 IF PN = 0 THEN PN = 1E-7
48 IF PH = 0 THEN PH = 1E-7
50 GN = G1 + R*T*LOG(PN/P0)
52 GH = G2 + R*T*LOG(PH/P0)
54 GA = G3 + R*T*LOG(PA/P0)
56 G = NN*GN + NH*GH + NA*GA
58 H = NN*HN + NH*HH + NA*HA
60 TS = H - G
62 PRINT "XI=";X;" G=";G;
   " H=";H;"TS=";TS
64 NEXT X
66 END

```

6.37 (a) Any reaction with $\Delta n = 0$; e.g., $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g})$. (b) From (6.36), to have K_p° independent of T requires that $\Delta H^\circ = 0$. Two mirror-image species have the same energy, so ΔH° is zero for $\text{d-CHFClBr}(\text{g}) \rightleftharpoons \text{l-CHFClBr}(\text{g})$. [Actually, because of the nonconservation of parity, two mirror-image molecules have an extremely tiny, experimentally undetectable energy difference.]

6.38 (a) The system discussed near the end of Sec. 6.5 with $n_{\text{N}_2} = 3.00$ mol, $n_{\text{H}_2} = 1.00$ mol, $n_{\text{NH}_3} = 1.00$ mol has $x_{\text{N}_2} = 3.00/5.00 = 0.600$. If the reaction $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ shifts slightly to the right with 0.100 mol of N_2 being consumed, the new amounts are $n_{\text{N}_2} = 2.90$ mol, $n_{\text{H}_2} = 0.70$ mol, $n_{\text{NH}_3} = 1.20$ mol, and $x_{\text{N}_2} = 2.90/4.80 = 0.604$. Thus x_{N_2} has increased even though n_{N_2} has decreased. (b) $x_i = n_i/n_{\text{tot}}$; $dx_i = dn_i/n_{\text{tot}} - (n_i/n_{\text{tot}}^2) dn_{\text{tot}}$. We have $dn_i = v_i d\xi$ and $dn_{\text{tot}} = d \sum_j n_j = \sum_j dn_j = \sum_j v_j d\xi = (\sum_j v_j) d\xi = (\Delta n/\text{mol}) d\xi$. So $dx_i = (v_i/n_{\text{tot}}) d\xi - (x_i/n_{\text{tot}})(\Delta n/\text{mol}) d\xi = n_{\text{tot}}^{-1} [v_i - x_i(\Delta n/\text{mol})] d\xi$.

6.39 (a) False. (b) False; G is minimized only if the system is held at constant T and P . (c) True; see Eq. (6.4). (d) False; see Sec. 6.5. (e) False; see Fig. 6.5. (f) True; see Fig. 6.5. (g) True. (h) False; this is true only if $\Delta n = 0$. (i) False. (j) True. (k) True; from (6.13) and (6.20), K_P° depends on P° but K_P does not.

Reminder: Use the solutions manual as an incentive to work problems, not as a way to avoid working problems.

CHAPTER 7

7.1 (a) $c = 2$ (water and sucrose), $p = 1$, $r = 0$, $a = 0$; $f = c - p + 2 - r - a = 3$. The degrees of freedom are temperature, pressure, and sucrose mole fraction. (b) $c = 3$, $p = 1$, $r = 0$, $a = 0$; $f = 4$. The degrees of freedom are T , P , x_{sucrose} , x_{ribose} . (c) $c = 3$ (sucrose, ribose, water), $p = 2$ (solid sucrose, the solution); $f = 3 - 2 + 2 - 0 - 0 = 3$ (T , P , x_{ribose}). Note that x_{sucrose} in the solution saturated with sucrose is fixed. (d) $c = 3$ (sucrose, ribose, water), $p = 3$ (solid sucrose, solid ribose, the solution); $f = 3 - 3 + 2 - 0 - 0 = 2$ (T and P). (e) $c = 1$ (water), $p = 2$; $f = 1 - 2 + 2 - 0 - 0 = 1$. The degree of freedom can be taken as either T or P . (Once T is fixed, P is fixed at the vapor pressure of water.) (f) $c = 2$ (water, sucrose), $p = 2$; $f = 2 - 2 + 2 - 0 - 0 = 2$ [T and x_{sucrose} (or P and x_{sucrose})]. (g) $c = 2$, $p = 3$; $f = 2 - 3 + 2 - 0 - 0 = 1$ (either T or P).

7.2 (a) $c = 1$, $p = 2$; $f = 1 - 2 + 2 - 0 - 0 = 1$, as in Prob. 7.1e. (b) $c = 1$, $p = 1$; $f = 2$. (c) $c = 1$, $p = 3$; $f = 1 - 3 + 2 - 0 - 0 = 0$.

7.3 (a) $f = c_{\text{ind}} - p + 2$ and $p = c_{\text{ind}} + 2 - f$. The smallest possible f is zero, so $p_{\text{max}} = c_{\text{ind}} + 2$. (b) If $p = 10$, then c_{ind} must be at least 8.

7.4 (a) $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$, $\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_4^-$, $\text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-}$, $\text{HPO}_4^{2-} \rightleftharpoons \text{H}^+ + \text{PO}_4^{3-}$. The equilibrium conditions are: $\mu_{\text{H}_2\text{O}} = \mu_{\text{H}^+} + \mu_{\text{OH}^-}$, $\mu_{\text{H}_3\text{PO}_4} = \mu_{\text{H}^+} + \mu_{\text{H}_2\text{PO}_4^-}$, $\mu_{\text{H}_2\text{PO}_4^-} = \mu_{\text{H}^+} + \mu_{\text{HPO}_4^{2-}}$, $\mu_{\text{HPO}_4^{2-}} = \mu_{\text{H}^+} + \mu_{\text{PO}_4^{3-}}$. The electro-neutrality condition is $x_{\text{H}^+} = x_{\text{OH}^-} + x_{\text{H}_2\text{PO}_4^-} + 2x_{\text{HPO}_4^{2-}} +$

$3x_{\text{PO}_4^{3-}}$. There are 7 species (H_2O , H^+ , OH^- , H_3PO_4 , H_2PO_4^- , HPO_4^{2-} , PO_4^{3-}) and Eq. (7.10) gives $c_{\text{ind}} = 7 - 4 - 1 = 2$.

Hence $f = 2 - 1 + 2 = 3$. (b) $x_{\text{K}^+} = x_{\text{Br}^-}$ and $x_{\text{Na}^+} = x_{\text{Cl}^-}$ (assuming that no solid precipitates out of the solution).

We shall neglect the ionization of water. (Its inclusion would not change f .) The electroneutrality relation is

$x_{\text{K}^+} + x_{\text{Na}^+} = x_{\text{Br}^-} + x_{\text{Cl}^-}$ and is not an additional condition since it follows from the two preceding equations. The species are K^+ , Br^- , Na^+ , Cl^- , and H_2O . Equation (7.10) gives $c_{\text{ind}} = 5 - 0 - 2 = 3$. Hence $f = 3 - 1 + 2 = 4$.

7.5 (a) $c_{\text{ind}} = 3 - 0 - 0 = 3$ and $f = 3 - 1 + 2 = 4$. (b)

$2\text{NH}_3 \rightleftharpoons \text{N}_2 + 3\text{H}_2$, so $\mu_{\text{N}_2} + 3\mu_{\text{H}_2} = 2\mu_{\text{NH}_3}$ and $r = 1$. Hence

$c_{\text{ind}} = 3 - 1 - 0 = 2$ and $f = 2 - 1 + 2 = 3$.* (c) $2\mu_{\text{NH}_3} = \mu_{\text{N}_2} + 3\mu_{\text{H}_2}$ and $x_{\text{H}_2} = 3x_{\text{N}_2}$ (since all the N_2 and H_2 come from decomposition of NH_3). Hence $c_{\text{ind}} = 3 - 1 - 1 = 1$

and $f = 1 - 1 + 2 = 2$.* (d) We have the reaction equilibrium $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ and the phase equilibria $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaCO}_3(\text{g})$ and $\text{CaO}(\text{s}) \rightleftharpoons \text{CaO}(\text{g})$. There is 1 reaction equilibrium condition. The phase equilibrium conditions have already been taken into account in deriving the phase rule; see Eqs. (7.3)-(7.6). There are no relations between mole fractions. There are three species (CaCO_3 , CaO , CO_2) and $c_{\text{ind}} = 3 - 1 - 0 = 2$. Hence $f = 2 - 3 + 2 = 1$.

*In (b) and (c), the catalyst was not counted in finding c . If the catalyst is considered to be a species whose amount can be varied, then c and c_{ind} are each increased by 1; if the catalyst is a solid,

then p is increased by 1 and f is unchanged; if the catalyst is in the gas phase, then f is increased by 1.

7.6 (a) Here, the equilibrium conditions $p^\alpha = p^\beta = p^\gamma = \dots$ are eliminated. Instead of specifying 1 pressure, we must specify p pressures (where p is the number of phases). This increases f by $p - 1$, so $f = c_{\text{ind}} - p + 2 + p - 1 = c_{\text{ind}} + 1$. (b) Here, the equilibrium conditions of Eqs. (7.3) to (7.6) are eliminated. There are $c(p - 1)$ such conditions, so f is increased by $c(p - 1)$ and $f = c - p + 2 - r - a + cp - c = cp - p + 2 - r - a = c_{\text{ind}} - p + 2 + cp - c$.

7.7 We have the reactions (1) $\text{HCN} \rightleftharpoons \text{H}^+ + \text{CN}^-$ and (2) $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$. Let n_{1,H^+} and n_{2,H^+} denote the moles of H^+ coming from reactions 1 and 2, respectively. Stoichiometry gives $n_{1,\text{H}^+} = n_{\text{CN}^-}$ and $n_{2,\text{H}^+} = n_{\text{OH}^-}$, so $n_{\text{CN}^-} + n_{\text{OH}^-} = n_{1,\text{H}^+} + n_{2,\text{H}^+} = n_{\text{H}^+}$.

7.8 (a) $c = 2$ (H_2O and NaCl), $p = 2$, $f = 2 - 2 + 2 - 0 - 0 = 2$ (T and P). (b) $c = 4$ (H_2O , NaCl , Na^+ , Cl^-), $p = 2$; $r = 1$, since we have the equilibrium $\text{NaCl(s)} \rightleftharpoons \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$; $a = 1$, since we have the electroneutrality condition $x_{\text{Na}^+(\text{aq})} = x_{\text{Cl}^-(\text{aq})}$. So $f = 4 - 2 + 2 - 1 - 1 = 2$.

7.9 (a) $c = 4$, $p = 1$, $r = 2$ [$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ and $2\text{H}_2\text{O} \rightleftharpoons (\text{H}_2\text{O})_2$], and $a = 1$ ($x_{\text{H}^+} = x_{\text{OH}^-}$); $f = c - p + 2 - r - a = 4 - 1 + 2 - 2 - 1 = 2$ (T and P). $c_{\text{ind}} = c - r - a = 1$. (b) $c = 5$, $p = 1$, $r = 3$ [the reactions in (a) and $\text{H}_2\text{O} +$

$$(\text{H}_2\text{O})_2 \rightleftharpoons (\text{H}_2\text{O})_3], a = 1; f = 2. c_{\text{ind}} = 1.$$

7.10(a) Treat the vapor as an ideal gas. The liquid's volume is negligible compared to the container's volume. If the equilibrium vapor pressure is reached before all the liquid vaporizes, then the gas will be at 23.76 torr, and

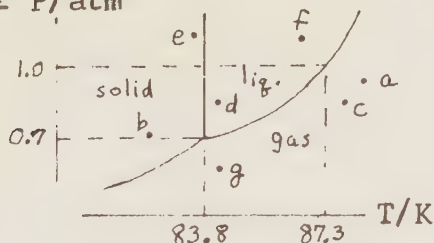
$$n_{\text{gas}} = \frac{PV}{RT} = \frac{(23.76/760) \text{ atm} (10,000 \text{ cm}^3)}{(82.06 \text{ cm}^3\text{-atm/mol-K})(298.15 \text{ K})} = 0.01278 \text{ mol}$$

$$m_{\text{gas}} = (0.01278 \text{ mol})(18.015 \text{ g/mol}) = 0.230 \text{ g}$$

There are 0.230 g of vapor and 0.130 g of liquid. (b)

With $V = 20,000 \text{ cm}^3$, we would get 0.460 g of vapor if the equilibrium vapor pressure of 23.76 torr were reached before all the liquid vaporized. However, there is only 0.360 g of water present initially, so all the liquid vaporizes to give a system with only vapor present.

7.11 P/atm



- (a) Gas; (b) solid; (c) gas;
 (d) liquid; (e) solid;
 (f) liquid; (g) gas.

7.12(a) Ar. The greater number of electrons means greater intermolecular attractions in Ar. (b) H_2O , due to hydrogen bonding. (c) C_3H_8 , which has more electrons.

$$\underline{7.13} \quad \Delta \bar{S}_{\text{vap}} \approx 21 \text{ cal mol}^{-1} \text{ K}^{-1} = 87 \text{ J mol}^{-1} \text{ K}^{-1} \approx$$

$$\Delta \bar{H}_{\text{vap}} / (319.4 \text{ K}), \text{ and } \Delta \bar{H}_{\text{vap}} \approx 6.7 \text{ kcal/mol} = 28 \text{ kJ/mol.}$$

7.14 The hydrogen bonding increases the degree of order in the liquid and hence decreases S of the liquid. Therefore, ΔS for the transition liquid \rightarrow gas is increased.

7.15 (a) The T-H-E rule (7.12) gives $\Delta \bar{H}_{\text{vap,nbp,CO}}/(81.7 \text{ K}) = (8.314 \text{ J/mol-K})(4.5 + \ln 81.7) = 74.0 \text{ J/mol-K}$ and

$\Delta \bar{H}_{\text{vap,nbp,CO}} = 6.05 \text{ kJ/mol}$. Similarly, we get 55.7 kJ/mol for anthracene, 168 kJ/mol for MgCl_2 , and 295 kJ/mol for Cu.

(b) Experimental values in kJ/mol (from Barin and Knacke, Reed et al., and the AIP handbook) are: CO—6.04, anthracene—56.5, MgCl_2 —156, and Cu—304.

7.16 Assuming ideal vapor and using (3.29) we have $\Delta \bar{S} = \text{const.} = \Delta \bar{S}_1 + \Delta \bar{S}_2 = \Delta \bar{S}_{\text{vap,nbp}} + R \ln (\bar{V}^\dagger / \bar{V}_1) = \Delta \bar{S}_{\text{vap,nbp}} + R \ln \bar{V}^\dagger - R \ln (RT_{\text{nbp}}/1 \text{ atm}) = \Delta \bar{S}_{\text{vap,nbp}} - R \ln (T_{\text{nbp}}/K) + R \ln \bar{V}^\dagger - R \ln (R K/1 \text{ atm}) = \text{const.},$ so $\Delta \bar{S}_{\text{vap,nbp}} = R \ln (T_{\text{nbp}}/K) + \text{const.} + R \ln \bar{V}^\dagger - R \ln (R K/1 \text{ atm}) = R \ln (T_{\text{nbp}}/K) + \text{const.}',$ which is the T-H-E rule.

7.17 Assuming ideal vapor, neglecting \bar{V}_{liq} in $\bar{V}_{\text{gas}} - \bar{V}_{\text{liq}}$, and neglecting the temperature dependence of $\Delta \bar{H}_{\text{vap}}$, we use the integrated Clausius-Clapeyron equation (7.21).

If state 1 is the normal boiling point 34.5°C and state 2 is 25.0°C , then $\ln (P_2/760 \text{ torr}) =$

$$-\{(6380 \text{ cal/mol})/(1.987 \text{ cal/mol-K})\}[(298.1 \text{ K})^{-1} - (307.6_5 \text{ K})^{-1}] = -0.332_5 = \ln (P_2/\text{torr}) - \ln 760 \text{ and}$$

$$\ln (P_2/\text{torr}) = 6.301; P_2/\text{torr} = 545; P_2 = 545 \text{ torr.}$$

7.18 (a) Integration of $dP/dT = \Delta H/(T \Delta V)$ gives $P_2 - P_1 =$

$(\Delta H/\Delta V) \ln (T_2/T_1)$, where ΔH and ΔV are assumed constant.

From Prob. 2.37, for one gram $\Delta H = 79.7 \text{ cal}$ and $\Delta V = (1.000)^{-1} \text{ cm}^3 - (0.917)^{-1} \text{ cm}^3 = -0.091 \text{ cm}^3$. We have

$$P_2 = 1 \text{ atm} + \frac{79.7 \text{ cal}}{-0.091 \text{ cm}^3} \frac{82.06 \text{ cm}^3 \text{ atm}}{1.987 \text{ cal}} \ln \frac{272.15 \text{ K}}{273.15 \text{ K}} = 134 \text{ atm}$$

(b) With 272.15 K replaced by 263.15 K, we get $P_2 = 1350 \text{ atm}$.

7.19 Use Eq. (7.24). For 1 g,

$$\Delta V_{\text{fus}} = (1 \text{ g})/(13.690 \text{ g/cm}^3) - (1 \text{ g})/(14.193 \text{ g/cm}^3) = 0.00259 \text{ cm}^3. \quad (\underline{a})$$

$$\ln \frac{T}{234.2_5 \text{ K}} = \frac{0.00259 \text{ cm}^3}{2.82 \text{ cal}} 99 \text{ atm} \frac{1.987 \text{ cal}}{82.06 \text{ cm}^3 \text{ atm}} = 0.00220$$

$$T/(234.2_5 \text{ K}) = 1.00220, \quad T = 234.7_7 \text{ K} = -38.4^\circ\text{C}$$

(b) Replacing 99 atm by 799 atm in the above equation, we get $T = 238.4_5 \text{ K} = -34.7^\circ\text{C}$.

7.20 $dP/dT = \Delta H/T\Delta V$. For solid-liquid transitions, ΔV is much smaller than for solid-vapor or liquid-vapor transitions.

7.21 Equation (7.21) gives

$$\ln \frac{760 \text{ torr}}{23.76 \text{ torr}} = - \frac{\Delta \bar{H}}{1.987 \text{ cal/mol-K}} \left(\frac{1}{373.15 \text{ K}} - \frac{1}{298.15 \text{ K}} \right)$$

$$\Delta \bar{H} = 10.2 \text{ kcal/mol} = 42.7 \text{ kJ/mol}$$

$$\underline{7.22} \quad \Delta \bar{H} = (539.4 \text{ cal/g})(18.015 \text{ g/mol}) = 9717 \text{ cal/mol}.$$

(a) Equation (7.21) gives

$$\ln \frac{P}{760 \text{ torr}} = - \frac{9717 \text{ cal/mol}}{1.987 \text{ cal/mol-K}} \left(\frac{1}{393.15 \text{ K}} - \frac{1}{373.15 \text{ K}} \right)$$

$$\ln (P/760 \text{ torr}) = 0.667, \quad P/760 \text{ torr} = 1.950, \quad P = 1480 \text{ torr}$$

$$(b) \ln \frac{446 \text{ torr}}{760 \text{ torr}} = - \frac{9717 \text{ cal/mol}}{1.987 \text{ cal/mol-K}} \left(\frac{1}{T} - \frac{1}{373.15 \text{ K}} \right)$$

$$1/T = 2.789 \times 10^{-3} \text{ K}^{-1}, \quad T = 358.6 \text{ K} = 85.4^\circ\text{C}$$

7.23 A plot of $\ln (P/\text{atm})$ vs. $1/T$ has slope $-\Delta\bar{H}/R$.

$\ln (P/\text{atm})$	-9.0547	-7.9320	-6.9268	-6.0208
$10^4/T$	28.317	26.799	25.436	24.204

K^{-1}

(a) The plot is linear with slope $-7380 \text{ K} = -\Delta\bar{H}/(1.987 \text{ cal/mol-K})$. $\Delta\bar{H} = 14,660 \text{ cal/mol}$. (b) Eq. (7.21) gives

$$\ln \frac{P}{1.845 \text{ torr}} = - \frac{14660 \text{ cal/mol}}{1.987 \text{ cal/mol-K}} \left(\frac{1}{433.15 \text{ K}} - \frac{1}{413.15 \text{ K}} \right)$$

$$\ln (P/1.845 \text{ torr}) = 0.8246, \quad P = 4.208 \text{ torr}$$

(Alternatively, the graph can be extrapolated.) (c) Use of Eq. (7.21) gives

$$\ln \frac{760 \text{ torr}}{1.845 \text{ torr}} = - \frac{14660 \text{ cal/mol}}{1.987 \text{ cal/mol-K}} \left(\frac{1}{T} - \frac{1}{413.15 \text{ K}} \right)$$

$$T = 623 \text{ K} = 350^\circ\text{C}$$

(The true normal boiling point is 356.6°C . The error arises because $\Delta\bar{H}$ is not constant over the long temperature interval from 140 to 350°C .)

7.24 A plot of $\ln (P/\text{atm})$ vs. $1/T$ has slope $-\Delta\bar{H}/R$.

$$\ln (P/\text{atm}) \quad -4.350 \quad -3.0886 \quad -1.9812 \quad -1.0003$$

$$10^3/T \quad 6.5295 \quad 6.1293 \quad 5.7753 \quad 5.4600 \quad \text{K}^{-1}$$

(a) The plot is a straight line with slope $-3130 \text{ K} =$

$$-\Delta\bar{H}/(8.314 \text{ J/mol-K}) \quad \text{and} \quad \Delta\bar{H} = 26.0 \text{ kJ/mol} = 6.22 \text{ kcal/}$$

mol. (b) Equation (7.21) gives $\ln (P/279.5 \text{ torr}) =$

$$-[(26000 \text{ J/mol})/(8.314 \text{ J/mol-K})][(198 \text{ K})^{-1} - (183 \text{ K})^{-1}]$$

and $P = 1020 \text{ torr}$.

7.25 Trouton's rule is $\Delta\bar{H}/T \approx 10.5 R$. At the normal

$$\text{boiling point, } \Delta\bar{V} = \bar{V}_{\text{gas}} - \bar{V}_{\text{liq}} \approx \bar{V}_{\text{gas}} \approx RT/P =$$

$RT_b/(1 \text{ atm})$. For a small change in P , we have $dP/dT \approx$

$\Delta P/\Delta T$ and the reciprocal of Eq. (7.18) becomes

$$\frac{\Delta T}{\Delta P} \approx \left(\frac{\Delta\bar{H}}{T} \right)^{-1} \Delta\bar{V} \approx (10.5R)^{-1} RT_b/(1 \text{ atm}) = T_b/(10\frac{1}{2} \text{ atm})$$

7.26 (a) The 0°C path solid \rightarrow liquid \rightarrow gas shows that

$$\Delta\bar{H}_{\text{sub}} = \Delta\bar{H}_{\text{fus}} + \Delta\bar{H}_{\text{vap}} = 51.07 \text{ kJ/mol. (Pressure changes}$$

have no significance since P has very little effect on

H .) (b) The Clapeyron equation is $dP/dT = \Delta\bar{H}/(T \Delta\bar{V})$. For

the solid-vapor line, $\Delta\bar{H} = \Delta\bar{H}_{\text{sub}}$ and $\Delta\bar{V} = \bar{V}_{\text{gas}} - \bar{V}_{\text{solid}} =$

$$RT/P - M_{\text{solid}}/\rho_{\text{solid}} = (82.06 \text{ cm}^3\text{-atm/mol-K})(273.16 \text{ K})/$$

$$[(4.585/760)\text{atm}] - (18.0 \text{ g/mol})/(0.92 \text{ g/cm}^3) = 3.716 \times 10^6$$

$$\text{cm}^3/\text{mol} - 19.6 \text{ cm}^3/\text{mol} = 3.716 \times 10^6 \text{ cm}^3/\text{mol, where ideal}$$

vapor was assumed. Then $(dP/dT)_{\text{solid-gas}} = \Delta\bar{H}/(T \Delta\bar{V}) =$

$$(51070 \text{ J/mol})/(273.16 \text{ K})(3.716 \times 10^6 \text{ cm}^3/\text{mol}) =$$

$$(5.031 \times 10^{-5} \text{ J/cm}^3\text{-K})(82.06 \text{ cm}^3\text{-atm}/8.3145 \text{ J}) = 4.966 \times$$

$$10^{-4} \text{ atm/K} = 0.3774 \text{ torr/K. For the liquid-vapor line,}$$

$\Delta\bar{H} = \Delta\bar{H}_{\text{vap}} = 45060 \text{ J/mol}$, $\Delta\bar{V} = 3.716 \times 10^6 \text{ cm}^3/\text{mol}$, and $(dP/dT)_{\text{liq-vap}} = 0.3330 \text{ torr/K}$. For the solid-liquid line, $\Delta\bar{H} = 6.01 \text{ kJ/mol}$, $\Delta\bar{V} = M/\rho_{\text{liq}} - M/\rho_{\text{solid}} = (18.015 \text{ g/mol}) \times (1.000 \text{ cm}^3/\text{g} - 1.0905 \text{ cm}^3/\text{g}) = -1.630 \text{ cm}^3/\text{mol}$, and $dP/dT = -1.012 \times 10^5 \text{ torr/K}$.

7.27 (a) At 25°C , $\ln(P/\text{torr}) = 18.3036 - 3816.44/(298.15 - 46.13) = 3.1602$ and $P = 23.58 \text{ torr}$; at 150°C , the Antoine equation gives $\ln(P/\text{torr}) = 8.1810$ and $P = 3572 \text{ torr}$. (b) The Clausius-Clapeyron equation is $d \ln P/dT = \Delta\bar{H}/RT^2$, with ideal vapor assumed and the liquid's volume neglected. Differentiation of the Antoine equation gives at 100°C $d \ln P/dT = B/(T/K + C)^2 \text{ K} = 3816.44/(373.15 - 46.13)^2 \text{ K} = 0.035687/\text{K} = \Delta\bar{H}/RT^2 = \Delta\bar{H}/(8.3145 \text{ J/mol-K})(373.15 \text{ K})^2$ and $\Delta\bar{H}_{\text{vap}} = 41.315 \text{ kJ/mol}$.

7.28 (a) We make the approximations that the solid and liquid volumes are negligible compared to the vapor volume, that $\Delta\bar{H}$ of vaporization and sublimation are constant, and that the vapor is ideal. Then Eqs. (7.21) and (7.22) apply and show that $\ln P$ varies linearly with $1/T$. We plot $\ln P$ vs. $1/T$ for the solid and join the two points by a straight line; we do the same for the liquid. At the triple point, the solid and liquid vapor pressures are equal, so the intersection point of the two lines gives the triple point; this is found to be $P = 15.4 \text{ torr}$, $T = 200 \text{ K}$. (b) Equation (7.21) gives

$$\ln \frac{10.0 \text{ torr}}{1.00 \text{ torr}} = \frac{\Delta \bar{H}_{\text{sub}}}{1.987 \text{ cal/mol-K}} \left(\frac{1}{177.0 \text{ K}} - \frac{1}{195.8 \text{ K}} \right)$$

$$\Delta \bar{H}_{\text{sub}} = 8430 \text{ cal/mol}$$

$$\ln \frac{100.0 \text{ torr}}{33.4 \text{ torr}} = \frac{\Delta \bar{H}_{\text{vap}}}{1.987 \text{ cal/mol-K}} \left(\frac{1}{209.6 \text{ K}} - \frac{1}{225.3 \text{ K}} \right)$$

$$\Delta \bar{H}_{\text{vap}} = 6550 \text{ cal/mol}. \quad \Delta \bar{H}_{\text{fus}} / (\text{cal/mol}) = 8430 - 6550 = 1880$$

7.29 The triple-point temperature differs only slightly from the normal melting point, so we take $T_{\text{tr}} = 1452^\circ\text{C} = 1725 \text{ K}$. We use Eq. (7.21) to find the liquid's vapor pressure at $T_{\text{tr}} = 1725 \text{ K}$; this must equal the solid's vapor pressure at 1725 K . Equation (7.21) gives for the liquid-vapor equilibrium: $\ln (P_2/P_1) = \Delta \bar{H}(T_2 - T_1)/RT_1T_2$ and $\ln (P_2/P_{\text{tr}}) = \Delta \bar{H}(T_2 - T_{\text{tr}})/RT_2T_{\text{tr}}$. Division gives

$$\frac{\ln (P_2/P_{\text{tr}})}{\ln (P_2/P_1)} = \frac{T_2 - T_{\text{tr}}}{T_2 - T_1} \frac{T_1}{T_{\text{tr}}}$$

$$\frac{\ln (1.00/P_{\text{tr}})}{\ln (1.00/0.100)} = \frac{2078 \text{ K} - 1725 \text{ K}}{2078 \text{ K} - 1879 \text{ K}} \frac{1879 \text{ K}}{1725 \text{ K}} = 1.932$$

$$P_{\text{tr}} = 0.0117 \text{ torr}$$

[Alternatively, we could find $\Delta \bar{H}$ of vaporization of the liquid and use (7.21) to get P_{tr} .] Now we use (7.21) for the solid:

$$\ln \frac{P}{0.0117 \text{ torr}} = - \frac{4250 \text{ cal/mol}}{1.987 \text{ cal/mol-K}} \left(\frac{1}{1473 \text{ K}} - \frac{1}{1725 \text{ K}} \right)$$

$$P = 0.0095 \text{ torr}$$

7.30 Since ice is the stable phase at -20°C , we have $\mu_{\text{ice}} < \mu_{\text{sc liq}}$, where sc = supercooled. The phase equilibrium condition gives $\mu_{\text{ice}} = \mu_{\text{vapor above ice}}$ and

$\mu_{\text{sc liq}} = \mu_{\text{vapor above sc liq}}$; therefore $\mu_{\text{vapor above ice}} < \mu_{\text{vapor above sc liq}}$. Use of $\mu_1 = \mu_1^{\circ} + RT \ln (P_1/P^{\circ})$ [Eq. (6.4)] for the vapors gives $\mu_1^{\circ} + RT \ln (P_{1,\text{above ice}}) < \mu_1^{\circ} + RT \ln (P_{1,\text{above sc liq}})$, so $\ln (P_{1,\text{above ice}}) < \ln (P_{1,\text{above sc liq}})$ and $P_{1,\text{above ice}} < P_{1,\text{above sc liq}}$.

7.31 $dP/dT = \Delta H/(T \Delta V)$. Since V of the solid or liquid is negligible compared to V of the gas, we have to a high degree of accuracy, $\Delta V_{\text{solid} \rightarrow \text{vapor}} = \Delta V_{\text{liq} \rightarrow \text{vapor}}$. As shown in Prob. 7.26, $\Delta \bar{H}_{\text{sub}}$ is greater than $\Delta \bar{H}_{\text{vap}}$ by $\Delta \bar{H}_{\text{fus}}$, which is not negligible. Therefore $\Delta H_{\text{solid} \rightarrow \text{gas}} > \Delta H_{\text{liq} \rightarrow \text{gas}}$ and $(dP/dT)_{\text{solid} \rightarrow \text{gas}} > (dP/dT)_{\text{liq} \rightarrow \text{gas}}$. The solid-vapor line has greater slope.

7.32 The pressure due to 10 cm of water is given by (1.9) as $P = \rho gh = [1.00 (10^{-3} \text{ kg})/(10^{-6} \text{ m}^3)](9.80 \text{ m/s}^2) \times (0.10 \text{ m}) = 980 \text{ N/m}^2 = (980 \text{ J/m}^3)(82.06 \times 10^{-6} \text{ m}^3 \text{ atm})/(8.314 \text{ J}) = 0.009_7 \text{ atm}$, where (2.7), (2.14), (1.19) and (1.20) were used. The total pressure 10 cm below the surface is 1.009_7 atm and Eq. (7.24) and data in the example that follows it give

$$0.009_7 \text{ atm} = \frac{79.7 \text{ cal}}{-0.091 \text{ cm}^3} \frac{82.06 \text{ cm}^3 \text{ atm}}{1.987 \text{ cal}} \ln \frac{T_2}{273.15 \text{ K}}$$

$$\ln (T_2/273.15 \text{ K}) = -2.7 \times 10^{-7}; T_2 = (273.15 \text{ K})e^{-2.7 \times 10^{-7}}$$

$$T_2 - 273.15 \text{ K} = (273.15 \text{ K})[\exp(-2.7 \times 10^{-7}) - 1] = -7.4 \times 10^{-5} \text{ K}.$$

7.33 Neglecting the change in water density with pressure and the change in g with depth, we have as the pressure at 3000 m: $P = \rho gh = (1.0 \text{ g/cm}^3)(1 \text{ kg}/10^3 \text{ g}) \times (10^6 \text{ cm}^3/1 \text{ m}^3)(9.8 \text{ m/s}^2)(3000 \text{ m}) = (2.9 \times 10^7 \text{ Pa}) \times (1 \text{ atm}/1.01 \times 10^5 \text{ Pa}) = 290 \text{ atm}$. P exceeds the 350°C vapor pressure of water and the stable phase is liquid water.

7.34 Let sc denote supercooled liquid water. All equations in this problem are for -10°C . The phase equilibrium condition and Eq. (6.4) give $\mu_{ice} = \mu_{\text{vapor above ice}} = \mu_i^\circ + RT \ln (1.950 \text{ torr}/750 \text{ torr})$ and $\mu_{sc} = \mu_{\text{vapor above sc}} = \mu_i^\circ + RT \ln (P_i/750 \text{ torr})$. Subtraction gives $\mu_{ice} - \mu_{sc} = RT \ln (1.95 \text{ torr}/P_i)$. But Prob. 4.26b gives $\mu_{ice} - \mu_{sc} = \bar{G}_{ice} - \bar{G}_{sc} = (-2.76 \text{ cal/g})(18.0 \text{ g/mol}) = -49.7 \text{ cal/mol}$. (This relation holds at 1 atm, but the effect of pressure on liquid and solid thermodynamic properties is slight and can be ignored.) Therefore $-49.7 \text{ cal/mol} = RT \ln (1.95 \text{ torr}/P_i) = (1.987 \text{ cal/mol-K})(263.1 \text{ K}) \times \ln (1.95 \text{ torr}/P_i)$. We find $1.95 \text{ torr}/P_i = 0.909_3$ and $P_i = 2.14 \text{ torr}$. (The experimental value is 2.15 torr.)

7.35 When the two forms are in equilibrium (and hence interconvertible), their chemical potentials are equal. We therefore want to make $\bar{G}_{di} = \bar{G}_{gr}$. For each form, $d\bar{G} = -\bar{S} dT + \bar{V} dP = \bar{V} dP$ at constant T . Since solids are quite

incompressible, we make the approximation of neglecting the change in \bar{V} with P ; for each form $\Delta\bar{G} = \bar{V} \Delta P$ or $\bar{G}(P_2) = \bar{G}(P_1) + \bar{V} \Delta P$, where $P_1 = P^\circ = 1 \text{ atm}$. Setting $\bar{G}_{\text{di}}(P_2) = \bar{G}_{\text{gr}}(P_2)$, we have

$$\bar{G}_{\text{di}}(P_1) + \bar{V}_{\text{di}} \Delta P = \bar{G}_{\text{gr}}(P_1) + \bar{V}_{\text{gr}} \Delta P$$

$$\Delta P = \frac{\bar{G}_{\text{gr}}(P^\circ) - \bar{G}_{\text{di}}(P^\circ)}{\bar{V}_{\text{di}} - \bar{V}_{\text{gr}}} = \frac{-\Delta G_{f,\text{di}}^\circ}{\bar{V}_{\text{di}} - \bar{V}_{\text{gr}}} \quad (\text{Use } \bar{V} = M/\rho)$$

$$= \frac{-2900 \text{ J/mol}}{(3.41_2 \text{ cm}^3/\text{mol}) - (5.33_8 \text{ cm}^3/\text{mol})} \frac{82.06 \text{ cm}^3 \text{ atm}}{8.3145 \text{ J}}$$

$$= 14900 \text{ atm} \quad \text{and} \quad P_2 = 14900 \text{ atm}$$

7.36 When gray (g) tin is more stable than white (w), we have $\mu_g < \mu_w$ and $\bar{G}_g < \bar{G}_w$. We have $d\bar{G} = -\bar{S} dT + \bar{V} dP = -\bar{S} dT$ at the constant P of 1 atm. Appendix data show that $\bar{S}_w > \bar{S}_g$, so \bar{G}_w decreases faster than \bar{G}_g as T increases, and \bar{G}_w increases more rapidly than \bar{G}_g as T decreases. At the temperature T_{eq} with $\bar{G}_g = \bar{G}_w$, the two forms are in equilibrium; below T_{eq} , we have $\bar{G}_g < \bar{G}_w$ and gray tin is more stable. Let $T_1 = 25^\circ\text{C}$, $T_2 = T_{\text{eq}}$, and $\Delta T = T_{\text{eq}} - 25^\circ\text{C}$. We have $\Delta\bar{G}_g = \bar{G}_g(T_{\text{eq}}) - \bar{G}_g(25^\circ\text{C})$ and $\Delta\bar{G}_w = \bar{G}_w(T_{\text{eq}}) - \bar{G}_w(25^\circ\text{C})$, so $\bar{G}_g(T_{\text{eq}}) = \bar{G}_w(T_{\text{eq}})$ becomes $\bar{G}_g(25^\circ\text{C}) + \Delta\bar{G}_g = \bar{G}_w(25^\circ\text{C}) + \Delta\bar{G}_w$ or $\Delta\bar{G}_g - \Delta\bar{G}_w = \bar{G}_w(25^\circ\text{C}) - \bar{G}_g(25^\circ\text{C}) = 0 - 0.13 \text{ kJ/mol} = -0.13 \text{ kJ/mol}$, where Appendix data were used. Since $\Delta\bar{G} = -\int_1^2 \bar{S} dT$ at constant P , we have $\Delta\bar{G}_g - \Delta\bar{G}_w = -\int_1^2 (\bar{S}_g - \bar{S}_w) dT \approx (\bar{S}_w - \bar{S}_g)(T_2 - T_1) = (51.55 - 44.14) \times$

$(\text{J/mol-K})(T_2 - 25^\circ\text{C})$, if we neglect the T dependence of $\bar{S}_g - \bar{S}_w$. Then $-130 \text{ J/mol} \approx (7.41 \text{ J/mol-K})(T - 25^\circ\text{C})$ and $T_{\text{eq}} - 25^\circ\text{C} \approx -17.5 \text{ K} = -17.5^\circ\text{C}$, so $T_{\text{eq}} \approx 7\frac{1}{2}^\circ\text{C}$.

7.37 0.01°C is the triple-point temperature, so ice has a vapor pressure of 4.585 torr at 0.01°C .

7.38 (a) The initial state (state 1) has partial pressures P_A and P_B above liquid A; the liquid is subject to a pressure $P = P_A + P_B$. The final state (state 2) has partial pressures $P_A + dP_A$ and $P_B + dP_B$ above liquid A, which experiences a pressure $P + dP$, where $dP = dP_A + dP_B$. Let the changes in liquid and vapor A chemical potentials on going from state 1 to 2 be $d\mu(A^l)$ and $d\mu(A^g)$. The phase equilibrium conditions for states 1 and 2 are $\mu_1(A^l) = \mu_1(A^g)$ and $\mu_2(A^l) = \mu_2(A^g) = \mu_1(A^l) + d\mu(A^l) = \mu_1(A^g) + d\mu(A^g)$. Hence $d\mu(A^l) = d\mu(A^g)$. We have $d\mu(A^l) = d\bar{G}(A^l) = -\bar{S}(A^l) dT + \bar{V}(A^l) dP = \bar{V}(A^l) dP$, since T is constant. Also, $\mu(A^g) = \mu^\circ(A^g) + RT \ln (P_A/\text{atm})$ and $d\mu(A^g) = (RT/P_A) dP_A$ at constant T . Hence $\bar{V}(A^l) dP = (RT/P_A) dP_A = \bar{V}(A^g) dP_A$. Q.E.D.

(b) $dP_A/P_A = [\bar{V}(A^l)/RT] dP$. Integration with $\bar{V}(A^l)$ assumed constant gives $\ln (P_{A,2}/P_{A,1}) = [\bar{V}(A^l)/RT](P_2 - P_1)$.

$$\ln \frac{P_{A,2}}{23.76 \text{ torr}} = \frac{18.1 \text{ cm}^3/\text{mol}}{(82.06 \text{ cm}^3\text{-atm/mol-K})(298 \text{ K})} (1 \text{ atm}) = 0.000740$$

$$P_{A,2}/(23.76 \text{ torr}) = 1.00074, \quad P_{A,2} = 23.78 \text{ torr}$$

7.39 Use the 25°C path

$$\text{liq}(1 \text{ bar}) \xrightarrow{a} \text{liq}(23.766 \text{ torr}) \xrightarrow{b} \text{vap}(23.766 \text{ torr}) \xrightarrow{c} \text{vap}(1 \text{ bar})$$

We have $d\bar{G} = -\bar{S} dT + \bar{V} dP = \bar{V} dP$ at constant T . For the liquid, $\Delta\bar{G}_a = \bar{V} \Delta P$, and

$$\Delta\bar{G}_a = (18.1 \text{ cm}^3/\text{mol})(-0.956 \text{ atm}) \frac{8.314 \text{ J}}{82.06 \text{ cm}^3 \text{ atm}} = -1.8 \text{ J/mol}$$

Step b is a constant- T -and- P equilibrium process, so

$$\begin{aligned} \Delta\bar{G}_b &= 0. \text{ For step c, } \Delta\bar{G}_c = \int_1^2 \bar{V} dP = \int_1^2 (RT/P) dP = \\ &RT \ln(P_2/P_1) = (8.3145 \text{ J/mol-K})(298.15 \text{ K}) \ln(750.062/23.766) \\ &= 8557.2 \text{ J/mol. } \Delta\bar{G}_a + \Delta\bar{G}_b + \Delta\bar{G}_c = 8555.4 \text{ J/mol. From} \\ &\text{the Appendix, } \Delta\bar{G}/(\text{J/mol}) = -228572 + 237129 = 8557. \end{aligned}$$

7.40 (a) Trouton's rule is $\Delta\bar{H}/T_b = 10.5R = c$. Substitution into Eq. (7.22) gives

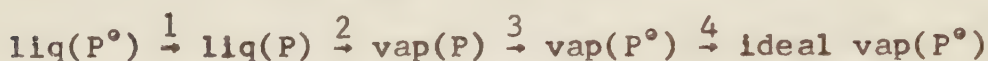
$$\ln \frac{P}{\text{atm}} = -\frac{c}{R} \frac{T_b}{T} + \frac{c}{R} = -(10.5R/R)T_b/T + 10.5R/R = 10.5 \times (1 - T_b/T)$$

$$P/\text{atm} = \exp \{10.5[1 - (353.2_5 \text{ K})/T]\}$$

$$\begin{aligned} \text{(b) } P/\text{atm} &= \exp [10.5(1 - 353.2_5/298.15)] = 0.1436 \text{ and} \\ P &= 109 \text{ torr. } \text{(c) } \ln(620/760) = 10.5(1 - 353.2_5/T) \\ \text{and } T &= 346.5 \text{ K} = 73.4^\circ\text{C.} \end{aligned}$$

$$\begin{aligned} \text{7.41 (a) Use of (7.21) gives at } 0^\circ\text{C: } \ln(4.926/4.258) &= \\ -[\Delta\bar{H}/(1.987 \text{ cal/mol-K})][(274.15 \text{ K})^{-1} - (272.15 \text{ K})^{-1}] &\text{ and} \\ \Delta\bar{H}_{273} &= 10.80 \text{ kcal/mol} = 45.20 \text{ kJ/mol. Similarly, } \Delta\bar{H}_{373} \\ &= 9.89 \text{ kcal/mol} = 41.37 \text{ kJ/mol. We have } \Delta\bar{S}_{273} = \Delta\bar{H}_{273}/T \\ &= (10800 \text{ cal/mol})/(273.1 \text{ K}) = 39.5 \text{ cal/mol-K} = 165 \text{ J/mol-K;} \\ \Delta\bar{S}_{373} &= \Delta\bar{H}_{373}/T = 26.5 \text{ cal/mol-K} = 111 \text{ J/mol-K.} \end{aligned}$$

$\Delta\bar{G} = \Delta\bar{H} - T \Delta\bar{S} = 0$, as it must be for equilibrium processes at constant T and P . The calculated 100°C $\Delta\bar{H}$ value is slightly in error, since the approximations used to derive Eq. (7.21) are less accurate the higher the vaporization temperature and the closer the temperature is to the critical point; for example, $\text{H}_2\text{O}(\text{g})$ is denser and hence less ideal at 1 atm and 373 K than at 5 torr and 0°C . (b) ΔH° and ΔS° are for the process $\text{liq} \rightarrow \text{ideal gas}$ at 1 bar. Let P be the 0°C vapor pressure. A convenient path is the following 0°C path:



Since moderate pressure changes have little effect on liq. thermodynamic properties, we can take $\Delta H_1 = 0$, $\Delta S_1 = 0$.

Gas nonideality is slight at 1 bar, so we take $\Delta H_4 = 0$, $\Delta S_4 = 0$.

Since the vapor is nearly ideal and H of an ideal gas depends on T only, we take $\Delta H_3 = 0$. Thus $\Delta H_{273}^\circ = \Delta\bar{H}_2 = 45.20 \text{ kJ/mol}$. Use of (3.27), (3.29), and Boyle's law gives $\Delta S_{273}^\circ = \Delta\bar{S}_2 + \Delta\bar{S}_3 = \Delta\bar{H}_2/T + R \ln(P/P^\circ) =$

$$(45200 \text{ J/mol})/(273 \text{ K}) + (8.3145 \text{ J/mol-K}) \ln(4.58/750) = 123.2 \text{ J/mol-K}.$$

7.42 (a) $dn_A = dn_A^S - a d\xi$, $dn_B = dn_B^S - b d\xi$, $dn_E = e d\xi$,

$dn_F = f d\xi$. Then $\sum_i \mu_i dn_i = \mu_A(dn_A^S - a d\xi) +$

$\mu_B(dn_B^S - b d\xi) + \mu_E e d\xi + \mu_F f d\xi = \mu_A dn_A^S + \mu_B dn_B^S +$

$(-a\mu_A - b\mu_B + e\mu_E + f\mu_F) d\xi = \mu_A dn_A^S + \mu_B dn_B^S$, since the

equilibrium condition for the reaction is $\sum_i \nu_i \mu_i \equiv -a\mu_A -$

$b\mu_B + e\mu_E + f\mu_F = 0$. (b) $dG = -S dT + V dP + \sum_i \mu_i dn_i =$

$-S dT + V dP + \mu_A dn_A^S + \mu_B dn_B^S$; at constant T , P , and n_B^S ,

$dG = \mu_A dn_A^S$ and $\mu_A = (\partial G / \partial n_A^S)_{T,P,n_B^S}$.

7.43 (a) and (c). See Fig. 7.1a.

CHAPTER 8

8.1 As $\rho \rightarrow 0$, $\bar{V} \rightarrow \infty$. In Eq. (8.2), $-b$ can be neglected compared to \bar{V} to give $P = RT/\bar{V} - a/\bar{V}^2 = (1/\bar{V})(RT - a/\bar{V})$. As $\bar{V} \rightarrow \infty$, $RT - a/\bar{V}$ goes to RT and $P \rightarrow RT/\bar{V}$. (Note that it is harder to use the form (1.39) to get the limiting behavior since both P and a/\bar{V}^2 go to 0.) In (8.4), the terms B/\bar{V} , C/\bar{V}^2 , ... each go to 0, giving $P\bar{V} = RT$. When (8.3) is solved for P and b is neglected compared to \bar{V} , we get $P = RT/\bar{V} - a/\bar{V}^2 T^{\frac{1}{2}} = (1/\bar{V})(RT - a/\bar{V} T^{\frac{1}{2}}) \rightarrow RT/\bar{V}$.

8.2 (a) $n = (28.8 \text{ g})/(30.07 \text{ g/mol}) = 0.958 \text{ mol}$; $\bar{V} = V/n = (999 \text{ cm}^3)/(0.958 \text{ mol}) = 1043 \text{ cm}^3/\text{mol}$. $P = [(82.06 \text{ cm}^3\text{-atm/mol-K})(298.1 \text{ K})/(1043 \text{ cm}^3/\text{mol})] \times [1 - (186 \text{ cm}^3/\text{mol})/(1043 \text{ cm}^3/\text{mol}) + (1.06 \times 10^4 \text{ cm}^6/\text{mol}^2)/(1043 \text{ cm}^3/\text{mol})^2] = 19.5 \text{ atm}$. The ideal-gas P is $P = RT/\bar{V} = 23.5 \text{ atm}$. (b) $B^\dagger = B/RT = (-186 \text{ cm}^3/\text{mol})/(82.06 \text{ cm}^3\text{-atm/mol-K})(298.1 \text{ K}) = -0.00760 \text{ atm}^{-1}$; $C^\dagger = (C - B^2)/R^2 T^2 = (1.06 \times 10^4 \text{ cm}^6/\text{mol}^2 - 186^2 \text{ cm}^6/\text{mol}^2)/(82.06 \text{ cm}^3\text{-atm/mol-K})^2 (298.1 \text{ K})^2 = -4.01 \times 10^{-5} \text{ atm}^{-2}$. $\bar{V} = [(82.06 \text{ cm}^3\text{-atm/mol-K})(298.1 \text{ K})/(16.0 \text{ atm})] \times [1 - (0.00760 \text{ atm}^{-1})(16.0 \text{ atm}) - (4.01 \times 10^{-5} \text{ atm}^{-2})(16.0 \text{ atm})^2] = 1327 \text{ cm}^3/\text{mol}$. $V = n\bar{V} = 1272 \text{ cm}^3$. Also, $\bar{V}_{\text{ideal}} = 1529 \text{ cm}^3/\text{mol}$ and $V_{\text{ideal}} = 1465 \text{ cm}^3$.

8.3 Eq. (8.4) gives $P = RT(1/\bar{V} + B/\bar{V}^2 + C/\bar{V}^3 + \dots)$. Substitution into the right side of (8.5) gives $P\bar{V} = RT[1 + B^\dagger RT(1/\bar{V} + B/\bar{V}^2 + C/\bar{V}^3 + \dots) + C^\dagger R^2 T^2(1/\bar{V}^2 + 2B/\bar{V}^3 + \dots) + \dots]$. We compare this

expression for $P\bar{V}$ with (8.4); equating the $1/\bar{V}$ coefficients, we get $B = B^+RT$. Equating the $1/\bar{V}^2$ coefficients, we get $C = B^+RTB + C^+R^2T^2 = B^{+2}R^2T^2 + C^+R^2T^2 = R^2T^2(B^{+2} + C^+)$. Solving for B^+ and C^+ , we get: $B^+ = B/RT$; $C^+ = C/R^2T^2 - B^{+2} = (C - B^2)/R^2T^2$.

8.4 (a) $B_{12} \approx \frac{1}{2}(B_1 + B_2) = -387 \text{ cm}^3/\text{mol}$. Let gas 1 be CH_4 . Then $x_1 = 0.0300/0.1000 = 0.300$ and $x_2 = 0.700$. The equation at the end of Sec. 8.2 gives $B \approx (0.300)^2(-42 \text{ cm}^3/\text{mol}) + 2(0.300)(0.700)(-387 \text{ cm}^3/\text{mol}) + (0.700)^2(-732 \text{ cm}^3/\text{mol}) = -525 \text{ cm}^3/\text{mol}$. $V/n_{\text{tot}} = 10000 \text{ cm}^3/\text{mol}$. $P = [(82.06 \text{ cm}^3\text{-atm/mol-K})(298.1 \text{ K})/(10000 \text{ cm}^3/\text{mol})] \times [1 - (525 \text{ cm}^3/\text{mol})/(10000 \text{ cm}^3/\text{mol})] = 2.32 \text{ atm}$. (b) With $B_{12} = -180 \text{ cm}^3/\text{mol}$, we get $B = -438 \text{ cm}^3/\text{mol}$ and $P = 2.34 \text{ atm}$. Also, $P_{\text{ideal}} = RT/(V/n_{\text{tot}}) = 2.45 \text{ atm}$.

8.5 $n = (74.8 \text{ g})/(30.07 \text{ g/mol}) = 2.48_g \text{ mol}$.
 $\bar{V} = V/n = (200 \text{ cm}^3)/(2.48_g \text{ mol}) = 80.4 \text{ cm}^3/\text{mol}$.

$$(a) \quad P = \frac{RT}{\bar{V}} = \frac{(82.06 \text{ cm}^3\text{-atm/mol-K})(310.6 \text{ K})}{80.4 \text{ cm}^3/\text{mol}} = 317 \text{ atm}$$

(b) Equations (8.16) and (8.2) give

$$a = \frac{27(82.06 \text{ cm}^3\text{-atm/mol-K})^2(305.4 \text{ K})^2}{64(48.2 \text{ atm})} = 5.50 \times 10^6 \text{ cm}^6 \text{ atm mol}^{-2}$$

$$b = \frac{(82.06 \text{ cm}^3\text{-atm/mol-K})(305.4 \text{ K})}{8(48.2 \text{ atm})} = 65.0 \text{ cm}^3 \text{ mol}^{-1}$$

$$P = \frac{(82.06 \text{ cm}^3\text{-atm/mol-K})(310.6 \text{ K})}{80.4 \text{ cm}^3/\text{mol} - 65.0 \text{ cm}^3/\text{mol}} - \frac{5.50 \times 10^6 \text{ cm}^6\text{-atm/mol}^2}{(80.4 \text{ cm}^3/\text{mol})^2}$$

$$P = 1655 \text{ atm} - 851 \text{ atm} = 804 \text{ atm}$$

(c) Equations (8.18), (8.19), and (8.3) give

$$a = \frac{0.4275(82.06 \text{ cm}^3\text{-atm/mol-K})^2(305.4 \text{ K})^{5/2}}{48.2 \text{ atm}} = 9.73 \times 10^7 \text{ cm}^6\text{-atm-K}^{1/2}/\text{mol}^2$$

$$b = \frac{0.08664(82.06 \text{ cm}^3\text{-atm/mol-K})(305.4 \text{ K})}{48.2 \text{ atm}} = 45.0 \text{ cm}^3/\text{mol}$$

$$P = RT/(\bar{V} - b) - a/\bar{V}(\bar{V} + b)T^{1/2} = 720 \text{ atm} - 548 \text{ atm} = 172 \text{ atm}$$

(d) Interpolation gives at $37\frac{1}{2}^\circ\text{C}$: $B = -179 \text{ cm}^3/\text{mol} +$

$$(7.5/20)(22 \text{ cm}^3/\text{mol}) = -171 \text{ cm}^3/\text{mol} \text{ and } C = 10119 \text{ cm}^6/\text{mol}^2.$$

$$P = [(82.06 \text{ cm}^3\text{-atm/mol-K})(310.6 \text{ K})/(80.4 \text{ cm}^3/\text{mol})] \times$$

$$[1 - (171 \text{ cm}^3/\text{mol})/(80.4 \text{ cm}^3/\text{mol}) +$$

$$(10119 \text{ cm}^6/\text{mol}^2)/(80.4 \text{ cm}^3/\text{mol})^2] = 139 \text{ atm. Note: The}$$

observed pressure is 135 atm.

$$8.6 \quad n_{\text{tot}} = 0.2000 \text{ mol}, V/n_{\text{tot}} = 3500 \text{ cm}^3/\text{mol}. \text{ (a) } P =$$

$$RT/\bar{V} = (82.06 \text{ cm}^3\text{-atm/mol-K})(313.1 \text{ K})/(3500 \text{ cm}^3/\text{mol}) =$$

$$7.34 \text{ atm. (b) Let } \text{C}_2\text{H}_4 \text{ be gas 1. For } \text{C}_2\text{H}_4, a_1 = 27R^2T_C^2/$$

$$64P_C = 4.56 \times 10^6 \text{ cm}^6 \text{ atm/mol}^2, b_1 = RT_C/8P_C = 58.3 \text{ cm}^3/$$

$$\text{mol. For } \text{CO}_2, \text{ we find } a_2 = 3.61 \times 10^6 \text{ cm}^6 \text{ atm/mol}^2 \text{ and}$$

$$b_2 = 42.9 \text{ cm}^3/\text{mol. Also, } x_1 = 0.0786/0.200 = 0.393, x_2 =$$

$$0.607. \text{ From the last paragraph of Sec. 8.2, } a =$$

$$[(0.393)^2(4.56 \times 10^6) + 2(0.393)(0.607)(4.56 \times 10^6 \times 3.61 \times 10^6)^{1/2} +$$

$$(0.607)^2(3.61 \times 10^6)](\text{cm}^6\text{-atm/mol}^2) = 3.97 \times 10^6 \text{ cm}^6\text{-atm/mol}^2;$$

$$b = 0.393(58.3 \text{ cm}^3/\text{mol}) + 0.607(42.9 \text{ cm}^3/\text{mol}) = 49.0 \text{ cm}^3/\text{mol. } P =$$

$$(82.06 \text{ cm}^3\text{-atm/mol-K})(313.1 \text{ K})/[(3500 - 49)\text{cm}^3/\text{mol}] -$$

$$(3.97 \times 10^6 \text{ cm}^6\text{-atm/mol}^2)/(3500 \text{ cm}^3/\text{mol})^2 = 7.12 \text{ atm. } (\underline{c}) \quad Z = \bar{P}\bar{V}/RT \text{ so } P = ZRT/\bar{V} = 0.9689(82.06 \text{ cm}^3\text{-atm/mol-K}) \times (313.1 \text{ K})/(3500 \text{ cm}^3/\text{mol}) = 7.11 \text{ atm.}$$

$$\underline{8.7} \quad P = RT/\bar{V} + RTB(T)/\bar{V}^2 + RTC(T)/\bar{V}^3.$$

$$(\partial P/\partial \bar{V})_T = 0 = -RT/\bar{V}^2 - 2RTB/\bar{V}^3 - 3RTC/\bar{V}^4$$

$$(\partial^2 P/\partial \bar{V}^2)_T = 0 = 2RT/\bar{V}^3 + 6RTB/\bar{V}^4 + 12RTC/\bar{V}^5$$

$$RT_c \bar{V}_c^2 + 2RT_c B \bar{V}_c + 3RT_c C = 0 \quad (1)$$

$$2RT_c \bar{V}_c^2 + 6RT_c B \bar{V}_c + 12RT_c C = 0 \quad (2)$$

Subtract twice equation (1) from equation (2) to get

$B = -3C/\bar{V}_c$ at $T = T_c$. Substitution of this expression

for B into equation (1) gives $C(T_c) = \bar{V}_c^2/3$. Also,

$$B(T_c) = -3C(T_c)/\bar{V}_c = -\bar{V}_c. \text{ We have } Z_c = P_c \bar{V}_c/RT_c = 1 + B(T_c)/\bar{V}_c + C(T_c)/\bar{V}_c^2 = 1 - 1 + 1/3 = 1/3.$$

8.8 (a) From (8.16), $b = RT_c/8P_c = (82.06 \text{ cm}^3\text{-atm/mol-K}) \times (150.9 \text{ K})/8(48.3 \text{ atm}) = 32.0 \text{ cm}^3/\text{mol}$; $a = 27R^2T_c^2/64P_c = 27(82.06 \text{ cm}^3\text{-atm/mol-K})^2(150.9 \text{ K})^2/64(48.3 \text{ atm}) = 1.34 \times 10^6 \text{ cm}^6 \text{ atm/mol}^2$. (b) Comparison of (8.9) with (8.4) gives as the van der Waals estimate: $B = b - a/RT$.

$$B_{100 \text{ K}} = 32.0 \text{ cm}^3/\text{mol} - (1.34 \times 10^6 \text{ cm}^6\text{-atm/mol}^2)/(82.06 \text{ cm}^3\text{-atm/mol-K})(100 \text{ K}) = -131 \text{ cm}^3/\text{mol}. \text{ Also,}$$

$$B_{200 \text{ K}} = -49.6 \text{ cm}^3/\text{mol}, B_{300 \text{ K}} = -22.4 \text{ cm}^3/\text{mol}, B_{500 \text{ K}} = -0.7 \text{ cm}^3/\text{mol}, B_{1000 \text{ K}} = 15.7 \text{ cm}^3/\text{mol}. \text{ Agreement with experiment is fair.}$$

8.9 We have: $\Delta \bar{U}_{\text{vap}} \approx a/\bar{V} = a\rho/M$ and $\Delta \bar{H}_{\text{vap}} \approx a\rho/M + RT$. For N_2 at its normal boiling point, $\Delta \bar{H}_{\text{vap}} \approx (1.35 \times 10^6 \text{ cm}^6 \text{ atm/mol}^2)(0.805 \text{ g/cm}^3)/(28 \text{ g/mol}) + RT = (3.9 \times 10^4 \text{ cm}^3 \text{ atm/mol})(1.987 \text{ cal/82.06 cm}^3 \text{ atm}) + (1.987 \text{ cal/mol-K})(77.4 \text{ K}) = 1.1 \text{ kcal/mol}$. For HCl , $\Delta \bar{H}_{\text{vap}} \approx (3.65 \times 10^6 \text{ cm}^6 \text{ atm/mol}^2)(1.193 \text{ g/cm}^3)/(36.5 \text{ g/mol}) + RT = 2.89 \text{ kcal/mol} + 0.37 \text{ kcal/mol} = 3.3 \text{ kcal/mol}$. For H_2O , $\Delta \bar{H}_{\text{vap}} \approx (5.46 \times 10^6 \text{ cm}^6 \text{ atm/mol}^2)(0.96 \text{ g/cm}^3)/(18 \text{ g/mol}) + RT = 7.8 \text{ kcal/mol}$. Agreement with experiment is fairly good.

8.10 $(P + 27R^2T_c^2/64P_c\bar{V}^2)(\bar{V} - RT_c/8P_c) = RT$

$$\left(P + \frac{27T_c^2}{64P_c\bar{V}^2} \frac{64P_c^2\bar{V}_c^2}{9T_c^2} \right) \left(\bar{V} - \frac{\bar{V}_c}{3} \right) = \frac{8P_c\bar{V}_c}{3T_c} T$$

$$(P + 3P_c/\bar{V}_r^2)(\bar{V} - \bar{V}_c/3) = 8P_c\bar{V}_cT_r/3$$

$$(P_r + 3/\bar{V}_r^2)(\bar{V}_r - 1/3) = 8T_r/3$$

8.11 (a) $P = RT/(\bar{V} - b) - a/T\bar{V}^2$. The critical-point conditions $(\partial P/\partial \bar{V})_T = 0$ and $(\partial^2 P/\partial \bar{V}^2)_T = 0$ lead to

$$\frac{RT_c}{(\bar{V}_c - b)^2} = \frac{2a}{T_c\bar{V}_c^3} \quad \text{and} \quad \frac{RT_c}{(\bar{V}_c - b)^3} = \frac{3a}{T_c\bar{V}_c^4}$$

Division of the first equation by the second gives $\bar{V}_c - b = 2\bar{V}_c/3$ and $\bar{V}_c = 3b$. Substitution in the first equation gives $RT_c/4b^2 = 2a/27b^3T_c$ and $T_c = (2/3)(2a/3bR)^{1/2}$. Substitution in the Berthelot equation at the critical point gives

$$P_c = \frac{R}{2b} \frac{2}{3} \left(\frac{2a}{3bR} \right)^{\frac{1}{2}} - \frac{a}{9b^2} \frac{3}{2} \left(\frac{3bR}{2a} \right)^{\frac{1}{2}} = \frac{\sqrt{2}}{12\sqrt{3}} \frac{a^{\frac{1}{2}} R^{\frac{1}{2}}}{b^{3/2}}$$

Division of this P_c equation by the preceding T_c expression gives $P_c/T_c = R/8b$, so $b = RT_c/8P_c$. The above P_c expression gives

$$a = \frac{144 \times 3}{2} \frac{P_c^2 b^3}{R} = \frac{216 P_c^2 R^3 T_c^3}{8^3 P_c^3 R} = \frac{27}{64} \frac{R^2 T_c^3}{P_c}$$

$$(b) \quad Z_c = \frac{P_c \bar{V}_c}{RT_c} = \frac{\sqrt{2}}{12\sqrt{3}} \frac{a^{\frac{1}{2}} R^{\frac{1}{2}}}{b^{3/2}} \frac{3b}{R} \frac{3}{2} \left(\frac{3bR}{2a} \right)^{\frac{1}{2}} = \frac{3}{8} = 0.375$$

(c) Substitution of $R = 8P_c \bar{V}_c / 3T_c$ and the above expressions for a and b into the Berthelot equation followed by division by $P_c \bar{V}_c$ gives

$$\left(P + \frac{27}{64} \frac{R^2 T_c^3}{P_c} \frac{1}{T \bar{V}^2} \right) \left(\bar{V} - \frac{RT_c}{8P_c} \right) = RT$$

$$\left(P + \frac{27}{64} \frac{64}{9} \frac{P_c^2 \bar{V}_c^2}{T_c^2} \frac{T_c^3}{P_c} \frac{1}{T \bar{V}^2} \right) \left(\bar{V} - \frac{8P_c \bar{V}_c}{3T_c} \frac{T_c}{8P_c} \right) = \frac{8P_c \bar{V}_c}{3T_c} T$$

$$\left(P_r + \frac{3}{V_r^2 T_r} \right) \left(V_r - \frac{1}{3} \right) = \frac{8}{3} T_r$$

8.12 From (8.23), $P_r = 8T_r/3(V_r - \frac{1}{3}) - 3/V_r^2$. $T_r = T/T_c = 310.6/305.4 = 1.017$; $V_r = \bar{V}/\bar{V}_c = V/n\bar{V}_c = (200 \text{ cm}^3)/(2.488 \text{ mol})(148 \text{ cm}^3/\text{mol}) = 0.543$. Then $P_r = 8(1.017)/3(0.543 - 0.333) - 3/(0.543)^2 = 2.75 = P/P_c$ and $P = 2.75P_c = 132\frac{1}{2} \text{ atm}$.

8.13 Eq. (8.26) gives $B = (82.06 \text{ cm}^3\text{-atm/mol-K}) \times (150.9 \text{ K})(48.3 \text{ atm})^{-1} [0.597 - 0.462e^{0.7002(150.9 \text{ K})/T}] = [153.1 - 118.4e^{(105.66 \text{ K})/T}] \text{ cm}^3/\text{mol}$. At $T = 100, 200, 300, 500, \text{ and } 1000 \text{ K}$, we get (in cm^3/mol) $-187.5, -47.7, -15.3, 6.8, 21.5$. Agreement with experiment is very good.

8.14 As noted in Sec. 8.6, at T and P° , $\bar{H}_{1d} - \bar{H} = \int_0^{P^\circ} [T(\partial \bar{V}/\partial T)_P - \bar{V}] dP$. Differentiation of (8.5) gives $(\partial \bar{V}/\partial T)_P = RP^{-1}(1 + B^\dagger P + C^\dagger P^2 + \dots) + RTP^{-1}(PB^\dagger + P^2 C^\dagger + \dots)$, where the prime indicates differentiation with respect to T . Use of (8.5) gives $T(\partial \bar{V}/\partial T)_P - \bar{V} = RT^2 P^{-1}(PB^\dagger + P^2 C^\dagger + \dots)$. Then $\bar{H}_{1d} - \bar{H} = \int_0^{P^\circ} RT^2 (B^\dagger + PC^\dagger + \dots) dP = RT^2 [P^\circ B^\dagger + \frac{1}{2}(P^\circ)^2 C^\dagger + \dots]$. $\bar{S}_{1d} - \bar{S} = \int_0^{P^\circ} [(\partial \bar{V}/\partial T)_P - R/P] dP = \int_0^{P^\circ} [R(B^\dagger + C^\dagger P + \dots) + RT(B^\dagger + PC^\dagger + \dots)] dP = R(B^\dagger + TB^\dagger)P^\circ + \frac{1}{2}R(C^\dagger + TC^\dagger)P^\circ{}^2 + \dots$. Finally, $\bar{G}_{1d} - \bar{G} = (\bar{H}_{1d} - \bar{H}) - T(\bar{S}_{1d} - \bar{S})$ and substitution of the preceding results gives $\bar{G}_{1d} - \bar{G} = -RT[B^\dagger P^\circ + \frac{1}{2}C^\dagger(P^\circ)^2 + \dots]$.

8.15 (a) Comparison of (8.9) with (8.4) gives the van der Waals estimates of the virial coefficients as $B = b - a/RT$, $C = b^2$, Use of (8.6) gives $B^\dagger = b/RT - a/R^2 T^2$, Differentiation gives $B^{\dagger'} = -b/RT^2 + 2a/R^2 T^3$, Substitution in the results of Prob. 8.14 gives $\bar{H}_{1d} - \bar{H} = RT^2(-b/RT^2 + 2a/R^2 T^3)P^\circ + \dots = (2a/RT - b)P^\circ + \dots$ and gives $\bar{S}_{1d} - \bar{S} = (a/RT^2)P^\circ + \dots$. (b) From (8.16), $a = 27R^2 T_c^2 / 64P_c = 5.50 \times 10^6 \text{ cm}^6 \text{ atm/mol}^2$ and $b =$

$RT_c/8P_c = 65.0 \text{ cm}^3/\text{mol}$. Then $\bar{H}_{id} - \bar{H} = (0.987 \text{ atm}) \times [2(5.50 \times 10^6 \text{ cm}^6 \text{ atm/mol}^2)/(82.06 \text{ cm}^3 \text{ atm/mol-K})(298 \text{ K}) - 65.0 \text{ cm}^3/\text{mol}] = (379 \text{ cm}^3 \text{ atm/mol})(1.987 \text{ cal}/82.06 \text{ cm}^3 \text{ atm}) = 9.2 \text{ cal/mol}$. Also, $\bar{S}_{id} - \bar{S} = [(5.50 \times 10^6 \text{ cm}^6 \text{ atm/mol}^2)/(82.06 \text{ cm}^3 \text{ atm/mol-K})(298 \text{ K})^2](0.987 \text{ atm}) = (0.74 \text{ cm}^3 \text{ atm/mol-K})(1.987 \text{ cal}/82.06 \text{ cm}^3 \text{ atm}) = 0.018 \text{ cal/mol-K}$. These are substantially smaller than the experimental values.

8.16 (a) The Berthelot equation when solved for P and multiplied by \bar{V}/RT is $P\bar{V}/RT = \bar{V}/(\bar{V} - b) - a/RT^2\bar{V} = 1/(1 - b/\bar{V}) - a/RT^2\bar{V}$. Use of (8.8) with $x = b/\bar{V}$ gives $P\bar{V}/RT = 1 + (b - a/RT^2)/\bar{V} + b^2/\bar{V}^2 + \dots$. Comparison with (8.4) gives the Berthelot estimates of the virial coefficients as $B = b - a/RT^2$, $C = b^2$, Use of (8.6) gives $B^\dagger = b/RT - a/RT^3$, Differentiation gives $B^{\dagger'} = -b/RT^2 + 3a/RT^4$. Use of Prob. 8.14 results gives $\bar{H}_{id} - \bar{H} = (3a/RT^2 - b)P^\circ + \dots$ and $\bar{S}_{id} - \bar{S} = (2a/RT^3)P^\circ + \dots$. **(b)** Substitution of the a and b expressions of Prob. 8.11a gives $\bar{H}_{id} - \bar{H} = (81RT_c^3/64P_c T^2 - RT_c/8P_c)P^\circ + \dots$ and $\bar{S}_{id} - \bar{S} = (27RT_c^3/32P_c T^3)P^\circ + \dots$. **(c)** Substitution in the results of (b) gives $\bar{S}_{id} - \bar{S} = (27/32) \times (1.987 \text{ cal/mol-K})(305.4 \text{ K}/298 \text{ K})^3(0.987/48.2) = 0.037 \text{ cal/mol-K}$ and $\bar{H}_{id} - \bar{H} = 15 \text{ cal/mol}$. Agreement with experiment is excellent. **(d)** $\bar{S}_{id} - \bar{S} = (27/32) \times (1.987 \text{ cal/mol-K})(430.8/298)^3(1/77.8) = 0.065 \text{ cal/mol-K}$.

8.17 (a) We use the following isothermal path (r.g. = real gas, i.g. = ideal gas):

$$\text{r.g.}(\bar{V}^\circ) \xrightarrow{1} \text{r.g.}(\bar{V}=\infty) \xrightarrow{2} \text{i.g.}(\bar{V}=\infty) \xrightarrow{3} \text{i.g.}(\bar{V}^\circ) \xrightarrow{4} \text{i.g.}(\bar{V}_{\text{id}}^\circ)$$

From $d\bar{A} = -\bar{S} dT - P d\bar{V}$, we have $(\partial\bar{A}/\partial\bar{V})_T = -P$. Then

$$\Delta\bar{A}_1 = -\int_{\bar{V}^\circ}^{\infty} P d\bar{V} = \int_{\infty}^{\bar{V}^\circ} P d\bar{V}; \Delta\bar{A}_2 = 0 \text{ (since } \Delta U_2 = 0 \text{ and}$$

$$\Delta S_2 = 0, \text{ as noted in Chap. 5); } \Delta\bar{A}_3 = -\int_{\infty}^{\bar{V}^\circ} P_{\text{id}} d\bar{V} =$$

$$-\int_{\infty}^{\bar{V}^\circ} (RT/\bar{V}) d\bar{V}, \Delta\bar{A}_4 = -\int_{\bar{V}^\circ}^{\bar{V}_{\text{id}}^\circ} (RT/\bar{V}) d\bar{V} = -RT \ln (\bar{V}_{\text{id}}^\circ/\bar{V}^\circ) =$$

$$-RT \ln (RT/P^\circ\bar{V}^\circ). \text{ Then } \bar{A}_{\text{id}}(T, P^\circ) - \bar{A}(T, P^\circ) = \Delta\bar{A}_1 + \Delta\bar{A}_2$$

$$+ \Delta\bar{A}_3 + \Delta\bar{A}_4 = \int_{\infty}^{\bar{V}^\circ} (P - RT/\bar{V}) d\bar{V} - RT \ln (RT/P^\circ\bar{V}^\circ). \text{ (b)}$$

Solving (8.3) for P and substituting in the result of (a),

$$\text{we get } \bar{A}_{\text{id}} - \bar{A} = \int_{\infty}^{\bar{V}^\circ} [RT/(\bar{V} - b) - a/\bar{V}(\bar{V} + b)T^{\frac{1}{2}} - RT/\bar{V}] d\bar{V}$$

- $RT \ln (RT/P^\circ\bar{V}^\circ)$. Use of a table of integrals gives

$$\bar{A}_{\text{id}} - \bar{A} = [RT \ln (\bar{V} - b) - (a/T^{\frac{1}{2}})(-1/b) \ln (1 + b/\bar{V}) - RT \ln \bar{V}]_{\infty}^{\bar{V}^\circ}$$

$$- RT \ln (RT/P^\circ\bar{V}^\circ) = [RT \ln (1 - b/\bar{V}) + (a/bT^{\frac{1}{2}}) \ln (1 + b/\bar{V})]_{\infty}^{\bar{V}^\circ}$$

$$- RT \ln (RT/P^\circ\bar{V}^\circ) = RT \ln (1 - b/\bar{V}^\circ) + (a/bT^{\frac{1}{2}}) \ln (1 + b/\bar{V}^\circ)$$

$$- RT \ln (RT/P^\circ\bar{V}^\circ). \text{ (c) } \bar{S}_{\text{id}} - \bar{S} = -(\partial/\partial T)(\bar{A}_{\text{id}} - \bar{A}) =$$

$$-R \ln (1 - b/\bar{V}^\circ) + (a/2bT^{3/2}) \ln (1 + b/\bar{V}^\circ) + R \ln (RT/P^\circ\bar{V}^\circ)$$

$$+ R. \bar{U}_{\text{id}} - \bar{U} = (\bar{A}_{\text{id}} - \bar{A}) + T(\bar{S}_{\text{id}} - \bar{S}) =$$

$$(3a/2bT^{\frac{1}{2}}) \ln (1 + b/\bar{V}^\circ) + RT.$$

8.18 Differentiation of (8.26) gives $dB/dT = (RT_c/P_c) \times$

$$(-0.462)(-0.7002T_c/T^2)e^{0.7002T_c/T} = 0.3235(RT_c^2/P_cT^2) \times$$

$$e^{0.7002T_c/T}. \text{ From (8.6), } B^\dagger = B/RT \text{ and } dB^\dagger/dT =$$

$$(dB/dT)/RT - B/RT^2. \text{ Substitution of } T_c = 305.4 \text{ K, } P_c =$$

48.2 atm, and $T = 298 \text{ K}$ in (8.26) and in the dB/dT equa-

tion gives $B = -182 \text{ cm}^3/\text{mol}$ and $dB/dT = 1.186 \text{ cm}^3/\text{mol-K}$.

Then $B^\dagger = B/RT = -0.00744 \text{ atm}^{-1}$ and $dB^\dagger/dT =$
 $(1.186 \text{ cm}^3/\text{mol-K})/(82.06 \text{ cm}^3\text{-atm/mol-K})(298 \text{ K}) +$
 $(182 \text{ cm}^3/\text{mol})/(82.06 \text{ cm}^3\text{-atm/mol-K})(298 \text{ K})^2 = 7.35 \times 10^{-5}$
 $\text{atm}^{-1} \text{ K}^{-1}$. From Prob. 8.14, $\bar{H}_{id} - \bar{H} = RT^2 P^\circ dB^\dagger/dT =$
 $(1.987 \text{ cal/mol-K})(298 \text{ K})^2 (750/760) \text{ atm} (7.35 \times 10^{-5} \text{ atm}^{-1} \text{ K}^{-1})$
 $= 13 \text{ cal/mol}$ and $\bar{S}_{id} - \bar{S} = RP^\circ (B^\dagger + T dB^\dagger/dT) =$
 $(1.987 \text{ cal/mol-K})(0.987 \text{ atm})[-0.00744 + 298(7.35 \times 10^{-5})] \text{ atm}^{-1}$
 $= 0.028 \text{ cal/mol-K}$.

8.19 $f(x) = (1 - x)^{-1}$, $f'(x) = (1 - x)^{-2}$, $f''(x) =$
 $2(1 - x)^{-3}$, $f'''(x) = 3 \cdot 2(1 - x)^{-4}$, ...
 $f(0) = 1$, $f'(0) = 1$, $f''(0) = 2$, $f'''(0) = 3 \cdot 2$, ...
 $f(x) = 1 + (x - 0) + 2(x - 0)^2/2! + 3 \cdot 2(x - 0)^3/3! + \dots$
 $= 1 + x + x^2 + x^3 + \dots$

8.20 $f(x) = \ln x$, $f'(x) = 1/x$, $f''(x) = -1/x^2$,
 $f'''(x) = 2/x^3$, $f^{(iv)}(x) = -3 \cdot 2/x^4$, ...
 $f(1) = 0$, $f'(1) = 1$, $f''(1) = -1$, $f'''(1) = 2$,
 $f^{(iv)}(1) = -3 \cdot 2$, ...
 $\ln x = 0 + (x - 1) - (x - 1)^2/2! + 2(x - 1)^3/3 \cdot 2 - 3 \cdot 2(x - 1)^4/4 \cdot 3 \cdot 2 + \dots$
 $= (x - 1) - (x - 1)^2/2 + (x - 1)^3/3 - (x - 1)^4/4 + \dots$

8.21 $f(x) = e^x$, $f'(x) = e^x$, $f''(x) = e^x$, ...
 $f(0) = 1$, $f'(0) = 1$, $f''(0) = 1$, ...
 $e^x = 1 + x + x^2/2! + x^3/3! + \dots$

8.22 $(d/dx)(\sin x) = \cos x = 1 - 3x^2/3! + 5x^4/5! - \dots$
 $= 1 - x^2/2! + x^4/4! - \dots$.

8.23 x is in radians; $1^\circ = 0.0174533$ rad. Substitution in (8.29) gives $\sin 1^\circ = 0.01745$.

8.24 The function $1/(x^2 + 4)$ has singularities at $x = 2i$ and $x = -2i$ (where $x^2 + 4 = 0$). The distance between the origin (point a) and either of these singularities is 2, so $b = 2$.

8.25 (a) $\sum_{n=0}^5 1^n/n! = 2.7166667$, $\sum_{n=0}^{10} 1^n/n! = 2.7182818$, $\sum_{n=0}^{20} 1^n/n! = 2.7182818$. The exact value is $e = 2.7182818$.

(b) For $x = 10$, we find 1477.6667, 12842.305, and 21991.482 for $n = 5$, 10, and 20. The exact value is $e^{10} = 22026.466$. (For $n = 30$, one finds 22026.464.)

A BASIC program is

```

10 INPUT "X=";X
20 FOR M = 5 TO 20 STEP 5
30 S = 1
40 NF = 1
50 FOR N = 1 TO M
60 NF = N*NF
70 S = S + X^N/NF
80 NEXT N
90 PRINT "M=";M;" SUM=";S
100 NEXT M
110 END

```

8.26 From Sec. 8.3, $T_c \approx 1.6T_b = 1.6(353 \text{ K}) = 565 \text{ K}$;

$$\bar{V}_c \approx 2.7\bar{V}_b = 2.7(78 \text{ g/mol})/(0.81 \text{ g/cm}^3) = 260 \text{ cm}^3/\text{mol}.$$

From Sec. 8.4, Z_c is usually between 0.25 and 0.30, so we take $Z_c = P_c \bar{V}_c / RT_c \approx 0.275$. Thus

$$P_c \approx 0.275 \frac{RT_c}{\bar{V}_c} \approx \frac{(82.06 \text{ cm}^3\text{-atm/mol-K})(565 \text{ K}) 0.275}{260 \text{ cm}^3/\text{mol}} = 49 \text{ atm}$$

(The experimental values are 562 K, 259 cm³/mol, 48 atm.)

8.27 Use the isothermal path: $\text{liq}(1 \text{ bar}) \xrightarrow{a}$

$\text{liq}(23.766 \text{ torr}) \xrightarrow{\text{b}} \text{vap}(23.766 \text{ torr}) \xrightarrow{\text{c}} \text{ideal vap}(23.766 \text{ torr}) \xrightarrow{\text{d}} \text{ideal vap}(1 \text{ bar})$. For step (a), Prob. 7.39 gives $\Delta \bar{G}_a = -1.8 \text{ J/mol}$. For step (b), $\Delta \bar{G}_b = 0$, since this is a reversible constant-T-and-P process. For step (c), Prob. 8.15a gives $\Delta \bar{G}_c = \Delta \bar{H}_c - T \Delta \bar{S}_c \approx (a/RT - b)P =$

$$\left[\frac{5.47 \times 10^6 \text{ cm}^6\text{-atm/mol}^2}{(82.06 \text{ cm}^3\text{-atm/mol-K})(298 \text{ K})} - 30.5 \frac{\text{cm}^3}{\text{mol}} \right] \frac{23.766}{760} \text{ atm}$$

$$= 6.04 \frac{\text{cm}^3 \text{ atm}}{\text{mol}} \frac{8.314 \text{ J}}{82.06 \text{ cm}^3 \text{ atm}} = 0.6 \text{ J/mol}$$

For step (d), Prob. 7.39 gives $\Delta \bar{G}_d = 8557.2 \text{ J/mol}$. The net $\Delta \bar{G}$ is 8556.0 J/mol compared with 8555.4 J/mol in Prob. 7.39 and 8557 J/mol from data in the Appendix.

8.28 Use of Eqs. (4.52) and (8.5) gives

$$\begin{aligned}
 \mu_{JT} &= (1/\bar{C}_P)[T(\partial \bar{V}/\partial T)_P - \bar{V}] = \\
 &\bar{C}_P^{-1} \{ T[(R/P)(1 + B^\dagger P + C^\dagger P^2 + \dots) + (RT/P)(P dB^\dagger/dT + \\
 &\quad P^2 dC^\dagger/dT + \dots)] - (RT/P)(1 + B^\dagger P + C^\dagger P^2 + \dots) \} \\
 &= (RT^2/\bar{C}_P)(dB^\dagger/dT + P dC^\dagger/dT + P^2 dD^\dagger/dT + \dots) \\
 \lim_{P \rightarrow 0} \mu_{JT} &= (RT^2/\bar{C}_P) dB^\dagger/dT
 \end{aligned}$$

(b) Equations (4.47) and (8.4) give $(\partial U/\partial V)_T = T(\partial P/\partial T)_V - P =$

$$\begin{aligned}
 &T \left[\frac{R}{\bar{V}} \left(1 + \frac{B}{\bar{V}} + \dots \right) + \frac{RT}{\bar{V}} \left(\frac{1}{\bar{V}} \frac{dB}{dT} + \dots \right) \right] - \frac{RT}{\bar{V}} \left(1 + \frac{B}{\bar{V}} + \dots \right) \\
 &= \frac{RT^2}{\bar{V}} \left(\frac{1}{\bar{V}} \frac{dB}{dT} + \dots \right). \text{ As } P \rightarrow 0, \bar{V} \rightarrow \infty \text{ and } (\partial U/\partial V)_T \rightarrow 0.
 \end{aligned}$$

8.29 From (8.4), $\bar{V} - \bar{V}_{\text{id}} = (RT/P)(1 + B/\bar{V} + C/\bar{V}^2 + \dots)$
 $- RT/P = RT(B/P\bar{V} + C/P\bar{V}^2 + \dots)$. In the limit $P \rightarrow 0$, we
 have $P\bar{V} = RT$ and $\bar{V} - \bar{V}_{\text{id}} \rightarrow B + C/\bar{V} + \dots \rightarrow B$, since
 $\bar{V} \rightarrow \infty$ as $P \rightarrow 0$.

8.30 (a) As found in Prob. 8.15a, the van der Waals equa-
 tion gives $B^\dagger = b/RT - a/R^2T^2$ and $B^{\ddagger} = -b/RT^2 + 2a/R^2T^3$.
 Substitution in the equation of Prob. 8.28a with all
 terms but the first neglected gives $\mu_{\text{JT}} = (2a/RT - b)/\bar{C}_P$
 as the low-P estimate of μ_{JT} . (b) At the inversion tem-
 perature, the low-P μ_{JT} is zero, so $(2a/RT - b)/\bar{C}_P = 0$
 and $T_{1,P \rightarrow 0} = 2a/bR = 2(1.35 \times 10^6 \text{ atm cm}^6 \text{ mol}^{-2})/$
 $(38.6 \text{ cm}^3/\text{mol})(82.06 \text{ cm}^3\text{-atm/mol-K}) = 852 \text{ K}$, where N_2
 a and b values in Sec. 8.4 were used. The low-P 298-K
 estimate of μ_{JT} is $\mu_{\text{JT}} = [2(1.35 \times 10^6 \text{ atm cm}^6 \text{ mol}^{-2})/$
 $(82.06 \text{ cm}^3\text{-atm/mol-K})(298 \text{ K}) - 38.6 \text{ cm}^3/\text{mol}]/$
 $(6.96 \text{ cal/mol-K}) = (10.3 \text{ cm}^3 \text{ K/cal})(1.987 \text{ cal})/$
 $(82.06 \text{ cm}^3 \text{ atm}) = 0.250 \text{ K/atm}$, where \bar{C}_P is from the Ap-
 pendix and (1.19) and (1.21) were used. Agreement with
 the experimental μ_{JT} is good, but T_1 is poorly predicted.

8.31 (a) Ne has more electrons and greater intermolecular
 attractions than He, so Ne has a greater a, a greater T_c
 and a greater $\Delta\bar{H}_{\text{vap}}$. Ne atoms are larger than He atoms,
 so Ne has a greater b value. (b) C_3H_8 has greater inter-
 molecular attractions and larger size, and so has the
 greater a, T_c , $\Delta\bar{H}_{\text{vap}}$, and b. (c) Due to hydrogen bonds,

H₂O has greater intermolecular attractions, and so has the greater a , T_c , and $\Delta \bar{H}_{\text{vap}}$. The H₂S molecule is larger than the H₂O molecule, so $b_{\text{H}_2\text{S}} > b_{\text{H}_2\text{O}}$.

8.32 From (8.16), $b = RT_c/8P_c = (82.06 \text{ cm}^3\text{-atm/mol-K}) \times (190.6 \text{ K})/8(45.4 \text{ atm}) = 43.1 \text{ cm}^3/\text{mol}$; $a = 27R^2T_c^2/64P_c = 2.27 \times 10^6 \text{ cm}^6 \text{ atm mol}^{-2}$. $\bar{V}_0 = b + RT/P = 43.1 \text{ cm}^3/\text{mol} + (82.06 \text{ cm}^3\text{-atm/mol-K})(273 \text{ K})/(100 \text{ atm}) = 267 \text{ cm}^3/\text{mol}$.

$\bar{V}_1 = b + RT/(P + a/\bar{V}_0^2) = 43.1 \text{ cm}^3/\text{mol} + (82.06 \text{ cm}^3\text{-atm/mol-K})(273 \text{ K})/[100 \text{ atm} + (2.27 \times 10^6 \text{ cm}^6 \text{ atm mol}^{-2})/(267 \text{ cm}^3/\text{mol})^2] = 213 \text{ cm}^3/\text{mol}$;
 $\bar{V}_2 = b + RT/(P + a/\bar{V}_1^2) = 192 \text{ cm}^3/\text{mol}$; $\bar{V}_3 = 182 \text{ cm}^3/\text{mol}$;
 $\bar{V}_4 = 176 \text{ cm}^3/\text{mol}$; $\bar{V}_5 = 172 \text{ cm}^3/\text{mol}$; $\bar{V}_6 = 170 \text{ cm}^3/\text{mol}$;
 $\bar{V}_7 = 169 \text{ cm}^3/\text{mol}$; $\bar{V}_8 = 168 \text{ cm}^3/\text{mol}$; $\bar{V}_9 = 167 \text{ cm}^3/\text{mol}$;
 $\bar{V}_{10} = 166.6 \text{ cm}^3/\text{mol}$; $\bar{V}_{11} = 166 \text{ cm}^3/\text{mol}$; $\bar{V}_{12} = 166 \text{ cm}^3/\text{mol}$.

From Fig. 8.1a, for CH₄ at 100 atm and 0°C, $Z = 0.78_5 = P\bar{V}/RT$ and $\bar{V} = 0.78_5 RT/P = 0.78_5 (82.06 \text{ cm}^3\text{-atm/mol-K}) \times (273 \text{ K})/(100 \text{ atm}) = 176 \text{ cm}^3/\text{mol}$. A BASIC program is

```

10 DIM V(100)
20 INPUT "A=";A
22 INPUT "B=";B
24 INPUT "P=";P
26 INPUT "T=";T
30 R = 82.06
40 V(1) = B + R*T/P
50 FOR I = 1 TO 99
60 V(I+1) = B + R*T/(P + A/V(I)^2)
70 PRINT "I=";I;" V=";V(I+1)
80 IF ABS(V(I+1) - V(I))/V(I) < 1E-5
    THEN STOP
90 NEXT I
95 END

```

8.33 $T_r = T/T_c = (286 \text{ K})/(190.6 \text{ K}) = 1.50$ and $P_r = P/P_c = (91 \text{ atm})/(45.4 \text{ atm}) = 2.00$. At these T_r and P_r values, Fig. 8.5 gives $Z = 0.84$ or 0.85 . We have $Z = P\bar{V}/RT$ and $\bar{V} = ZRT/P = 0.84_5 (82.06 \text{ cm}^3\text{-atm/mol-K})(286 \text{ K})/(91 \text{ atm})$

$$= 218 \text{ cm}^3/\text{mol}.$$

8.34 (a) As in Prob. 7.27b, $d \ln P/dT = (1/P)(dP/dT) = 0.035687/\text{K}$ and $dP/dT = (0.035687/\text{K})(1 \text{ atm}) = 0.035687 \text{ atm/K}$ at 100°C . (b) $\Delta \bar{V} = (82.058 \text{ cm}^3\text{-atm/mol-K})(373.15 \text{ K})/(1 \text{ atm}) - 452 \text{ cm}^3/\text{mol} - 19 \text{ cm}^3/\text{mol} = 30149 \text{ cm}^3/\text{mol}$. Then $\Delta \bar{H} = (T \Delta \bar{V})(dP/dT) = (373.15 \text{ K})(30149 \text{ cm}^3/\text{mol}) \times (0.035687 \text{ atm/K}) = (4.0148 \times 10^5 \text{ cm}^3\text{-atm/mol}) \times (8.3145 \text{ J}/82.058 \text{ cm}^3\text{-atm}) = 40.68_0 \text{ kJ/mol}$.

CHAPTER 9

9.1 (a) $n_1 = c_1 V = (0.800 \text{ mol/L})(0.145 \text{ L}) = 0.116 \text{ mol}.$

(b) $(145 \text{ g}) \times 10.0\% = 14.5 \text{ g}; 0.398 \text{ mol}.$ (c) $m_1 = n_1/w_A = n_1/(w - w_1) = n_1/(w - n_1 M_1)$, where w is the mass of the solution, w_1 is the mass of the HCl, n_1 is the number of moles of HCl, and M_1 is the HCl molar mass. Solving for n_1 , we get $n_1 = m_1 w / (1 + m_1 M_1) = (4.85 \text{ mol/kg})(0.145 \text{ kg}) / [1 + (4.85 \text{ mol/kg})(0.03646 \text{ kg/mol})] = 0.598 \text{ mol HCl}.$

Alternatively, a solution with 1000 g of solvent has 4.85 mol of HCl, which is 176.8₃ g of HCl. The weight percent of HCl is $[176.8_3 / (1000 + 176.8_3)] 100\% = 15.03\%.$ 15.03% of 145 g is 21.7₉ g of HCl, which is 0.598 mol HCl.

9.2 (a) All quantities involved are intensive, so we can work with any convenient amount of solution. Let us choose 1 dm³ of solution. This amount of solution has 8.911 mol of CH₃OH, which is 285.5 g of CH₃OH. Since the solution is 30% CH₃OH, the solution's mass is $(100/30) \times (285.5 \text{ g}) = 951.8 \text{ g}.$ Its density is $(951.8 \text{ g}) / (1 \text{ dm}^3) = 0.9518 \text{ g/cm}^3.$ (b) $m_1 = n_1/w_A = (8.911 \text{ mol}) / (951.8 \text{ g} - 285.5 \text{ g}) = 0.01337 \text{ mol/g} = 13.37 \text{ mol/kg}.$ (c) $\rho_{\text{CH}_3\text{OH}} = m_{\text{CH}_3\text{OH}}/V = (285.5 \text{ g}) / (1 \text{ dm}^3) = 285.5 \text{ g/L}.$

9.3 Let us take 1000 g of solution. This contains $(0.800 \%) (1000 \text{ g}) = 8.00 \text{ g of NH}_3$ and $1000 \text{ g} - 8 \text{ g} = 992 \text{ g of water}.$ This is 0.469₇ mol of NH₃ and 55.06 mol

of water. Then $m_1 = n_1/w_A = (0.469_7 \text{ mol})/(992 \text{ g}) = 0.000474 \text{ mol/g} = 0.474 \text{ mol/kg}$. Also, $x_1 = 0.469_7/(0.469_7 + 55.06) = 0.00846$.

9.4 $c_1 = n_1/V = n_1/(w/\rho) = \rho n_1/w$, where w is the solution's mass. Because the solution is very dilute, we have $w = w_1 + w_A \approx w_A = n_A M_A$, where A is the solvent. Then $c_1 \approx \rho n_1/n_A M_A$. Also, $x_1 = n_1/(n_A + n_1) \approx n_1/n_A$, so $c_1 \approx \rho x_1/M_A$. For the molality, we have $m_1 = n_1/w_A = n_1/n_A M_A \approx x_1/M_A$. From $c_1 \approx \rho x_1/M_A$ and $m_1 \approx x_1/M_A$, we get $c_1 \approx \rho m_1$.

9.5 As noted after Eq. (1.4), $M_A = M_{r,A} \times 1 \text{ g/mol}$, so $m_B = n_B/n_A M_A = n_B/(n_A M_{r,A} \text{ g/mol}) = n_B/(n_A M_{r,A} 10^{-3} \text{ kg/mol}) = (1000 n_B/n_A M_{r,A}) \text{ mol/kg}$.

9.6 (a) $V = n_1 \bar{V}_1 + n_2 \bar{V}_2 = (0.500 \text{ mol})(18.63 \text{ cm}^3/\text{mol}) + (55.51 \text{ mol})(18.062 \text{ cm}^3/\text{mol}) = 1011.9 \text{ cm}^3$. (b) From Eq. (9.26), $C_P = n_1 \bar{C}_{P1} + n_2 \bar{C}_{P2}$. An amount of 0.1000-mol/kg solution that contains 1000 g of solvent has 0.1000 mol (5.844 g) of NaCl and has an NaCl weight percentage of $[5.844/(5.844 + 1000)]100\% = 0.581\%$. Taking 0.581% of 1000 g gives 5.81 g of NaCl in the 1000 g of solution, which is 0.0994 mol of NaCl. The percent water is $100 - 0.581 = 99.419\%$. The H_2O mass is 994.19 g, which is 55.186 mol H_2O . So $C_P = (55.186 \text{ mol})(17.992 \text{ cal/mol-K}) + (0.0994 \text{ mol})(-17.00 \text{ cal/mol-K}) = 991.22 \text{ cal/K}$.

9.7 Substitution of $G = \sum_i n_i \mu_i$ into $G \equiv U + PV - TS$

gives the desired result.

9.8 $\bar{A}_i = (\partial A / \partial n_i)_{T, P, n_{j \neq i}}$, where A is the Helmholtz energy of the solution, n_i is the number of moles of i in the solution, T and P are temperature and pressure, and $n_{j \neq i}$ indicates that all mole numbers except i are held fixed.

9.9 (a) $H \equiv U + PV$. Partial differentiation gives

$$(\partial H / \partial n_i)_{T, P, n_{j \neq i}} = (\partial U / \partial n_i)_{T, P, n_{j \neq i}} + P(\partial V / \partial n_i)_{T, P, n_{j \neq i}},$$

so $\bar{H}_i = \bar{U}_i + P\bar{V}_i$. (b) Taking $\partial / \partial T$ of (9.32), we get

$$\begin{aligned} (\partial \Delta G_{\text{mix}} / \partial T)_{P, n_i} &= (\partial / \partial T)_{P, n_i} \sum_i n_i (\bar{G}_i - \bar{G}_i^*) = \\ \sum_i n_i [(\partial \bar{G}_i / \partial T)_{P, n_i} - (\partial \bar{G}_i^* / \partial T)_{P, n_i}] &= \sum_i n_i (-\bar{S}_i + \bar{S}_i^*) = \\ \sum_i n_i \bar{S}_i^* - \sum_i n_i \bar{S}_i &= S^* - S = -\Delta S_{\text{mix}}, \text{ where (9.30) was used.} \end{aligned}$$

9.10 (a) $G = \sum_i n_i \mu_i = \sum_i n_i [\mu_i^\circ + RT \ln (P_i / P^\circ)]$. Taking

$P_1 = P^\circ$ and $P_2 = P_i$ in (4.65), we have for n_i moles of

pure gas i : $G_i^*(T, P_i, n_i) - G_i^*(T, P^\circ, n_i) = n_i RT \times$

$$\int_{P^\circ}^{P_i} P^{-1} dP = n_i RT \ln (P_i / P^\circ). \text{ So } G_i^*(T, P_i, n_i) =$$

$$G_i^*(T, P^\circ, n_i) + n_i RT \ln (P_i / P^\circ) = n_i \bar{G}_i^*(T, P^\circ) + n_i RT \times$$

$$\ln (P_i / P^\circ) = n_i [\mu_i^\circ + RT \ln (P_i / P^\circ)], \text{ since } \bar{G}_i = \mu_i \text{ for a}$$

pure substance. Hence the above sum for G of the mixture

$$\text{becomes } G = \sum_i G_i^*(T, P_i, n_i). \text{ (b) } S = -(\partial / \partial T)_{P, n_i} G =$$

$$\sum_i [-(\partial G_i^* / \partial T)_{P, n_i}] = \sum_i S_i^*(T, P_i, n_i), \text{ where (4.51) was}$$

$$\text{used. (c) } H = G + TS = \sum_i G_i^* + T \sum_i S_i^* = \sum_i (G_i^* + TS_i^*) =$$

$$\sum_i H_i^*(T, n_i), \text{ where } P_i \text{ is absent since } H \text{ is independent}$$

$$\text{of } P \text{ for an ideal gas. (d) } C_P = (\partial H / \partial T)_{P, n_i} =$$

$$(\partial / \partial T)_{P, n_i} \sum_i H_i^* = \sum_i (\partial H_i^* / \partial T)_{n_i} = \sum_i C_{P, i}^*(T, n_i). U =$$

$$\begin{aligned}
 H - PV &= \sum_1 H_1^* - P(\sum_1 n_i RT/P) = \sum_1 (H_1^* - n_i RT) = \\
 \sum_1 (H_1^* - P_i V) &= \sum_1 U_1^*(T, n_i). \quad (\underline{e}) \text{ Assuming the mixture} \\
 \text{is ideal, we have } C_P &= \sum_1 C_{P,i}^*(T, n_i) = C_{P,O_2}^* + C_{P,CO_2}^* = \\
 n_{O_2} \bar{C}_{P,O_2}^* + n_{CO_2} \bar{C}_{P,CO_2}^* &= (0.100 \text{ mol})(29.355 \text{ J/mol-K}) + \\
 (0.300 \text{ mol})(37.11 \text{ J/mol-K}) &= 14.07 \text{ J/K}.
 \end{aligned}$$

9.11 $n(H_2O) = 1.11_0 \text{ mol}$ and $n(C_2H_5OH) = 0.977 \text{ mol}$.

$x(C_2H_5OH) = 0.977/2.087 = 0.468$. For this composition, Fig. 9.5 gives $\bar{V}(H_2O) = 16.8 \text{ cm}^3/\text{mol}$, $\bar{V}(C_2H_5OH) = 57.0 \text{ cm}^3/\text{mol}$. $V = \bar{V}_1 n_1 + \bar{V}_2 n_2 = (16.8 \text{ cm}^3/\text{mol})(1.11 \text{ mol}) + (57.0 \text{ cm}^3/\text{mol})(0.977 \text{ mol}) = 74.3 \text{ cm}^3$.

9.12 $V = n_1 \bar{V}_1 + n_2 \bar{V}_2 = 307.09 \text{ cm}^3 = (72.061/18.0153) \text{ mol} \times (16.488 \text{ cm}^3/\text{mol}) + (192.252/32.0422) \text{ mol} \bar{V}_{CH_3OH}$ and $\bar{V}_{CH_3OH} = 40.19 \text{ cm}^3/\text{mol}$.

9.13 Take solutions that each contain 1000 g of H_2O (constant n_{H_2O}). Let w be the solution mass. For the 12% solution: $(1000 \text{ g})/w = 0.88000$ and $w = 1136.36 \text{ g}$; this solution contains 136.36 g of CH_3OH , which is 4.2557 mol of CH_3OH ; the solution has $V = (1136.36 \text{ g})/(0.97942 \text{ g/cm}^3) = 1160.24 \text{ cm}^3$. For the 13% solution: $(1000 \text{ g})/w = 0.87000$ and $w = 1149.43 \text{ g}$; this solution has 149.43 g of CH_3OH , which is 4.6636 mol of CH_3OH ; the solution's volume is $V = (1149.43 \text{ g})/(0.97799 \text{ g/cm}^3) = 1175.30 \text{ cm}^3$. We have $\bar{V}_{CH_3OH} \approx (\Delta V/\Delta n_{CH_3OH})_{T,P,n_{H_2O}} = (15.06 \text{ cm}^3)/(0.4079 \text{ mol}) = 36.92 \text{ cm}^3/\text{mol}$. To find \bar{V}_{H_2O} , we now take solutions with

100 g of CH_3OH (constant $n_{\text{CH}_3\text{OH}}$) and do the calculations the same way as for the constant $n_{\text{H}_2\text{O}}$ solutions. For the 12% solution, we find $n_{\text{H}_2\text{O}} = 40.706 \text{ mol}$ and $V = 850.84 \text{ cm}^3$. For the 13% solution, we find $n_{\text{H}_2\text{O}} = 37.148 \text{ mol}$ and $V = 786.54 \text{ cm}^3$. Hence $\bar{V}_{\text{H}_2\text{O}} \approx (\Delta V / \Delta n_{\text{H}_2\text{O}})_{T,P,n_{\text{CH}_3\text{OH}}} = (-64.30 \text{ cm}^3) / (-3.558 \text{ mol}) = 18.07 \text{ cm}^3/\text{mol}$.

9.14 (a) \bar{V} of MgSO_4 at a given composition equals the slope of Fig. 9.3 at that composition. The slope is zero at the minimum, which occurs at $n_{\text{MgSO}_4} = 0.07 \text{ moles}$ in 1000 g of water, which is a molality of 0.07 mol/kg. (b) Infinite dilution corresponds to $n_{\text{MgSO}_4} \rightarrow 0$. Drawing the tangent line to the curve at $n_{\text{MgSO}_4} = 0$, one finds its slope to be $-3.5 \text{ cm}^3/\text{mol}$, which is \bar{V}^∞ of MgSO_4 .

9.15 We draw the tangent line at $x_{\text{ethanol}} = 0.4$. This line intersects the $x_{\text{ethanol}} = 0$ axis at $-1.1 \text{ cm}^3/\text{mol} = \bar{V}_{\text{H}_2\text{O}} - \bar{V}_{\text{H}_2\text{O}}^* = \bar{V}_{\text{H}_2\text{O}} - 18.05 \text{ cm}^3/\text{mol}$, and $\bar{V}_{\text{H}_2\text{O}} = 16.95 \text{ cm}^3/\text{mol}$. The tangent line intersects the $x_{\text{ethanol}} = 1$ axis at $-1.15 \text{ cm}^3/\text{mol} = \bar{V}_{\text{ethanol}} - \bar{V}_{\text{ethanol}}^* = \bar{V}_{\text{ethanol}} - 58.4 \text{ cm}^3/\text{mol}$, and $\bar{V}_{\text{ethanol}} = 57.3 \text{ cm}^3/\text{mol}$.

9.16 The pure molar volumes are $\bar{V}_{\text{H}_2\text{O}}^* = M/\rho = (18.015 \text{ g/mol}) / (0.99705 \text{ g/cm}^3) = 18.07 \text{ cm}^3/\text{mol}$ and $\bar{V}_{\text{CH}_3\text{OH}}^* = 40.71 \text{ cm}^3/\text{mol}$. We plot $\Delta V_{\text{mix}}/n$ vs. $x_{\text{H}_2\text{O}}$ (similar to Fig. 9.4). (a) Drawing the tangent line at $x_{\text{H}_2\text{O}} = 0$, we find it intersects the $x_{\text{H}_2\text{O}} = 1$ line at $-4.1 \text{ cm}^3/\text{mol}$.

(With a reasonable choice of scale, the intersection occurs off the paper and can be calculated by extrapolation.) Therefore at $x_{\text{H}_2\text{O}} = 0$, $\bar{V}_{\text{H}_2\text{O}} - \bar{V}_{\text{H}_2\text{O}}^* = -4.1 \text{ cm}^3/\text{mol} = \bar{V}_{\text{H}_2\text{O}} - 18.1 \text{ cm}^3/\text{mol}$ and $\bar{V}_{\text{H}_2\text{O}} = 14.0 \text{ cm}^3/\text{mol}$. Of course, $\bar{V}_{\text{CH}_3\text{OH}} = \bar{V}_{\text{CH}_3\text{OH}}^* = 40.7 \text{ cm}^3/\text{mol}$ at $x_{\text{H}_2\text{O}} = 0$. (b) The tangent line at $x_{\text{H}_2\text{O}} = 0.4$ intersects the $x_{\text{H}_2\text{O}} = 0$ line at $-0.5 \text{ cm}^3/\text{mol}$ and intersects $x_{\text{H}_2\text{O}} = 1$ at $-1.6 \text{ cm}^3/\text{mol}$, so $\bar{V}_{\text{CH}_3\text{OH}} - \bar{V}_{\text{CH}_3\text{OH}}^* = -0.5 \text{ cm}^3/\text{mol}$ and $\bar{V}_{\text{CH}_3\text{OH}} = 40.2 \text{ cm}^3/\text{mol}$; also, $\bar{V}_{\text{H}_2\text{O}} = 16.5 \text{ cm}^3/\text{mol}$. (c) $\bar{V}_{\text{CH}_3\text{OH}} - \bar{V}_{\text{CH}_3\text{OH}}^* = -1.6 \text{ cm}^3/\text{mol}$ and $\bar{V}_{\text{CH}_3\text{OH}} = 39.1 \text{ cm}^3/\text{mol}$; $\bar{V}_{\text{H}_2\text{O}} - \bar{V}_{\text{H}_2\text{O}}^* = -0.6 \text{ cm}^3/\text{mol}$ and $\bar{V}_{\text{H}_2\text{O}} = 17.5 \text{ cm}^3/\text{mol}$.

9.17 (a) $\bar{V}_B = (\partial V / \partial n_B)_{T,P,n_A} = b + (3/2)cn_B^{1/2} + 2kn_B$ for $n_A M_A = 1 \text{ kg}$. (b) For $m_B = 1 \text{ mol/kg}$, we have $n_B = 1 \text{ mol}$ in a solution with $n_A M_A = 1 \text{ kg}$. $\bar{V}_B = 16.6253 \text{ cm}^3/\text{mol} + 1.5(1.7738 \text{ cm}^3/\text{mol}^{3/2})(1.0000 \text{ mol})^{1/2} + 2(0.1194 \text{ cm}^3/\text{mol}^2)(1.0000 \text{ mol}) = 19.5248 \text{ cm}^3/\text{mol}$.

(c) $V = n_A \bar{V}_A + n_B \bar{V}_B$ and $n_A \bar{V}_A = V - n_B \bar{V}_B = a + bn_B + cn_B^{3/2} + kn_B^2 - n_B b - 1.5cn_B^{3/2} - 2kn_B^2 = a - \frac{1}{2}cn_B^{3/2} - kn_B^2$.

Since $n_A = (1 \text{ kg})/M_A$, we get $\bar{V}_A = (M_A/1000 \text{ g}) \times (a - \frac{1}{2}cn_B^{3/2} - kn_B^2)$ for $n_A M_A = 1 \text{ kg}$. (d) $m_B = n_B/n_A M_A = n_B/(1 \text{ kg}) = n_B/\text{kg}$ and $n_B = m_B \text{ kg}$. Substitution in the results of (a) and (c) gives the desired equations. (e) $\bar{V}_{\text{H}_2\text{O}} = (18.0152 \text{ g/mol})[1002.96 \text{ cm}^3 - \frac{1}{2}(1.7738 \text{ cm}^3/\text{mol}^{3/2}) \times (1 \text{ mol/kg})^{3/2} \text{ kg}^{3/2} - (0.1194 \text{ cm}^3/\text{mol}^2)(1 \text{ mol/kg})^2 \text{ kg}^2]/(1000 \text{ g}) = 18.050 \text{ cm}^3/\text{mol}$. (f) In the infinite-dilution

limit, n_B goes to zero and \bar{V}_B in (d) becomes $\bar{V}_B^\infty = b = 16.6253 \text{ cm}^3/\text{mol}$.

9.18 $\bar{V}_{\text{NaCl}}^\infty = \bar{V}^\infty(\text{Na}^+) + \bar{V}^\infty(\text{Cl}^-)$, $\bar{V}_{\text{KNO}_3}^\infty = \bar{V}^\infty(\text{K}^+) + \bar{V}^\infty(\text{NO}_3^-)$, and $\bar{V}_{\text{NaNO}_3}^\infty = \bar{V}^\infty(\text{Na}^+) + \bar{V}^\infty(\text{NO}_3^-)$. Then $\bar{V}_{\text{KCl}}^\infty = \bar{V}^\infty(\text{K}^+) + \bar{V}^\infty(\text{Cl}^-) = \bar{V}_{\text{KNO}_3}^\infty + \bar{V}_{\text{NaCl}}^\infty - \bar{V}_{\text{NaNO}_3}^\infty = (38.0 + 16.6 - 27.8) \text{ cm}^3/\text{mol} = 26.8 \text{ cm}^3/\text{mol}$.

9.19 (a) $z \equiv \Delta V_{\text{mix}}/n = (V - V^*)/(n_A + n_B)$, so $V - V^* = (n_A + n_B)z$ and $V = (n_A + n_B)z + V^* = (n_A + n_B)z + n_A \bar{V}_A^* + n_B \bar{V}_B^*$. (b) Taking $(\partial/\partial n_A)_{n_B, T, P}$ of the result of (a) gives $(\partial V/\partial n_A)_{n_B, T, P} \equiv \bar{V}_A$ for the left side and $z + (n_A + n_B)(\partial z/\partial n_A)_{n_B} + \bar{V}_A^*$ for the right side. (Note that \bar{V}_A^* is a constant at fixed T and P and is independent of n_A .) Equating these expressions, we get $\bar{V}_A = z + n(\partial z/\partial n_A)_{n_B} + \bar{V}_A^*$. (c) Equation (1.35) gives $(\partial z/\partial n_A)_{n_B} = (dz/dx_B)(\partial x_B/\partial n_A)_{n_B}$. Since $x_B = n_B/(n_A + n_B)$, we have $(\partial x_B/\partial n_A)_{n_B} = -n_B/(n_A + n_B)^2 = -x_B/(n_A + n_B) = -x_B/n$. The result of (b) gives $(\partial z/\partial n_A)_{n_B} = (\bar{V}_A - \bar{V}_A^* - z)/n$. Substitution of these expressions for $\partial x_B/\partial n_A$ and $\partial z/\partial n_A$ into $\partial z/\partial n_A = (dz/dx_B)(\partial x_B/\partial n_A)$ gives $dz/dx_B = (\bar{V}_A^* - \bar{V}_A + z)/x_B$. The n_B subscript can be omitted from $(\partial z/\partial x_B)_{n_B}$ because $z \equiv (V - V^*)/n$ is an intensive quantity and so is a function of x_B only and is independent of the size of the system and hence of n_B . (d) The plotted quantity $\Delta V_{\text{mix}}/n$ is symmetric in A and B. Since the intercept at $x_B = 0$ is $\bar{V}_A' - \bar{V}_A^*$, the A-B symmetry means that the intercept at x_A

$= 0$ is $\bar{V}'_B - \bar{V}^*_B$. But $x_A = 0$ is $x_B = 1$.

9.20 The tangent to the ΔH_{mix} vs. $x_{\text{H}_2\text{SO}_4}$ curve at $x_{\text{H}_2\text{SO}_4} = 0.4$ intersects $x_{\text{H}_2\text{SO}_4} = 0$ at $-13.2 \text{ kJ/mol} =$

$\Delta \bar{H}_{\text{diff, H}_2\text{O}}$ and intersects $x_{\text{H}_2\text{SO}_4} = 1$ at $-16.1 \text{ kJ/mol} =$

$\Delta \bar{H}_{\text{diff, H}_2\text{SO}_4}$. Drawing the tangent at $x_{\text{H}_2\text{SO}_4} = 0.333$, we find $\Delta \bar{H}_{\text{diff, H}_2\text{O}} = -9.2 \text{ kJ/mol}$ and $\Delta \bar{H}_{\text{diff, H}_2\text{SO}_4} = -23.0 \text{ kJ/mol}$.

9.21 $\Delta H_{\text{mix}} = H - H^*$. $(\partial \Delta H_{\text{mix}} / \partial n_B)_{T, P, n_A} =$

$(\partial H / \partial n_B)_{T, P, n_A} - (\partial H^* / \partial n_B)_{T, P, n_A}$. But by definition, $\bar{H}_B =$

$(\partial H / \partial n_B)_{T, P, n_A}$. Also, $H^* = n_A \bar{H}_A^*(T, P) + n_B \bar{H}_B^*(T, P)$, so

$(\partial H^* / \partial n_B)_{T, P, n_A} = \bar{H}_B^*$. Therefore $(\partial \Delta H_{\text{mix}} / \partial n_B)_{T, P, n_A} =$

$\bar{H}_B - \bar{H}_B^* = \Delta \bar{H}_{\text{diff, B}}$, where (9.38) was used.

9.22 Subtraction of $\Delta H_{f, \text{NaCl}(s)}^\circ$ from the apparent ΔH_f° values give the following integral heats of solution per mole of NaCl vs. x_{NaCl} :

$\Delta \bar{H}_{\text{int, NaCl}} / (\text{kJ/mol})$	1.874	2.347	3.016	3.711
x_{NaCl}	0.1	0.0625	0.03846	0.019608

As in the last example in Sec. 9.3, multiplication of $\Delta \bar{H}_{\text{int, NaCl}}$ by x_{NaCl} gives $\Delta H_{\text{mix}}/n$:

$(\Delta H_{\text{mix}}/n) / (\text{J/mol})$	187.4	146.7	116.0	72.77	0
x_{NaCl}	0.1	0.0625	0.03846	0.019608	0

We plot ΔH_{mix} vs. x_{NaCl} and draw the tangent line at $x_{\text{NaCl}} = 0.05$. The tangent line intersects $x_{\text{NaCl}} = 0$ at $66\frac{1}{2} \text{ J/mol}$

$= \bar{H}_{H_2O} - \bar{H}_{H_2O}^*$ and intersects $x_{NaCl} = 0.1$ at $198\frac{1}{2}$ J/mol. Extrapolation gives the intersection at $x_{NaCl} = 1$ as $[66\frac{1}{2} - 10(198\frac{1}{2} - 66\frac{1}{2})]$ J/mol = 1.39 kJ/mol = $\bar{H}_{NaCl} - \bar{H}_{NaCl}^*$.

9.23 The NBS tables give $\Delta H_{f,298}^\circ = -92.307$ kJ/mol for $HCl(g)$ and $\Delta H_{f,298}^\circ = -121.55$ kJ/mol for HCl in 1 mol of H_2O . Thus $\Delta \bar{H}_{int,HCl} = -29.24$ kJ/mol for a solution with $x_{HCl} = 0.500$. From (9.37), $\Delta H_{mix} = n_{HCl} \Delta \bar{H}_{int,HCl}$ and $\Delta H_{mix}/n_{tot} = x_{HCl} \Delta \bar{H}_{int,HCl} = -14.62$ kJ/mol at $x_{HCl} = 0.5$. Using further data, we find (values in kJ/mol)

x_{HCl}	0.500	0.400	0.333	0.286	0.250	0.200
$\Delta \bar{H}_{int,HCl}$	-29.24	-40.36	-48.65	-53.17	-56.18	-60.61
$\Delta H_{mix}/n_{tot}$	-14.62	-16.15	-16.22	-15.19	-14.05	-12.12

We plot ΔH_{mix} vs. x_{HCl} and draw the tangent line at $x_{HCl} = 0.30$. The intercepts at $x_{HCl} = 0$ and $x_{HCl} = 1$ give $\Delta \bar{H}_{diff,H_2O} = -8.8$ kJ/mol and $\Delta \bar{H}_{diff,HCl} = -31.8$ kJ/mol.

9.24 No. Models show that the A-B intermolecular forces differ from the A-A and B-B intermolecular forces.

9.25 $n_{ben} = 1.280$ mol and $n_{tol} = 1.085$ mol. $x_{ben} = 0.5412$ and $x_{tol} = 0.4588$. Equation (9.44) gives $\Delta G_{mix} = (1.987 \text{ cal/mol-K})(293.1 \text{ K})[(1.280 \text{ mol}) \ln 0.5412 + (1.085 \text{ mol}) \ln 0.4588] = -950 \text{ cal}$. $\Delta V_{mix} = 0$, $\Delta H_{mix} = 0$. $\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix}$, so $\Delta S_{mix} = (950 \text{ cal})/(293.1 \text{ K}) = 3.24 \text{ cal/K}$.

9.26 (a) $n_{ben} = (100.0 \text{ g})/(78.11 \text{ g/mol}) = 1.280 \text{ mol}$.

$n_{\text{tol}} = 1.085 \text{ mol.}$ $x_{\text{ben}} = 1.280/(1.280 + 1.085) = 0.5412.$
 $x_{\text{tol}} = 0.4588.$ $P_{\text{ben}} = 0.5412(74.7 \text{ torr}) = 40.4 \text{ torr.}$
 $P_{\text{tol}} = 0.4588(22.3 \text{ torr}) = 10.2 \text{ torr.}$ (b) $P_{\text{tot}} =$
 $(40.4 + 10.2) \text{ torr} = 50.6 \text{ torr.}$ Use of $P_i = x_{i,\text{vap}} P$ gives
 $x_{\text{ben,vap}} = (40.4 \text{ torr})/(50.6 \text{ torr}) = 0.798.$ $x_{\text{tol,vap}} =$
 $0.202.$

9.27 $P = P_{\text{hex}} + P_{\text{oct}} = x_{\text{hex}} P_{\text{hex}}^* + (1 - x_{\text{hex}}) P_{\text{oct}}^*.$
 $x_{\text{hex}} = (P - P_{\text{oct}}^*) / (P_{\text{hex}}^* - P_{\text{oct}}^*) = (666 \text{ torr} - 354 \text{ torr}) /$
 $(1836 \text{ torr} - 354 \text{ torr}) = 0.211.$ $x_{\text{oct}} = 1 - 0.211 = 0.789.$

9.28 $P_i = x_{i,\text{vap}} P = x_i P_i^*.$ $0.555(95.0 \text{ torr}) = 0.305 P_{\text{hex}}^*$
and $P_{\text{hex}}^* = 173 \text{ torr.}$ $P = x_1 P_1^* + x_2 P_2^* = 95.0 \text{ torr} =$
 $0.305 P_{\text{hex}}^* + 0.695 P_{\text{hept}}^* = 0.305(173 \text{ torr}) + 0.695 P_{\text{hept}}^*$
and $P_{\text{hept}}^* = 60.8 \text{ torr.}$ We assumed an ideal solution, ideal
vapor, and the pressure independence of $\mu^*.$

9.29 (a) $P_A = x_{A,v} P = x_A P_A^*,$ so $x_{A,v} = x_A P_A^* / P.$ However,
 $P = P_A + P_B = x_A P_A^* + x_B P_B^* = x_A P_A^* + (1 - x_A) P_B^*,$ so $x_{A,v} =$
 $x_A P_A^* / (x_A P_A^* + P_B^* - x_A P_B^*) = (x_A P_A^* / P_B^*) / (x_A P_A^* / P_B^* + 1 - x_A).$
(b) If A is benzene, then $P_A^* / P_B^* = 74.7 / 22.3 = 3.35$ and
the equation in (a) gives $x_{A,v} = 3.35 x_A / (1 + 2.35 x_A).$ We get

$x_{A,v}$	0	0.456	0.691	0.834	0.931	1
x_A	0	0.2	0.4	0.6	0.8	1

The plot resembles the upper curve in Fig. 9.10b. For
toluene (t), we find $x_{t,v} = 0.299 x_t / (1 - 0.701 x_t)$ and

$$x_{t,v} \quad 0 \quad 0.070 \quad 0.166 \quad 0.310 \quad 0.545 \quad 1$$

$$x_t \quad 0 \quad 0.2 \quad 0.4 \quad 0.6 \quad 0.8 \quad 1$$

9.30 For an ideal solution, $V = V^* = n_1 \bar{V}_1^* + n_2 \bar{V}_2^* = n_1 M_1 / \rho_1^* + n_2 M_2 / \rho_2^* = m_1 / \rho_1^* + m_2 / \rho_2^* = (33.33 \text{ g}) / (0.8790 \text{ g/cm}^3) + (33.33 \text{ g}) / (0.8668 \text{ g/cm}^3) = 76.37 \text{ cm}^3$. Then $\rho = m/V = (66.66 \text{ g}) / (76.37 \text{ cm}^3) = 0.8729 \text{ g/cm}^3$.

9.31 (a) $\Delta C_{P,mix} = C_P - C_P^* = (\partial H / \partial T)_{P,n_i} - (\partial H^* / \partial T)_{P,n_i} = (\partial / \partial T)_{P,n_i} (H - H^*) = (\partial \Delta H_{mix} / \partial T)_{P,n_i} = 0$, since $\Delta H_{mix} = 0$ for an ideal solution. (b) $C_P = C_P^* = n_1 \bar{C}_{P1}^* + n_2 \bar{C}_{P2}^* = (100/78.11) \text{ mol} (136 \text{ J/mol-K}) + (100/92.14) \text{ mol} (156 \text{ J/mol-K}) = 343 \text{ J/mol-K}$.

9.32 At $x_B = 0.50$, the tangent is horizontal and intersects the $x_B = 0$ and $x_B = 1$ axes at $-0.41_5 \text{ kcal/mol} = \mu_A - \mu_A^* = \mu_B - \mu_B^*$; the calculated result is $\mu_i - \mu_i^* = RT \ln 0.5 = (1.987 \text{ cal/mol-K})(298.1 \text{ K}) \ln 0.5 = -0.411 \text{ kcal/mol}$. At $x_B = 0.25$, the tangent line's intercept at $x_B = 0$ is $-0.18_0 \text{ kcal/mol} = \mu_A - \mu_A^*$ and that at $x_B = 1$ is $-0.81_5 \text{ kcal/mol} = \mu_B - \mu_B^*$; the calculated values are $\mu_A - \mu_A^* = RT \ln 0.75 = -0.170 \text{ kcal/mol}$ and $\mu_B - \mu_B^* = RT \ln 0.25 = -0.821 \text{ kcal/mol}$.

9.33 From (9.30), (9.31), (9.42), and (9.28):

$$\begin{aligned} \bar{S}_i &= -(\partial \mu_i / \partial T)_{P,n_j} = -(\partial \mu_i^* / \partial T)_{P,n_j} - R \ln x_i = \bar{S}_i^* - R \ln x_i \\ \bar{V}_i &= (\partial \mu_i / \partial P)_{T,n_j} = (\partial \mu_i^* / \partial P)_T = \bar{V}_i^* \quad \bar{H}_i = \mu_i + T \bar{S}_i = \\ &\mu_i^* + RT \ln x_i + T \bar{S}_i^* - RT \ln x_i = \bar{H}_i^* \quad (\text{since } \mu_i^* = \bar{G}_i^*). \end{aligned}$$

9.34 $\mu_i = \mu_i^\circ + RT \ln (P_i/P^\circ) = \mu_i^\circ + RT \ln (x_i P/P^\circ) = \mu_i^\circ + RT \ln (P/P^\circ) + RT \ln x_i$. For $x_i = 1$, this equation becomes $\mu_i^* = \mu_i^\circ + RT \ln (P/P^\circ)$, so $\mu_i = \mu_i^* + RT \ln x_i$.

9.35 Substitution of Equation (9.42) into the phase-equilibrium condition $\mu_1^\alpha = \mu_1^\beta$ gives $\mu_1^* + RT \ln x_1^\alpha = \mu_1^* + RT \ln x_1^\beta$, so $x_1^\alpha = x_1^\beta$. Similarly, $x_2^\alpha = x_2^\beta$.

9.36 (a) The solvent A is ethanol and Raoult's law gives

$$P_A = x_A P_A^* = P_{\text{eth}} = 0.9900(172.76 \text{ torr}) = 171.03 \text{ torr}.$$

$$P_{\text{chl}} = P - P_{\text{eth}} = (177.95 - 171.03) \text{ torr} = 6.92 \text{ torr}.$$

(b) In a gas mixture, $P_i = x_i P$, so $x_{v,\text{eth}} = 171.03/177.95 = 0.9611$, and $x_{v,\text{chl}} = 6.92/177.95 = 0.0388$. (c) $P_i = K_i x_i$, so $K_{\text{chl}} = P_{\text{chl}}/x_{\text{chl}} = (6.92 \text{ torr})/0.0100 = 692 \text{ torr}$.

(d) $P_A = x_A P_A^* = P_{\text{eth}} = 0.9800(172.76 \text{ torr}) = 169.30 \text{ torr}$; $P_{\text{chl}} = K_{\text{chl}} x_{\text{chl}} = (692 \text{ torr})(0.0200) = 13.84 \text{ torr}$. $P = (169.30 + 13.84) \text{ torr} = 183.14 \text{ torr}$. $x_{v,\text{eth}} = P_{\text{eth}}/P = 169.30/183.14 = 0.9244$ and $x_{v,\text{chl}} = P_{\text{chl}}/P = 13.84/183.14 = 0.0756$.

9.37 (a) $P_{\text{chl}} = x_{\text{chl},v} P = 0.9794(438.59 \text{ torr}) = 429.56 \text{ torr}$; $P_{\text{eth}} = (1 - 0.9794)(438.59 \text{ torr}) = 9.03 \text{ torr}$. (b)

Raoult's law for the solvent chloroform gives $P_{\text{chl}} = x_{\text{chl}} P_{\text{chl}}^*$ and $P_{\text{chl}}^* = (429.56 \text{ torr})/0.9900 = 433.90 \text{ torr}$.

(c) $P_{\text{eth}} = K_{\text{eth}} x_{\text{eth}}$ and $K_{\text{eth}} = (9.03 \text{ torr})/0.0100 = 903 \text{ torr}$.

9.38 We have $K_i = P_i/x_i$ for very dilute solutions of i. For CS_2 as solute, we draw the line tangent to the $P(\text{CS}_2)$

curve at the point $x(\text{CS}_2) = 0$. Since $P_1 = K_1 x_1$, the slope of this tangent line equals K_{CS_2} ; the slope equals the intercept of the tangent line with the $x(\text{CS}_2) = 1$ line. We find $K_{\text{CS}_2} = 1.25 \times 10^3$ torr in acetone as solvent. Drawing the tangent line to the $P(\text{ac})$ curve at the point $x(\text{CS}_2) = 1$ and finding its intercept with $x(\text{CS}_2) = 0$, we get $K_{\text{ac}} = 2.0 \times 10^3$ torr in the solvent CS_2 .

9.39 From (9.68), $\mu_1^\circ - \mu_{1,v}^\circ = RT \ln (K_1/P^\circ) =$
 $(8.314 \text{ J/mol-K})(308 \text{ K}) \ln (145/750) = -4.21 \text{ kJ/mol}.$

9.40 (a) $n_{\text{H}_2} = 8.14 \times 10^{-5} \text{ mol}$, $n_{\text{H}_2\text{O}} = 5.55 \text{ mol}$; $x_{\text{H}_2} =$
 1.47×10^{-5} . $K_{\text{H}_2} = P_{\text{H}_2}/x_{\text{H}_2} = (1.00 \text{ atm})/(1.47 \times 10^{-5}) =$
 $6.82 \times 10^4 \text{ atm}$. (b) $x_{\text{H}_2} = P_{\text{H}_2}/K_{\text{H}_2} =$
 $(10.00 \text{ atm})/(68200 \text{ atm}) = 1.47 \times 10^{-4}$. $n_{\text{H}_2} = 8.14 \times 10^{-4}$
 mol and $m_{\text{H}_2} = 1.64 \text{ mg}.$

9.41 $x_{\text{N}_2} = P_{\text{N}_2}/K_{\text{N}_2} = (0.780 \times 760 \text{ torr})/(5.75 \times 10^7 \text{ torr})$
 $= 1.03 \times 10^{-5}$, $x_{\text{O}_2} = (0.210 \times 760 \text{ torr})/(2.95 \times 10^7 \text{ torr})$
 $= 5.41 \times 10^{-6}$. n_{O_2} and n_{N_2} are negligible compared to $n_{\text{H}_2\text{O}}$
 $= 5.55 \text{ mol}$, so $n_{\text{N}_2} = (1.03 \times 10^{-5})(5.55 \text{ mol}) = 5.72 \times 10^{-5}$
 mol and $n_{\text{O}_2} = (5.41 \times 10^{-6})(5.55 \text{ mol}) = 3.00 \times 10^{-5} \text{ mol}.$
 $m_{\text{N}_2} = 1.60 \text{ mg}$ and $m_{\text{O}_2} = 0.960 \text{ mg}.$

9.42 $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$. The initial amount of N_2O_4 is 0.0109
 mol ; also, $n(\text{CHCl}_3) = 1.68 \text{ mol}$. At equilibrium, $n(\text{N}_2\text{O}_4) =$
 $0.0109 \text{ mol} - y$ and $n(\text{NO}_2) = 2y$. Since $n(\text{CHCl}_3) \gg 0.0109$

mol, we have $n_{\text{tot}} = 1.69$ mol. The equilibrium mole fractions are $x(\text{N}_2\text{O}_4) = 0.00645 - z$ and $x(\text{NO}_2) = 2z$, where $z = y/(1.69 \text{ mol})$. We have $K_x = 5 \times 10^{-7} = [x(\text{NO}_2)]^2/x(\text{N}_2\text{O}_4) = 4z^2/(0.00645 - z)$. Using the quadratic formula, we find $z = 2.8 \times 10^{-5}$, so $x(\text{N}_2\text{O}_4) = 0.00645 - z = 0.0064$ and $x(\text{NO}_2) = 2z = 5.6 \times 10^{-5}$.

9.43 $K_x = 480 = x_{\text{trans}}/x_{\text{cis}} = (n_{\text{trans}}/n_{\text{tot}})/(n_{\text{cis}}/n_{\text{tot}}) = n_{\text{trans}}/n_{\text{cis}}$, so $n_{\text{trans}} = 480n_{\text{cis}}$. $n_{\text{trans}}/(n_{\text{cis}} + n_{\text{trans}}) = 480n_{\text{cis}}/(n_{\text{cis}} + 480n_{\text{cis}}) = 480/481 = 0.99792$. We have 99.792% trans and 0.208% cis.

9.44 Equations (9.30), (9.28), and (9.64) give: $\bar{S}_i = -(\partial\mu_i/\partial T)_{P,n_j} = -(\partial/\partial T)_{P,n_j}(\mu_i^\circ + RT \ln x_i) = \bar{S}_i^\circ - R \ln x_i$. The infinite-dilution limit of this equation gives

$$\bar{S}_i^\circ = (\bar{S}_i + R \ln x_i)^\infty. \quad \bar{H}_i = \bar{G}_i + T\bar{S}_i = \mu_i^\circ + RT \ln x_i + T\bar{S}_i^\circ - RT \ln x_i = \bar{H}_i^\circ. \quad \text{The infinite-dilution limit of this equation gives } \bar{H}_i^\infty = \bar{H}_i^\circ.$$

9.45 Equations (9.17), (9.73) and (9.72) give $\Delta V_{\text{mix}} = \sum_{i \neq A} n_i(\bar{V}_i - \bar{V}_i^*) + n_A(\bar{V}_A - \bar{V}_A^*) = \sum_{i \neq A} n_i(\bar{V}_i^\circ - \bar{V}_i^*)$. Equations (9.74) and (9.72) give $\Delta H_{\text{mix}} = \sum_{i \neq A} n_i(\bar{H}_i - \bar{H}_i^*) + n_A(\bar{H}_A - \bar{H}_A^*) = \sum_{i \neq A} n_i(\bar{H}_i^\circ - \bar{H}_i^*)$.

9.46 $\ln K_x = -\Delta G^\circ/RT$. (a) $(\partial \ln K_x/\partial T)_P = \Delta G^\circ/RT^2 - (\partial \Delta G^\circ/\partial T)_P/RT = \Delta G^\circ/RT^2 - (-\Delta S^\circ)/RT = (\Delta G^\circ + T\Delta S^\circ)/RT^2 = \Delta H^\circ/RT^2$, since $(\partial \Delta G^\circ/\partial T)_P = (\partial/\partial T) \sum_i \nu_i \mu_i^\circ = \sum_i \nu_i (\partial \mu_i^\circ/\partial T)_P = -\sum_i \nu_i \bar{S}_i^\circ = -\Delta S^\circ$. (b) $(\partial \ln K_x/\partial P)_T =$

$$-(\partial \Delta G^\circ / \partial P)_T / RT = -\Delta V^\circ / RT, \text{ since } (\partial \Delta G^\circ / \partial P)_T =$$

$$\sum_i \nu_i (\partial \mu_i^\circ / \partial P)_T = \sum_i \nu_i \bar{V}_i^\circ = \Delta V^\circ.$$

9.47 (a) $x_i = P_i / K_i$, so as K_i increases, x_i decreases. The solubility of O_2 in water decreases as T increases. (b)

$$(\bar{H}_{i,\text{vap}}^\circ - \bar{H}_i^\circ) / RT^2 = (\partial \ln K_i / \partial T)_P \approx (\Delta \ln K_i / \Delta T)_P.$$

$$\Delta \ln K_i = \ln (3.52 \times 10^7) - \ln (2.95 \times 10^7) = 0.177.$$

$$\bar{H}_i^\circ - \bar{H}_{i,\text{vap}}^\circ \approx -(8.314 \text{ J/mol-K})(298 \text{ K})^2 0.177 / (10 \text{ K}) =$$

$$-13.1 \text{ kJ/mol. (c) The log of (9.68) gives } RT \ln K_i / \text{bar}$$

$$= \mu_i^\circ - \mu_{i,\text{vap}}^\circ = \bar{G}_i^\circ - \bar{G}_{i,\text{vap}}^\circ, \text{ and we have } \bar{G}_i^\circ - \bar{G}_{i,\text{vap}}^\circ \approx$$

$$(8.314 \text{ J/mol-K})(298 \text{ K}) \ln (44100 \text{ bar/1 bar}) =$$

$$26.5 \text{ kJ/mol. (d) } \Delta S = (\Delta H - \Delta G) / T, \text{ so } \bar{S}_i^\circ - \bar{S}_{i,\text{vap}}^\circ \approx$$

$$[(-13100 - 26500) / 298] \text{ J/mol-K} = -133 \text{ J/mol-K}.$$

9.48 The log of Eq. (9.68) reads $\ln K_i = \ln P^\circ +$

$$(\mu_i^\circ - \mu_{i,\text{vap}}^\circ) / RT. \text{ Partial differentiation with respect to}$$

$$T \text{ gives } (\partial \ln K_i / \partial T)_P = -(\mu_i^\circ - \mu_{i,\text{vap}}^\circ) / RT^2 +$$

$$[(\partial \mu_i^\circ / \partial T)_P - d\mu_{i,\text{vap}}^\circ / dT] / RT = (\bar{G}_{i,\text{vap}}^\circ - \bar{G}_i^\circ) / RT^2 +$$

$$(-\bar{S}_i^\circ + \bar{S}_{i,\text{vap}}^\circ) / RT = (\bar{G}_{i,\text{vap}}^\circ + T\bar{S}_{i,\text{vap}}^\circ - \bar{G}_i^\circ - T\bar{S}_i^\circ) / RT^2 =$$

$$(\bar{H}_{i,\text{vap}}^\circ - \bar{H}_i^\circ) / RT^2 = (\bar{H}_{i,\text{vap}}^\circ - \bar{H}_i^\infty) / RT^2. \text{ Partial differen-}$$

$$\text{tiation of } \ln K_i \text{ with respect to } P \text{ gives } (\partial \ln K_i / \partial P)_T =$$

$$(\partial \mu_i^\circ / \partial P)_T / RT = \bar{V}_i^\circ / RT = \bar{V}_i^\infty / RT \text{ (since } \mu_{i,\text{vap}}^\circ \text{ depends only}$$

on T).

9.49 The phase-equilibrium condition $\mu_i^\alpha = \mu_i^\beta$ and (9.64)

$$\text{give } \mu_i^{\circ,\alpha} + RT \ln x_i^\alpha = \mu_i^{\circ,\beta} + RT \ln x_i^\beta \text{ and } \ln (x_i^\alpha / x_i^\beta) =$$

$$(\mu_i^{\circ,\beta} - \mu_i^{\circ,\alpha}) / RT. \text{ Hence } x_i^\alpha / x_i^\beta = \exp [(\mu_i^{\circ,\beta} - \mu_i^{\circ,\alpha}) / RT] \equiv$$

$N(T, P)$. (b) Equation (9.68) gives $K_1^{\beta}/K_1^{\alpha} = \exp [(\mu_1^{\circ, \beta} - \mu_{1, \text{vap}}^{\circ})/RT] \div \exp [(\mu_1^{\circ, \alpha} - \mu_{1, \text{vap}}^{\circ})/RT] = \exp [(\mu_1^{\circ, \beta} - \mu_1^{\circ, \alpha})/RT] = N(T, P)$. (c) $N = 30.3/0.068 = 446$.

9.50 Trouton's rule is $\Delta \bar{H}_{\text{vap}}/T_b \approx 21 \text{ cal/mol-K}$. We find the following heats of vaporization: $\Delta \bar{H}_{\text{ben}} \approx 7420 \text{ cal/mol}$, $\Delta \bar{H}_{\text{tol}} \approx 8060 \text{ cal/mol}$. Equation (7.21) gives for the vapor pressure of pure benzene at 120°C : $\ln [P_{\text{ben}}^*/(1 \text{ atm})] = (7420 \text{ cal/mol})(1/353.2 \text{ K} - 1/393.1 \text{ K})/(1.987 \text{ cal/mol-K}) = 1.073$ and $P_{\text{ben}}^* = 2.92 \text{ atm}$. Similarly, we find $P_{\text{tol}}^* = 1.29 \text{ atm}$, $P_{\text{ben}} = x_{\text{ben}} P_{\text{ben}}^* = 0.68(2.92 \text{ atm}) = 1.99 \text{ atm}$, $P_{\text{tol}} = 0.32(1.29 \text{ atm}) = 0.41 \text{ atm}$, $P = 2.40 \text{ atm}$, $x_{\text{vap, ben}} = P_{\text{ben}}/P = (1.99 \text{ atm})/(2.40 \text{ atm}) = 0.83$. We assumed the accuracy of Trouton's rule, the T independence of ΔH of vaporization, ideal gases, an ideal solution, and the pressure independence of μ^* .

9.51 $\Delta G_{\text{mix}} = G - G^* = G - n_A \mu_A^* - n_B \mu_B^*$. Then $\mu_A = (\partial G / \partial n_A)_{T, P, n_B} = (\partial / \partial n_A)_{T, P, n_B} (n_A \mu_A^* + n_B \mu_B^* + \Delta G_{\text{mix}}) = \mu_A^* + RT \ln x_A + n_A RT (\partial \ln x_A / \partial n_A)_{n_B} + n_B RT (\partial \ln x_B / \partial n_A)_{n_B} = \mu_A^* + RT \ln x_A + n_A RT [1/n_A - 1/(n_A + n_B)] + n_B RT [-1/(n_A + n_B)] = \mu_A^* + RT \ln x_A + RT - x_A RT - x_B RT = \mu_A^* + RT \ln x_A$, since $x_A + x_B = 1$. (The partial derivatives of the logs are found as in Prob. 9.54b.)

9.52 (a) Use of $(\partial G / \partial P)_T = V$ gives $\Delta G_1 = \int_P^{P_A^*} V_A^* dP' + \int_P^{P_B^*} V_B^* dP'$. We have $\Delta G_2 = 0$ for this constant- T -and- P equilibrium process. $\Delta G_3 = \Delta H_3 - T \Delta S_3 = -T \Delta S_3 =$

$-n_A RT \ln (P_A^*/P_A) - n_B RT \ln (P_B^*/P_B)$, where (3.29) and Boyle's law were used. $\Delta G_4 = 0$ (see the end of Sec. 6.1). $\Delta G_5 = 0$ (constant-T-and-P equilibrium process). $\Delta G_6 = \int_{P_{A+B}}^P V_{A+B} dP'$. (b) They are small because G of a liquid varies only slowly with P . (c) With ΔG_1 and ΔG_6 neglected, $\Delta G \equiv \Delta G_{\text{mix}} \approx \Delta G_3 = n_A RT \ln (P_A/P_A^*) + n_B RT \ln (P_B/P_B^*)$. (d) Use (9.51).

9.53 Equation (9.82) becomes $\Delta G_{\text{mix}}/(n_A + n_B) = RT[x_A \ln(x_{A,v} P/P_A^*) + x_B \ln(x_{B,v} P/P_B^*)]$. At $x_{\text{eth}} = 0.200$, $\Delta G_{\text{mix}}/(n_A + n_B) = (8.314 \text{ J/mol-K})(318 \text{ K}) \times \{0.200 \ln[(0.1552)454.53/172.76] +$

$0.800 \ln[(1 - 0.1552)454.53/433.54]\} = -731 \text{ J/mol}$. At $x_{\text{eth}} = 0.400, 0.600, 0.800$, we get $\Delta G_{\text{mix}}/n_{\text{tot}} = -1034 \text{ J/mol}, -1154 \text{ J/mol}, -997 \text{ J/mol}$, respectively. At $x_{\text{eth}} = 0$ and 1, $\Delta G_{\text{mix}}/n_{\text{tot}} = 0$.

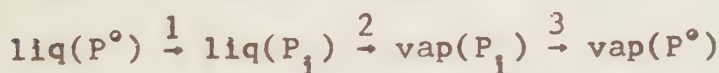
9.54 (a) From (9.35), $\Delta S_{\text{mix}} = -(\partial \Delta G_{\text{mix}}/\partial T)_{P, n_j} = -n_A R \ln x_A - n_B R \ln x_B - (n_A + n_B)x_A x_B (\partial W/\partial T)_P$. From (9.33), $\Delta H_{\text{mix}} = \Delta G_{\text{mix}} + T \Delta S_{\text{mix}} = (n_A + n_B)x_A x_B [W - T(\partial W/\partial T)_P]$. From (9.34), $\Delta V_{\text{mix}} = (\partial \Delta G_{\text{mix}}/\partial P)_{T, n_j} = (n_A + n_B)x_A x_B (\partial W/\partial P)_T$. (b) $\Delta G_{\text{mix}} = G - G^*$, so $G = G^* + \Delta G_{\text{mix}} = n_A u_A^*(T, P) + n_B u_B^*(T, P) + \Delta G_{\text{mix}}$. Then $u_A = (\partial G/\partial n_A)_{T, P, n_B} = u_A^* + (\partial \Delta G_{\text{mix}}/\partial n_A)_{T, P, n_B}$. We have $\ln x_A = \ln n_A - \ln(n_A + n_B)$ and $\ln x_B = \ln n_B - \ln(n_A + n_B)$, so $\partial \ln x_A/\partial n_A = 1/n_A - 1/(n_A + n_B)$ and $\partial \ln x_B/\partial n_A = -1/(n_A + n_B)$. Also, $x_A x_B (n_A + n_B) = n_A n_B/(n_A + n_B)$. Using these equations, we find $\mu_A = \mu_A^* + RT \ln x_A +$

$$n_A RT [1/n_A - 1/(n_A + n_B)] - n_B RT / (n_A + n_B) + W(T, P) \times [n_B / (n_A + n_B) - n_A n_B / (n_A + n_B)^2] = \mu_A^* + RT \ln x_A + W(T, P) x_B^2.$$

Since ΔG_{mix} is symmetric in A and B, by analogy to μ_A we have $\mu_B = \mu_B^* + RT \ln x_B + W(T, P) x_A^2$. (c) Equating μ_A in the solution to μ_A in the vapor above the solution, we get $\mu_A^* + RT \ln x_A + W x_B^2 = \mu_{A, \text{gas}}^\circ + RT \ln (P_A / P^\circ)$. Also, for pure liquid A in equilibrium with its vapor at T:

$\mu_A^* = \mu_{A, \text{gas}}^\circ + RT \ln (P_A^* / P^\circ)$. Subtraction of this equation from the preceding one gives $RT \ln x_A + W x_B^2 = RT \ln (P_A / P_A^*)$, so $\ln (P_A / P_A^*) = \ln x_A + W x_B^2 / RT$, $P_A / P_A^* = \exp(\ln x_A) \exp(W x_B^2 / RT)$, and $P_A = x_A P_A^* \exp(W x_B^2 / RT)$. By symmetry, $P_B = x_B P_B^* \exp(W x_A^2 / RT)$.

9.55 $\Delta G_{\text{vap}}^\circ$ involves isothermal conversion of liquid at 1 bar to vapor at 1 bar. We use this isothermal path:



$\Delta G_1 \approx 0$, since moderate pressure changes have little effect on liquid thermodynamic properties. $\Delta G_2 = 0$, since this is an equilibrium process at constant T and P.

Assuming ideal vapor, we have $\Delta G_3 = \Delta H_3 - T \Delta S_3 = -T \Delta S_3 = -nRT \ln (P_1 / P^\circ)$, where (3.29) and Boyle's law were used. Therefore $\Delta G_{\text{vap}}^\circ = \Delta \bar{G}_1 + \Delta \bar{G}_2 + \Delta \bar{G}_3 = -RT \ln (P_1 / P^\circ)$ and $P_1 = P^\circ \exp(-\Delta G_{\text{vap}}^\circ / RT)$.

9.56 (a) $\bar{U}_1, \bar{H}_1, \bar{V}_1$. (b) $\bar{U}_A, \bar{H}_A, \bar{V}_A$. (c) None.

9.57 (a) All; (b) ideal; (c) ideal and ideally dilute; (d) all; (e) ideal; (f) ideal; (g) ideal.

9.58 (a) True, since the equilibrium condition at constant T and P is minimization of G. (b) False; as noted in Sec. 9.2, ΔS_{mix} is occasionally negative. (c) False. In a liquid solution, intermolecular interactions are large. (d) True. (e) False.

CHAPTER 10

10.1 (a) No. (b) Yes. (c) Yes. $\gamma_i = a_i/x_i$ and a_i in (10.3) depends on μ_i° . (d) Yes.

10.2 (a) $\gamma_{I,i} = x_{i,vap} P/x_i P_i^*$. $\gamma_{I,chl} = (1 - 0.138)(304.2 \text{ torr})/(1 - 0.200)(295.1 \text{ torr}) = 1.11$.

$\gamma_{I,eth} = 0.138(304.2 \text{ torr})/0.200(102.8 \text{ torr}) = 2.04$.

$a_{I,chl} = \gamma_{I,chl} x_{chl} = 1.11(0.800) = 0.889$; $a_{I,eth} = 2.04(0.200) = 0.408$. (b) $\mu_i = \mu_i^\circ + RT \ln a_i = \mu_i^* + RT \ln a_{I,i}$, so $\mu_i - \mu_i^* = RT \ln a_{I,i}$. $\mu_{eth} - \mu_{eth}^* = (8.3145 \text{ J/mol-K})(308.1 \text{ K}) \ln 0.408 = -2300 \text{ J/mol}$. $\mu_{chl} - \mu_{chl}^* = RT \ln 0.889 = -301 \text{ J/mol}$. (c) Eqs. (9.32), (10.7), and (10.4) give $\Delta G_{mix} = \sum_i n_i (\mu_i - \mu_i^*) = \sum_i n_i RT \ln a_{I,i} = (8.3145 \text{ J/mol-K})(308.1 \text{ K})[(0.200 \text{ mol}) \ln 0.408 +$

$(0.800 \text{ mol}) \ln 0.889] = -700 \text{ J/mol}$. Alternatively,

$\Delta G_{mix} = (0.200 \text{ mol})(-2300 \text{ J/mol}) + (0.800 \text{ mol})(-301 \text{ J/mol}) = -701 \text{ J}$. (d) For an ideal solution, $\gamma_{I,i} = 1$ and

$a_{I,i} = x_i$, so $\Delta G_{mix} = (8.3145 \text{ J/mol-K})(308.1 \text{ K}) \times [(0.200 \text{ mol}) \ln 0.200 + (0.800 \text{ mol}) \ln 0.800] = -1280 \text{ J}$.

10.3 (a) $a_{I,i} = P_i/P_i^* = x_{i,vap} P/P_i^*$. $a_{I,ben} = 0.363(1.68 \text{ atm})/(2.98 \text{ atm}) = 0.205$. $\gamma_{I,ben} = a_{I,ben}/x_{ben} = 0.205/0.262 = 0.781$. $a_{I,tol} = (1 - 0.363)(1.68 \text{ atm})/(1.34 \text{ atm}) = 0.799$; $\gamma_{I,tol} = 0.799/(1 - 0.262) = 1.08$.

(b) Since toluene is the solvent, $\gamma_{II,tol} = \gamma_{I,tol} = 1.08$. The p. 268 example gives $\gamma_{II,ben} = (P_{ben}^*/K_{ben})\gamma_{I,ben}$,

where $K_{\text{ben}} = (P_{\text{ben}}/x_{\text{ben}})^{\infty}$. We plot $x_{\text{ben,vap}}^{P/x_{\text{ben,liq}}}$ and extrapolate to $x_{\text{ben,liq}} = 0$; we find $K_{\text{ben}} = 2.1_2$ atm. So $\gamma_{\text{II,ben}} = (2.98 \text{ atm}/2.1_2 \text{ atm})0.78_1 = 1.1_0$. $a_{\text{II,ben}} = 1.1_0(0.262) = 0.28_8$. $a_{\text{II,tol}} = a_{\text{I,tol}} = 0.799$. (c) We have $\Delta G_{\text{mix}} = G - G^* = \sum_i n_i(\mu_i - \mu_i^*) = \sum_i n_i(\mu_i - \mu_{\text{I},i}^{\circ}) = \sum_i n_i RT \ln a_{\text{I},i}$. An amount of solution with $n_{\text{tot}} = 1$ mol has 0.262 mol of benzene and 0.738 mol of toluene, which is 20.4₇ g of benzene and 68.0₀ g of toluene. The benzene wt. % is $[20.4_7/(20.4_7 + 68.0_0)]100\% = 23.1_4\%$; so 125 g of solution has 0.231₄(125 g) = 28.9 g of benzene and 96.1 g of toluene; thus $n_{\text{ben}} = 0.370$ mol and $n_{\text{tol}} = 1.04$ mol. Then $\Delta G_{\text{mix}} = (8.314 \text{ J/mol-K})(393 \text{ K}) \times [(0.370 \text{ mol}) \ln 0.205 + (1.04 \text{ mol}) \ln 0.799] = -2.68 \text{ kJ}$.

10.4 (a) Let $b = 3.92$. Equation (10.21) with $B = \text{Hg}$ and $A = \text{Zn}$ and state 1 being pure Hg gives $\ln \gamma_{\text{Hg}} = -\int_1^2 [x_{\text{Zn}}/(1 - x_{\text{Zn}})] d \ln (1 - bx_{\text{Zn}}) =$

$$b \int_0^{x_{\text{Zn}}} [x/(1 - x)(1 - bx)] dx =$$

$$[b/(1 - b)][-\ln(1 - x) + b^{-1} \ln(1 - bx)]_0^{x_{\text{Zn}}} =$$

$$[b/(b - 1)] \ln(1 - x_{\text{Zn}}) - [1/(b - 1)] \ln(1 - bx_{\text{Zn}}) = (3.92/2.92) \ln(1 - x_{\text{Zn}}) - (1/2.92) \ln(1 - 3.92x_{\text{Zn}}).$$

$$(b) \gamma_{\text{II,Zn}} = 1 - 3.92(0.0400) = 0.843; a_{\text{II,Zn}} = \gamma_{\text{II,Zn}} x_{\text{Zn}} = (.843)(.0400) = 0.0337. \ln \gamma_{\text{Hg}} = (1/2.92)\{3.92 \ln 0.960 - \ln [1 - (3.92)(0.0400)]\} = 0.00360; \gamma_{\text{Hg}} = 1.0036.$$

$$a_{\text{Hg}} = 1.0036(0.9600) = 0.9635.$$

10.5 (a) $\mu_1 = \mu_1^* + RT \ln \gamma_{I,1} x_1 = \mu_1^* + RT \ln x_1 + RT \ln \exp(bx_2^2) = \mu_1^* + RT \ln x_1 + bRTx_2^2$. (b) Let the components 1 and 2 be called A and B, respectively (to avoid confusion with states 1 and 2). We use Eq. (10.21) written for Convention I. We choose state 1 as pure B, so $\gamma_{I,B,1} = 1$. From part (a), $\ln \gamma_{I,A} = bx_B^2$, and we have $\ln \gamma_{I,B,2} = -\int_1^2 [x_A/(1 - x_A)] 2bx_B dx_B = -2b \int_1^{x_B,2} (1 - x_B) dx_B = -2b[(x_{B,2} - \frac{1}{2}x_{B,2}^2) - 1 + \frac{1}{2}] = bx_A^2$, where $x_B = 1 - x_A$ was used. Dropping the superfluous subscript 2, we have $\ln \gamma_{I,B} = bx_A^2$ and $\gamma_{I,B} = \exp(bx_A^2)$. (c) In the limit $x_{chl} = 0$ and $x_{ac} = 1$, Fig. 10.2 gives $\gamma_{I,chl} = 0.50$. Hence $0.50 = e^b$ and $b = \ln 0.50 = -0.693$. For $x_{chl} = 0.494$, the simple-solution model gives $\gamma_{ac} = e^{-0.693(0.494)^2} = 0.844$, and $\gamma_{chl} = e^{-0.693(0.506)^2} = 0.837$; the true values are 0.824 and 0.772.

10.6 As noted after Eq. (10.11), $G^E = RT \sum_i n_i \ln \gamma_{I,i}$. So $G^E/n = RT \sum_i x_i \ln \gamma_{I,i} = RT(x_{ac} \ln \gamma_{I,ac} + x_{chl} \ln \gamma_{I,chl})$. Values of γ_I listed in Sec. 10.2 give at 35.2°C:

x_{ac}	0	0.082	0.200	0.336	0.506	0.709	
G^E/n_{tot}	0	-42.8	-96.1	-133.1	-138.3	-102.6	cal/mol
x_{ac}	0.815	0.940	1				
G^E/n_{tot}	-69.8	-24.7	0	cal/mol			

10.7 (a) In the second example in Sec. 10.2, it was shown that $\gamma_{II,i}/\gamma_{I,i} = P_i^*/K_i$ for $i \neq A$. In the infinite-dilu-

tion ($x_A \rightarrow 1$) limit, we have $\gamma_{II,i} \rightarrow 1$ [Eq. (10.10)] and $\gamma_{I,i} \rightarrow \gamma_{I,i}^\infty$; in this limit, the boxed equation becomes $1/\gamma_{I,i}^\infty = P_i^*/K_i$. Equating the two expressions for P_i^*/K_i , we get $\gamma_{II,i} = \gamma_{I,i}/\gamma_{I,i}^\infty$. (b) From Fig. 10.2a, $\gamma_{I,chl} \rightarrow 0.50$ as $x_{ac} \rightarrow 1$. Therefore $\gamma_{II,chl} = 2.0\gamma_{I,chl}$ in acetone.

10.8 (a) Eq. (10.13) gives $P_{H_2O} = a_{H_2O}P_{H_2O}^*$ and $a_{H_2O} = (23.34 \text{ torr})/(23.76 \text{ torr}) = 0.9823$. (b) $a_{H_2O} = 22.75/23.76 = 0.9575$. An amount of solution with 1 kg of solvent has 2.00 mol of sucrose and 55.51 mol of H_2O , so $x_{H_2O} = 55.51/(55.51 + 2.00) = 0.9652$. Then $a_{H_2O} = \gamma_{H_2O}x_{H_2O} = 0.9575 = \gamma_{H_2O}(0.9652)$ and $\gamma_{H_2O} = 0.9920$.

10.9 For an amount of solution containing 1 kg of water, $n_{\text{sucrose}} = 1.50 \text{ mol}$ and $n_{H_2O} = 55.51 \text{ mol}$, so $x_{H_2O} = 55.51/57.01 = 0.9737$ and $x_{\text{suc}} = 0.0263$. From Eq. (10.23), $\gamma_{II,\text{suc}} = \gamma_{m,\text{suc}}/x_A = 1.292/0.9737 = 1.327$. Then $a_{II,\text{suc}} = \gamma_{II,\text{suc}}x_{\text{suc}} = 1.327(0.0263) = 0.0349$. Also, $a_{m,\text{suc}} = \gamma_{m,\text{suc}}(m_{\text{suc}}/m^\circ) = 1.292(1.50) = 1.94$.

10.10 Equations (9.31) and (10.23) give $\bar{V}_{m,i}^\circ = (\partial\mu_{m,i}^\circ/\partial P)_T = (\partial\mu_{II,i}^\circ/\partial P)_T = \bar{V}_{II,i}^\circ = \bar{V}_i^\infty$, where an equation on page 263 in the text was used. From (9.30) and (10.23), $\bar{S}_{m,i}^\circ = -(\partial\mu_{m,i}^\circ/\partial T)_P = -(\partial\mu_{II,i}^\circ/\partial T)_P - R \ln M_A^{m^\circ} = \bar{S}_{II,i}^\circ - R \ln M_A^{m^\circ} = (\bar{S}_i + R \ln x_i)^\infty - R \ln M_A^{m^\circ} = [\bar{S}_i + R \ln (x_i/M_A^{m^\circ})]^\infty$, where an equation on p. 263 was used. We have $x_i/M_A = n_i/n_{\text{tot}}M_A$; in the infinite-dilution limit, $n_{\text{tot}} = n_A$ and $x_i/M_A = n_i/n_A M_A = n_i/w_A$

$= m_1$, where w_A is the solvent mass and m_1 is the solute molality. Then $\bar{S}_{m,1}^\circ = [\bar{S}_1 + R \ln (m_1/m^\circ)]^\infty$. Finally, (9.28), (10.23), the above relation between $\bar{S}_{m,1}^\circ$ and $\bar{S}_{II,1}^\circ$, and the relation $\bar{H}_{II,1}^\circ = \bar{H}_1^\circ$ (p. 263) give $\bar{H}_{m,1}^\circ = \mu_{m,1}^\circ + T\bar{S}_{m,1}^\circ = \mu_{II,1}^\circ + RT \ln M_A m^\circ + T(\bar{S}_{II,1}^\circ - R \ln M_A m^\circ) = \mu_{II,1}^\circ + T\bar{S}_{II,1}^\circ = \bar{H}_{II,1}^\circ = \bar{H}_1^\circ$.

10.11 $\mu_{c,i}^\circ + RT \ln (\gamma_{c,i} c_i / c^\circ) = \mu_{II,i}^\circ + RT \ln \gamma_{II,i} x_i$.

In the limit $x_A \rightarrow 1$, Eqs. (10.29) and (10.10) show that the activity coefficients go to 1; so this limit gives

$\mu_{c,i}^\circ = \mu_{II,i}^\circ + RT \ln (x_i c^\circ / c_i)^\infty$. We have $x_i = n_i / n_{\text{tot}} \approx n_i / n_A$ and $c_i = n_i / V \approx n_i / V_A^*$ for x_A near 1. Hence, $(x_i c^\circ / c_i)^\infty = c^\circ n_i V_A^* / n_i n_A = c^\circ \bar{V}_A^*$, and $\mu_{c,i}^\circ = \mu_{II,i}^\circ + RT \ln \bar{V}_A^* c^\circ$. Substitution of this result in (10.28) gives

$\mu_i = \mu_{II,i}^\circ + RT \ln \bar{V}_A^* c^\circ + RT \ln (\gamma_{c,i} c_i / c^\circ) = \mu_{II,i}^\circ + RT \ln (\bar{V}_A^* \gamma_{c,i} c_i)$. Comparison with (10.22) shows that

$$\bar{V}_A^* \gamma_{c,i} c_i = \gamma_{II,i} x_i \text{ and } \gamma_{c,i} = (x_i / \bar{V}_A^* c_i) \gamma_{II,i}.$$

We have $x_i = n_i / n_{\text{tot}} = w_A n_i / w_A n_{\text{tot}} = w_A m_i / n_{\text{tot}} = \rho_A V_A^* m_i / n_{\text{tot}}$ (where w is mass) and $\bar{V}_A^* = V_A^* / n_A$, so $x_i / \bar{V}_A^* = \rho_A m_i n_A / n_{\text{tot}} = \rho_A m_i x_A$. Then $\gamma_{c,i} = (x_i / \bar{V}_A^* c_i) \gamma_{II,i} = (\rho_A m_i x_A / c_i) (\gamma_{m,i} / x_A) = (\rho_A m_i / c_i) \gamma_{m,i}$. Also, $\gamma_{c,i} c_i = \rho_A m_i \gamma_{m,i}$ and $(\gamma_{c,i} c_i / c^\circ) c^\circ = \rho_A (m_i \gamma_{m,i} / m^\circ) m^\circ$, so $a_{c,i} c^\circ = \rho_A a_{m,i} m^\circ$ and $a_{c,i} = (\rho_A m^\circ / c^\circ) a_{m,i}$.



(c) $\text{MgSO}_4 \rightarrow \text{Mg}^{2+} + \text{SO}_4^{2-}$; $v_+ = 1$, $v_- = 1$, $z_+ = 2$, $z_- = -2$.

(d) $\text{Ca}_3(\text{PO}_4)_2 \rightarrow 3\text{Ca}^{2+} + 2\text{PO}_4^{3-}$; $v_+ = 3$, $v_- = 2$, $z_+ = 2$,

$z_- = -3$. (e) For a 1:1 electrolyte, $z_+ = |z_-| = 1$. KCl

is a 1:1 electrolyte.

10.13 $\gamma_{\pm} = [(\gamma_+)^{v_+}(\gamma_-)^{v_-}]^{1/(v_+ + v_-)}$. (a) $\gamma_{\pm} = \gamma_+^{\frac{1}{2}}\gamma_-^{\frac{1}{2}}$.

(b) $\gamma_{\pm} = (\gamma_+)^{1/3}(\gamma_-)^{2/3}$. (c) $\gamma_{\pm} = \gamma_+^{\frac{1}{2}}\gamma_-^{\frac{1}{2}}$. (d) $\gamma_{\pm} = (\gamma_+)^{3/5}(\gamma_-)^{2/5}$.

10.14 $\mu_1 = v_+\mu_+ + v_-\mu_- = \mu_+ + 2\mu_-$.

10.15 $(v_{\pm})^v = (v_+)^{v_+}(v_-)^{v_-}$. (a) $(v_{\pm})^2 = 1^1 1^1$ and $v_{\pm} = 1$.

(b) $(v_{\pm})^3 = 1^1 2^2$ and $v_{\pm} = 1.587$. (c) $v_{\pm} = 1$. (d) $(v_{\pm})^5 = 3^3 2^2$ and $v_{\pm} = 2.551$.

10.16 With $v_+ = v_- = 1$, (10.53) is $\gamma_1 = \alpha^{\frac{1}{2}}[1 - (1 - \alpha)]^{\frac{1}{2}}\gamma_{\pm}$
 $= \alpha^{\frac{1}{2}}\alpha^{\frac{1}{2}}\gamma_{\pm} = \alpha\gamma_{\pm}$.

10.17 Substituting the m_+ and m_- expressions preceding (10.52) into (10.46) and using (1.68), we find $\mu_1 = \mu_1^{\circ} + RT \ln \{(\gamma_{\pm})^v (\alpha v_+ m_1 / m^{\circ})^{v_+} [v_- - (1 - \alpha)v_+]^{v_-} (m_1 / m^{\circ})^{v_-}\} = \mu_1^{\circ} + RT \ln \{(\gamma_{\pm})^v \alpha^{v_+} (m_1 / m^{\circ})^{v_+ + v_-} (v_+)^{v_+} (v_-)^{v_-} \times [1 - (1 - \alpha)v_+ / v_-]^{v_-}\} = \mu_1^{\circ} + vRT \ln \{\gamma_{\pm} \alpha^{v_+ / v} (v_+)^{v_+ / v} (v_-)^{v_- / v} [1 - (1 - \alpha)v_+ / v_-]^{v_- / v} m_1 / m^{\circ}\} = \mu_1^{\circ} + vRT \ln \{v_{\pm} \gamma_{\pm} \alpha^{v_+ / v} [1 - (1 - \alpha)v_+ / v_-]^{v_- / v} m_1 / m^{\circ}\},$
 which is (10.53) and (10.52).

10.18 From the m_+ and m_- equations preceding (10.52) and

from $m_+^\infty = v_+ m_1$ and $m_-^\infty = v_- m_1$, we have $m_+/m_+^\infty = \alpha$ and $m_-/m_-^\infty = 1 - (1 - \alpha)v_+/v_-$. Then $(m_+/m_+^\infty)^{v_+/v_-} (m_-/m_-^\infty)^{v_-/v_+} \gamma_\pm = \alpha^{v_+/v_-} [1 - (1 - \alpha)v_+/v_-]^{v_-/v_+} \gamma_\pm$, which equals γ_1 [Eq. (10.53)].

10.19 Use of the reaction-equilibrium condition $\mu_{IP} = \mu_+ + \mu_-$, Eq. (10.36), and Eq. (10.38) gives $G = n_A \mu_A + (v_+ n_1 - n_{IP}) \mu_+ + (v_- n_1 - n_{IP}) \mu_- + n_{IP} (\mu_+ + \mu_-) = n_A \mu_A + (v_+ \mu_+ + v_- \mu_-) n_1 = n_A \mu_A + n_1 \mu_1$.

10.20 (a) Equation (10.58) gives

$$\phi = \frac{1}{(0.018015 \text{ kg/mol})^2 (4.800 \text{ mol/kg})} \ln \frac{23.76 \text{ torr}}{20.02 \text{ torr}} = 0.990$$

(b) From Eq. (10.56), $a_A = P_A/P_A^* = (20.02 \text{ torr})/(23.76 \text{ torr}) = 0.843$. One kg of water contains 55.51 mol of H_2O .

There is no significant ion pairing in the KCl solution, so $x_A = 55.51/(55.51 + 4.80 + 4.80) = 0.853$. Equation (10.5) gives $\gamma_A = a_A/x_A = 0.843/0.853 = 0.988$.

(c) $a_A = 0.843$. $x_A = 55.51/(55.51 + 4.80) = 0.920$. $\gamma_A = 0.843/0.920 = 0.916$.

10.21 (a) $\ln \gamma_m = am/m^\circ + b(m/m^\circ)^2 + c(m/m^\circ)^3 + d(m/m^\circ)^4 + \int_0^m (a/m^\circ + bm'/m^{\circ 2} + cm'^2/m^{\circ 3} + dm'/m^{\circ 4}) dm' = 2am/m^\circ + (3/2)b(m/m^\circ)^2 + (4/3)c(m/m^\circ)^3 + (5/4)d(m/m^\circ)^4$. (b) Substitution of $m/m^\circ = 6.00$ gives $\log \gamma_m = 0.45415$ and $\gamma_m = 2.85$. One kg of H_2O has 55.51 mol H_2O , and $x(H_2O) = 55.51/(55.51 + 6.00) = 0.9025$. Equation (10.23) gives

$$\gamma_{II,i} = \gamma_{m,i}/x_A = 2.85/0.9025 = 3.16.$$

10.22 (a) At constant T and P, $0 = n_A d\mu_A + n_i d\mu_i = n_A(-\phi RTM_A v dm_i - RTM_A v m_i d\phi) + n_i[(vRT/m_i) dm_i + vRT d \ln \gamma_i]$ and $0 = (n_i/m_i - \phi n_A M_A) dm_i - n_A M_A m_i d\phi + n_i d \ln \gamma_i$. We have $m_i = n_i/n_A M_A$. Substitution of $n_A M_A = n_i/m_i$ into the preceding equation and division by n_i gives $d \ln \gamma_i = d\phi + [(\phi - 1)/m_i] dm_i$ at constant T and P.

(b) $\phi = (u_A^* - \mu_A)/RTM_A v m_i = -RT \ln \gamma_{x,A} x_A / RTM_A v m_i = -\ln (\gamma_{x,A} x_A) / M_A v m_i$. At high dilution, $\gamma_{x,A} \rightarrow 1$ and $\ln (\gamma_{x,A} x_A) \rightarrow \ln x_A$. Equation (8.30) gives for x_A near 1: $\ln x_A \approx x_A - 1$. At high dilution, there is no ion pairing

and the electrolyte gives $v n_i$ moles of ions. Hence $x_A = 1 - v n_i / n_{\text{tot}} \approx 1 - v n_i / n_A$. We have $\ln x_A \approx -v n_i / n_A$ and $\phi \rightarrow (v n_i / n_A) / M_A v (n_i / n_A M_A) = 1$. (c) Integration from the infinite-dilution state (where $\gamma_i = 1$ and $\phi = 1$) to a solution with molality m gives $\ln \gamma_i(m) = \phi(m) - 1 + \int_0^m [(\phi - 1)/m_i] dm_i$.

10.23 $m(\text{Cl}^-) = [0.0100 + 2(0.0050)] \text{mol} / (0.100 \text{ kg}) = 0.200 \text{ mol/kg}$. $m(\text{K}^+) = 0.100 \text{ mol/kg}$. $m(\text{Mg}^{2+}) = 0.070 \text{ mol/kg}$. $m(\text{SO}_4^{2-}) = 0.020 \text{ mol/kg}$. $I_m = \frac{1}{2} \sum_i z_i^2 m_i = \frac{1}{2}[0.200 + 0.100 + 2^2(0.070) + (-2)^2 0.020] \text{ mol/kg} = 0.330 \text{ mol/kg}$.

10.24 For the electrolyte $M_{v_+} X_{v_-}$ with stoichiometric molality m_i and no ion pairing, we have $m_+ = v_+ m_i$ and $m_- =$

v_{-m_i} . Hence $I_m = \frac{1}{2}(z_+^2 v_{+m_i} + z_-^2 v_{-m_i}) = \frac{1}{2}m_i(v_+ z_+^2 + v_- z_-^2) = \frac{1}{2}z_+ |z_-| (v_+ + v_-)m_i = \frac{1}{2}z_+ |z_-| v m_i$, where (10.65) and (10.45) were used.

10.25 (a) With ion pairing neglected, $I_m = \frac{1}{2}[2^2(0.01 \text{ mol/kg}) + 2^2(0.01 \text{ mol/kg})] = 0.04 \text{ mol/kg}$. Then $\log \gamma_{\pm} = -0.510(2)2[(0.04)^{\frac{1}{2}}/[1 + (0.04)^{\frac{1}{2}}] - 0.30(0.04)] = -0.31_6$; $\gamma_{\pm} = 0.48$. (b) (b) $I_m = \frac{1}{2}[2^2(0.01) + 2^2(0.01) + 2^2(0.01) + 1^2(0.02) + 3^2(0.01) + 1^2(0.03)] \text{ mol/kg} = 0.13 \text{ mol/kg}$. $\log \gamma_{\pm} = -0.510(2)2[(0.13)^{\frac{1}{2}}/[1 + (0.13)^{\frac{1}{2}}] - 0.30(0.13)] = -0.46_1$; $\gamma_{\pm} = 0.35$.

10.26 From (10.61), we have at 25°C: $C_{\text{CH}_3\text{OH}}/C_{\text{H}_2\text{O}} = (\rho_{\text{CH}_3\text{OH}}/\rho_{\text{H}_2\text{O}})^{\frac{1}{2}}(\epsilon_{r,\text{H}_2\text{O}}/\epsilon_{r,\text{CH}_3\text{OH}})^{3/2} = (0.787/0.997)^{\frac{1}{2}} \times (78.4/32.6)^{3/2} = 3.31$ and $B_{\text{CH}_3\text{OH}}/B_{\text{H}_2\text{O}} = (0.787/0.997)^{\frac{1}{2}} \times (78.4/32.6)^{\frac{1}{2}} = 1.37_8$, where data following (10.66) were used. Using the $C_{\text{H}_2\text{O}}$ and $B_{\text{H}_2\text{O}}$ values after (10.66), we get $C_{\text{CH}_3\text{OH}} = 3.89 \text{ (kg/mol)}^{\frac{1}{2}}$ and $B_{\text{CH}_3\text{OH}} = 4.52 \times 10^9 \text{ (kg/mol)}^{\frac{1}{2}} \text{ m}^{-1}$. Substitution in (10.66) gives for CH_3OH at 25°C: $\ln \gamma_{\pm} = -3.89z_+ |z_-| (I_m/\text{m}^\circ)^{\frac{1}{2}}/[1 + 0.452(a/\text{\AA})(I_m/\text{m}^\circ)^{\frac{1}{2}}]$ Substitution of $I_m/\text{m}^\circ = 0.0200$ and $a/\text{\AA} = 3$ gives $\ln \gamma_{\pm} = -0.462$ and $\gamma_{\pm} = 0.630$.

10.27 (a) $m(\text{Pb}^{2+}) = 0.100 \text{ mol/kg} - 0.43(0.100 \text{ mol/kg}) = 0.057 \text{ mol/kg}$; $m(\text{NO}_3^-) = 0.200 \text{ mol/kg} - 0.043 \text{ mol/kg} = 0.157 \text{ mol/kg}$; $m(\text{PbNO}_3^+) = 0.043 \text{ mol/kg}$. $I_m = \frac{1}{2}[4(0.057) + 1(0.157) + 1(0.043)] \text{ mol/kg} = 0.214$. (b) $\log \gamma_{\pm} = -0.257$

and $\gamma_{\pm} = 0.553$. Equation (10.53) gives

$$\gamma_i = (0.57)^{1/3} [1 - 0.43(1/2)]^{2/3} 0.553 = 0.390.$$

10.28 (a) In Eq. (10.76), $\gamma_{m,i,sat}$ and $m_{i,sat}$ are for $P = P^\circ = 1$ bar. Since the solution is very dilute and nonionic, we can approximate $\gamma_{m,i,sat}$ as 1 and (10.76) gives

$$\Delta G_{f,298}^\circ [O_2(aq)] = 0 - RT \ln 0.00115 = 16.8 \text{ kJ/mol. (b) } x_i = P_i/K_i = (1 \text{ bar})/(30300 \text{ bar}) = 3.30 \times 10^{-5} = n_i/n_{tot} \approx n_i/n_{H_2O} \text{ and } n_{C_2H_6} = n_{H_2O}(3.30 \times 10^{-5}) = (55.51 \text{ mol}) \times (3.30 \times 10^{-5}) = 0.00183 \text{ mol in 1000 kg of water, so } m_{C_2H_6} = 0.00183 \text{ mol/kg. Then (10.76) gives } \Delta G_{f,298}^\circ [C_2H_6(aq)] = -32.82 \text{ kJ/mol} - RT \ln (0.00183) = -17.2 \text{ kJ/mol.}$$

10.29 Use of Eq. (10.24) for μ_i gives the following results. $\bar{S}_i = -(\partial \mu_i / \partial T)_{P,n_j} = -(\partial \mu_{m,i}^\circ / \partial T)_P - (\partial / \partial T)_{P,n_j} [RT \ln (\gamma_{m,i} m_i / m^\circ)] = \bar{S}_{m,i}^\circ - R \ln (\gamma_{m,i} m_i / m^\circ) - RT (\partial \ln \gamma_{m,i} / \partial T)_{P,n_j}$. $\bar{V}_i = (\partial \mu_i / \partial P)_{T,n_j} = (\partial \mu_{m,i}^\circ / \partial P)_{T,n_j} + RT (\partial \ln \gamma_{m,i} / \partial P)_{T,n_j} = \bar{V}_{m,i}^\circ + RT (\partial \ln \gamma_{m,i} / \partial P)_{T,n_j}$. $\bar{H}_i = \mu_i + T\bar{S}_i = \mu_{m,i}^\circ + T\bar{S}_{m,i}^\circ - RT^2 (\partial \ln \gamma_{m,i} / \partial T)_{P,n_j} = \bar{H}_{m,i}^\circ - RT^2 (\partial \ln \gamma_{m,i} / \partial T)_{P,n_j}$.

10.30 (a) $\Delta G_{298}^\circ / (\text{kJ/mol}) = -237.129 - 0 - (-157.244) = -79.885$. $\Delta H_{298}^\circ / (\text{kJ/mol}) = -285.830 - 0 - (-229.994) = -55.836$. $\Delta S_{298}^\circ / (\text{J/mol-K}) = 69.91 - 0 - (-10.75) = 80.66$. (b) $\Delta G_{298}^\circ / (\text{kJ/mol}) = -237.129 - 394.359 - 2(0) - (-527.81) = -103.68$. $\Delta H_{298}^\circ / (\text{kJ/mol}) = -285.830 - 393.509 - 2(0) - (-677.14) = -2.20$. $\Delta S_{298}^\circ / (\text{J/mol-K}) = 69.90 + 213.74 -$

$$2(0) - (-56.9) = 340.5.$$

10.31 $\bar{S}_l^\circ = -(\partial \mu_l^\circ / \partial T)_P = -(\partial / \partial T)_P (v_+ \mu_+^\circ + v_- \mu_-^\circ) =$
 $v_+ (-\partial \mu_+^\circ / \partial T)_P + v_- (-\partial \mu_-^\circ / \partial T)_P = v_+ \bar{S}_+^\circ + v_- \bar{S}_-^\circ$. Subtraction of S_{el}° from each side gives $\Delta S_{f,l}^\circ = v_+ \Delta S_{f,+}^\circ + v_- \Delta S_{f,-}^\circ$.
 Then $\Delta H_{f,l}^\circ = \Delta G_{f,l}^\circ + T \Delta S_{f,l}^\circ = v_+ (\Delta G_{f,+}^\circ + T \Delta S_{f,+}^\circ) +$
 $v_- (\Delta G_{f,-}^\circ + T \Delta S_{f,-}^\circ) = v_+ \Delta H_{f,+}^\circ + v_- \Delta H_{f,-}^\circ$.

10.32 Since the two ways of writing the reaction refer to the same process, ΔS° must be the same for each. Hence $\bar{S}^\circ(\text{H}^+) + \bar{S}^\circ(\text{OH}^-) - \bar{S}^\circ(\text{H}_2\text{O}) = \bar{S}^\circ(\text{H}_3\text{O}^+) + \bar{S}^\circ(\text{OH}^-) - 2\bar{S}^\circ(\text{H}_2\text{O})$ and $\bar{S}^\circ[\text{H}_3\text{O}^+(\text{aq})] = \bar{S}^\circ(\text{H}^+) + \bar{S}^\circ(\text{H}_2\text{O}) = 0 + 69.91 \text{ J/mol-K} = 69.91 \text{ J/mol-K at } 25^\circ\text{C}$.

10.33 (a) Use of (10.86), (10.87), and (10.88) gives $\Delta G_f^\circ / (\text{kJ/mol}) = 65.49 + 2(-111.25) = -157.01$. $\Delta H_f^\circ / (\text{kJ/mol}) = 64.77 + 2(-207.36) = -349.95$. $\bar{S}^\circ / (\text{J/mol-K}) = -99.6 + 2(146.4) = 193.2$. (b) $\Delta H^\circ / (\text{kJ/mol}) = -240.12 - 167.159 - (-411.153) = 3.87$.

10.34 From (10.86) with $i = \text{HCl}$, $-131.23 \text{ kJ/mol} = \Delta G_f^\circ[\text{HCl}(\text{aq})] = \Delta G_f^\circ[\text{H}^+(\text{aq})] + \Delta G_f^\circ[\text{Cl}^-(\text{aq})] = 0 + \Delta G_f^\circ[\text{Cl}^-(\text{aq})]$ and $\Delta G_f^\circ[\text{Cl}^-(\text{aq})] = -131.23 \text{ kJ/mol}$. Similarly, (10.88) gives $\Delta H_f^\circ[\text{Cl}^-(\text{aq})] = -167.16 \text{ kJ/mol}$. Use of $T\Delta S_f^\circ[\text{HCl}(\text{aq})] = \Delta H_f^\circ[\text{HCl}(\text{aq})] - \Delta G_f^\circ[\text{HCl}(\text{aq})]$ gives $\Delta S_f^\circ[\text{HCl}(\text{aq})] = -120.5_1 \text{ J/mol-K} = \bar{S}^\circ[\text{HCl}(\text{aq})] - \frac{1}{2}\bar{S}^\circ[\text{H}_2(\text{g})] - \frac{1}{2}\bar{S}^\circ[\text{Cl}_2(\text{g})] = \bar{S}^\circ[\text{HCl}(\text{aq})] - 176.88 \text{ J/mol-K}$, so $\bar{S}^\circ[\text{HCl}(\text{aq})] = 56.3_6 \text{ J/mol-K} = \bar{S}^\circ[\text{H}^+(\text{aq})] + \bar{S}^\circ[\text{Cl}^-(\text{aq})] = \bar{S}^\circ[\text{Cl}^-(\text{aq})]$.

10.35 From (10.79),

$$\Delta G_f^\circ [i(A)] = \Delta G_f^\circ (i^*) - vRT \ln (v_{\pm} \gamma_{m,i,sat} m_{i,sat} / m^\circ), \text{ so}$$

$$\Delta G_{f,298}^\circ [KCl(aq)] = -409140 \text{ J/mol} - 2RT \ln [1(0.588)4.82]$$

$$= -414.30 \text{ kJ/mol. Equation (10.86) gives } -414.30 \text{ kJ/mol}$$

$$= \Delta G_{f,298}^\circ [K^+(aq)] - 131.23 \text{ kJ/mol and } \Delta G_{f,298}^\circ [K^+(aq)] =$$

$$-283.07 \text{ kJ/mol. Equation (9.38) at 1 bar gives}$$

$$\Delta \bar{H}_{diff,KCl(aq)}^\infty = 17.22 \text{ kJ/mol} = \bar{H}^\infty [KCl(aq)] - \bar{H}^\circ [KCl(s)]$$

$$= \bar{H}^\circ [KCl(aq)] - \bar{H}^\circ [KCl(s)] = \bar{H}^\circ [K^+(aq)] + \bar{H}^\circ [Cl^-(aq)] -$$

$$\bar{H}^\circ [KCl(s)]. \text{ Subtraction and addition of the standard en-}$$

$$\text{thalpies of K, } \frac{1}{2}Cl_2, \text{ and } e^- \text{ on the right side of the last}$$

$$\text{equation gives } 17.22 \text{ kJ/mol} = \Delta H_{f,298}^\circ [K^+(aq)] +$$

$$\Delta H_{f,298}^\circ [Cl^-(aq)] - \Delta H_{f,298}^\circ [KCl(s)] = \Delta H_{f,298}^\circ [K^+(aq)] -$$

$$167.16 \text{ kJ/mol} + 436.75 \text{ kJ/mol and } \Delta H_{f,298}^\circ [K^+(aq)] =$$

$$-252.37 \text{ kJ/mol. To find } \bar{S}^\circ [K^+(aq)], \text{ we use the fact that}$$

$$\Delta G_{298}^\circ \text{ for dissolving KCl in water equals } \Delta G_{f,298}^\circ [KCl(aq)]$$

$$- \Delta G_{f,298}^\circ [KCl(s)] = (-283.07 - 131.23 + 409.14) \text{ kJ/mol} =$$

$$-5.16 \text{ kJ/mol. Since } \Delta H_{298}^\circ \text{ for the solution process is}$$

$$17.22 \text{ kJ/mol, we have } \Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T = 75.06 \text{ J/K-}$$

$$\text{mol for dissolving KCl in water. Then } 75.06 \text{ J/mol-K} =$$

$$\bar{S}^\circ [KCl(aq)] - \bar{S}^\circ [KCl(s)] = \bar{S}^\circ [K^+(aq)] + \bar{S}^\circ [Cl^-(aq)] -$$

$$\bar{S}^\circ [KCl(s)] = \bar{S}^\circ [K^+(aq)] + 53.36 \text{ J/mol-K} - 82.59 \text{ J/}$$

$$\text{mol-K and } \bar{S}^\circ [K^+(aq)] = 104.3 \text{ J/mol-K.}$$

10.36 (a) From (10.99), $\ln \phi_2 = \int_0^{P_2} (\bar{V}/RT - 1/P) dP =$

$$\int_0^{P_2} (1/P + B^\dagger + C^\dagger P + D^\dagger P^2 + \dots - 1/P) dP =$$

$$\int_0^{P_2} (B^\dagger + C^\dagger P + D^\dagger P^2 + \dots) dP = B^\dagger P_2 + C^\dagger P_2^2/2 + D^\dagger P_2^3/3 +$$

.... Dropping the unnecessary subscript 2 on ϕ and P, we get the desired equation. (b) Comparison of (8.9) with (8.4) gives $B = b - a/RT$, $C = b^2$, ...; use of (8.6) gives $B^\dagger = (bRT - a)/R^2 T^2$, $C^\dagger = (2abRT - a^2)/R^4 T^4$, ... and substitution into the result of (a) gives the desired result.

10.37 (a) From Eq. (8.16), $b = RT_c/8P_c = 42.9 \text{ cm}^3/\text{mol}$ and $a = 27R^2 T_c^2/64P_c = 3.61 \times 10^6 \text{ cm}^6 \text{ atm mol}^{-2}$. At 75°C , $RT = 28570 \text{ cm}^3\text{-atm/mol}$ and Prob. 10.36b gives $\ln \phi =$

$$- [(2.38 \times 10^6)/(8.16 \times 10^8 \text{ atm})](1 \text{ atm})$$

$$- [(4.18 \times 10^{12})/(1.33 \times 10^{18} \text{ atm}^2)](1 \text{ atm})^2 = -0.00292 \text{ and}$$

$\phi = 0.997$ (compared to $\phi_{\text{exper}} = 0.997$). Replacing 1 atm by 25 atm in the preceding equation, we get $\ln \phi =$

$$-0.0749 \text{ and } \phi = 0.928 \text{ (compared to } \phi_{\text{exper}} = 0.92).$$

(b) $\phi_1 = \phi_1^*(T, P) = \phi_1^*(75^\circ\text{C}, 25 \text{ atm}) = 0.928$, where the result of (a) was used. $f_1 = \phi_1 P_1 = \phi_1 x_1 P =$

$$0.928(0.100)(25.0 \text{ atm}) = 2.32 \text{ atm}.$$

10.38 From (10.97) and (10.98), $\bar{G} = \mu = \mu^\circ + RT \ln (f/P^\circ)$
 $= \mu^\circ + RT \ln (\phi P/P^\circ) = \mu^\circ + RT \ln (P/P^\circ) + RT \ln \phi$. For the corresponding ideal gas, $\phi = 1$ and $\bar{G}^{\text{id}} = \mu^{\text{id}} = \mu^\circ + RT \ln (P/P^\circ)$. Therefore $\bar{G} = \bar{G}^{\text{id}} + RT \ln \phi$ and $\ln \phi = (\bar{G} - \bar{G}^{\text{id}})/RT$.

10.39 (a) Equation (4.65) gives $\Delta G = \int_1^2 V dP = \int_1^2 (nRT/P) dP = nRT \ln (P_2/P_1) = (1.000 \text{ mol}) \times (8.314 \text{ J/mol-K})(273.15 \text{ K}) \ln 1000 = 15.69 \text{ kJ} = 3.75 \text{ kcal}$.

$$\begin{aligned}
 \text{(b)} \quad \Delta G &= n \Delta \mu = n [\mu^\circ + RT \ln (f_2/P^\circ) - \mu^\circ - RT \ln (f_1/P^\circ)] \\
 &= nRT \ln (f_2/f_1) = nRT \ln (\phi_2 P_2 / \phi_1 P_1) = (1.000 \text{ mol}) \times \\
 &\quad (8.314 \text{ J/mol-K})(273.15 \text{ K}) \ln [1.84(1000)/0.9996(1.000)] \\
 &= 17.1 \text{ kJ} = 4.08 \text{ kcal.}
 \end{aligned}$$

10.40 From (10.99), $\ln \phi$ equals the area under the $\bar{V}/RT - 1/P$ vs. P curve from 0 to 120 atm. The data are:

$10^3 \text{ atm} (\bar{V}/RT - 1/P)$	-4.79	-4.81	-4.78	-5.01	-5.36
P/atm	1	10	20	40	60
$10^3 \text{ atm} (\bar{V}/RT - 1/P)$	-5.47	-5.01	-4.17		
P/atm	80	100	120		

Plotting the points and measuring the area, we find:

The rectangular area between the P axis and the line $\bar{V}/RT - 1/P = -0.00417 \text{ atm}^{-1}$ is $(-0.00417 \text{ atm}^{-1})(120 \text{ atm}) = -0.500$. The area between the line $\bar{V}/RT - 1/P = -0.00417 \text{ atm}^{-1}$ and the curve is found to be -0.104 . The total area is $-0.604 = \ln \phi$ and $\phi = 0.547$. Also, $f = \phi P = 0.547 \times 120 \text{ atm} = 65.6 \text{ atm}$. [Alternatively, numerical integration can be used. We take $-4.79 \times 10^{-3} \text{ atm}^{-1}$ as the zero-pressure limit of $\bar{V}/RT - 1/P$. The trapezoidal rule gives -0.00479 as the area from 0 to 1 atm, -0.0432 as the area from 1 to 10 atm, -0.0479_5 as the area from 10 to 20 atm, and -0.0979 as the area from 20 to 40 atm; Simpson's rule gives -0.4107 as the area from 40 to 120 atm. The total area is -0.604_5 .] (b) Problem 8.29 gives $B =$

$$\lim_{P \rightarrow 0} (\bar{V} - \bar{V}_{id}) = \lim_{P \rightarrow 0} (\bar{V} - RT/P). \text{ The data in part (a)}$$

give $\lim_{P \rightarrow 0} (\bar{V}/RT - 1/P) = -0.0048 \text{ atm}^{-1}$. Hence $B(-50^\circ\text{C}) = (-0.0048 \text{ atm}^{-1})(82.06 \text{ cm}^3\text{-atm/mol-K})(223 \text{ K}) = -88 \text{ cm}^3/\text{mol}$.

10.41 (a) $B = [82.06 \text{ cm}^3\text{-atm/mol-K}](126.2 \text{ K})/(33.5 \text{ atm}) \times [0.597 - 0.462e^{0.7002(126.2)/273.15}] = -12.8 \text{ cm}^3/\text{mol}$.

(b) $B^\dagger = B/RT = -5.7 \times 10^{-4} \text{ atm}^{-1}$. At 1 atm, $\ln \phi = B^\dagger P = (-5.7 \times 10^{-4} \text{ atm}^{-1})(1 \text{ atm}) = -5.7 \times 10^{-4}$ and $\phi = 0.99943$.

At 25 atm, $\ln \phi = -0.014_3$ and $\phi = 0.9859$.

10.42 (a) $B^\dagger_{\text{chl}} = B_{\text{chl}}/RT = (-1040 \text{ cm}^3/\text{mol})/RT = -0.04048 \text{ atm}^{-1} = -5.326 \times 10^{-5} \text{ torr}^{-1}$. $B^\dagger_{\text{car}} = -0.0569_8 \text{ atm}^{-1} =$

$-7.497 \times 10^{-5} \text{ torr}^{-1}$. In the mixture: $\ln \phi_{\text{chl}} =$

$\ln \phi_{\text{chl}}^*(T, P) \approx B^\dagger_{\text{chl}} P = (-5.326 \times 10^{-5} \text{ torr}^{-1})(301.84 \text{ torr}) = -0.01608$ and $\phi_{\text{chl}} = 0.9841$; $\ln \phi_{\text{car}} =$

$(-7.497 \times 10^{-5} \text{ torr}^{-1})(301.84 \text{ torr}) = -0.02263$ and $\phi_{\text{car}} =$

0.9776 . In the pure vapors: $\ln \phi_{\text{chl}}^* = (-5.326 \times 10^{-5}) \times (360.51) = -0.01920$ and $\phi_{\text{chl}}^* = 0.9810$; $\ln \phi_{\text{car}}^* = -0.01599$; $\phi_{\text{car}}^* = 0.9841$.

(b) $f_i = \gamma_{I,i} x_i f_i^*$ and $\phi_i x_{i,v} P = \gamma_{I,i} x_i \phi_i^* P_i^*$, so $\gamma_{I,i} = \phi_i x_{i,v} P / x_i \phi_i^* P_i^*$. Then $\gamma_{I,\text{chl}} = (0.9841)(0.6456) \times$

$(301.84 \text{ torr}) / (0.5242)(0.9810)(360.51 \text{ torr}) = 1.034$ and

$\gamma_{I,\text{car}} = (0.9776)(0.3544)(301.84 \text{ torr}) /$

$0.4758(0.9841)(213.34 \text{ torr}) = 1.047$. (c) Here we take ϕ_i

and $\phi_i^* = 1$ and $\gamma_{I,i} = x_{i,v} P / x_i P_i^*$. We get $\gamma_{I,\text{chl}} = 1.031$

and $\gamma_{I,\text{car}} = 1.054$.

10.43 $\Delta G_{\text{mix}} = G - G^* = \sum_i n_i \mu_i - \sum_i n_i \mu_i^* = \sum_i n_i (\mu_i - \mu_i^*) = \sum_i n_i (RT \ln \gamma_{I,i} x_i) = \sum_i n_i RT \ln (P_i / P_i^*)$.

10.44 At constant T and P , we have $d\mu_i = d(\mu_i^* + RT \ln x_i) = RT d \ln x_i = (RT/x_i) dx_i$. Therefore $\sum_i n_i d\mu_i = RT \sum_i (n_i/x_i) dx_i = RT \sum_i (n_i n_{\text{tot}}/n_i) dx_i = RT n_{\text{tot}} \sum_i dx_i$. From $\sum_i x_i = 1$, it follows that $\sum_i dx_i = 0$. Hence $\sum_i n_i d\mu_i = 0$ at constant T and P . Q.E.D.

10.45 There are $2N_A = 12 \times 10^{23}$ ions in 1000 cm^3 of solution. With uniform distribution, each ion is in the center of a cube of volume $(1000 \text{ cm}^3)/(12 \times 10^{23}) = 8.3 \times 10^{-22} \text{ cm}^3$ and edge length $(8.3 \times 10^{-22} \text{ cm}^3)^{1/3} = 9 \times 10^{-8} \text{ cm} = 9 \text{ \AA}$, and this is the nearest-neighbor distance.

10.46 (a) The following become 1 in the limit $x_W \rightarrow 1$:

$\gamma_{I,W}, \gamma_{II,W}, \gamma_{II,E}, \gamma_{m,E}$. (b) Only $\gamma_{I,E}$ becomes 1.

10.47 (a) Because A-B attractions are weaker than A-A and B-B attractions, U and H of the solution will be higher than U and H of the corresponding ideal solution. Hence $\Delta H_{\text{mix}} > 0 = \Delta H_{\text{mix}}^{\text{id}}$. (b) Because A-A and B-B attractions are stronger than A-B attractions and the molecules have similar sizes and shapes, A molecules in the solution will tend to surround themselves preferentially with other A molecules (and similarly for B molecules). Hence the degree of order in the solution is greater than in an ideal solution (where there is complete randomness in distribution of A and B molecules), and S of the solution is less than S^{id} ; $S < S^{\text{id}}$; $S - S^* < S^{\text{id}} - S^*$, $\Delta S_{\text{mix}} < \Delta S_{\text{mix}}^{\text{id}}$. (c) $\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}}$. Since $\Delta H_{\text{mix}} > \Delta H_{\text{mix}}^{\text{id}}$ and $\Delta S_{\text{mix}} < \Delta S_{\text{mix}}^{\text{id}}$, we have $\Delta G_{\text{mix}} > \Delta G_{\text{mix}}^{\text{id}}$.

10.48 (a) An increase in z_+ increases the attractions be-

tween the positive ion and the negative atmosphere that surrounds it, thereby stabilizing the solution and hence lowering μ_+ and lowering γ_+ . (b) An increase in ionic diameter decreases the closest distance of approach between positive and negative ions, decreasing the attractions between them and hence increasing μ_+ and increasing γ_+ . (c) An increase in ionic strength means an increase in the attractions between each cation and the anions in its atmosphere, which lowers μ_+ and hence lowers γ_+ . (d) An increase in solvent dielectric constant decreases the interactions between positive and negative ions, increasing μ_+ and increasing γ_+ . (e) As T increases, the kinetic energy of random ionic motion increases, which tends to distribute the ions more randomly and to thereby break up the ordered ionic atmospheres. This destabilizes the solution and increases μ_+ and γ_+ .

10.49 (a) True. When $\mu_i = \mu_i^\circ$ in (10.3), then $a_i = 1$. (b) False. For example, for Convention I, with $x_i < 1$, γ_i might be such that $\gamma_i x_i = 1 = a_i$. (c) True. See Eq. (10.3). (d) True. See Eq. (10.5). (e) True. See (10.3) and (10.5).

10.50 (a) $\mu_{i(\text{sln})} = \mu_{i(\text{v})}$ and use of (10.52) gives $\mu_{m,i}^\circ + vRT \ln(v_{\pm} \gamma_i m_i / m^\circ) = \mu_i^{\circ, \text{v}} + RT \ln(P_i / P^\circ)$, so $\ln(P_i / P^\circ) = (\mu_{m,i}^\circ - \mu_i^{\circ, \text{v}}) / RT + \ln(v_{\pm} \gamma_i m_i / m^\circ)^v$ and $P_i = P^\circ \exp [(\mu_{m,i}^\circ - \mu_i^{\circ, \text{v}}) / RT] (v_{\pm} \gamma_i m_i / m^\circ)^v = K_i (v_{\pm} \gamma_i m_i / m^\circ)^v$. For HCl, $v_+ = 1 = v_-$, $v = 2$, and $v_{\pm} = 1$, so $P_i =$

$$\begin{aligned}
 & K_i (\gamma_i m_i / m^\circ)^2. \quad (\underline{b}) \quad K_i = P^\circ \exp [(\mu_{m,i}^\circ - \mu_i^{\circ,V})/RT]. \quad \mu_i^{\circ,V} = \\
 & \mu_{\text{HCl}(g)}^\circ. \quad \mu_{m,i}^\circ = \mu^\circ[\text{H}^+(\text{aq})] + \mu^\circ[\text{Cl}^-(\text{aq})]. \quad \mu_{m,i}^\circ - \mu_i^{\circ,V} = \\
 & \Delta G_f^\circ[\text{H}^+(\text{aq})] + \Delta G_f^\circ[\text{Cl}^-(\text{aq})] - \Delta G_f^\circ[\text{HCl}(g)] = [0 - 131.228 - \\
 & (-95.299)] \text{ kJ/mol} = -35.929 \text{ kJ/mol}. \quad K_i = (1 \text{ bar}) \times \\
 & \exp [(-35929 \text{ J/mol})/RT] = 5.08 \times 10^{-7} \text{ bar}. \quad P_i = \\
 & (5.08 \times 10^{-7} \text{ bar}) [0.80(0.100 \text{ mol/kg}) / (1 \text{ mol/kg})]^2 = \\
 & 3.25 \times 10^{-7} \text{ bar} = 0.00024 \text{ torr}.
 \end{aligned}$$

CHAPTER 11

11.1 (a) $m_i = n_i/w_A = (4.603 \text{ g})(1 \text{ mol}/46.026 \text{ g})/(0.5000 \text{ kg}) = 0.2000 \text{ mol/kg}$. We neglect H^+ from H_2O . Let $x = m(\text{H}^+) = m(\text{HCOO}^-)$. Then (11.15) gives $K_a = 1.80 \times 10^{-4} \text{ mol/kg} = \gamma_{\pm}^2 x^2 / (0.2000 \text{ mol/kg} - x)$. With the initial approximation $\gamma_{\pm} \approx 1$, we find $x = 0.0059_1 \text{ mol/kg}$. Hence $I_m \approx 0.0059_1 \text{ mol/kg}$ and the Davies equation gives $\gamma_{\pm} = 0.92_2$. Use of this γ_{\pm} in the K_a equation gives $x = 0.0064_0 \text{ mol/kg}$. Then $I_m = 0.0064_0 \text{ mol/kg}$, $\gamma_{\pm} = 0.91_9$, $x = 0.0064_2 \text{ mol/kg}$. (b) $m(\text{KCl}) = (0.1000 \text{ mol})/(0.500 \text{ kg}) = 0.200 \text{ mol/kg}$. The KCl contribution to I_m is 0.200 mol/kg and the H^+ and HCOO^- contribution to I_m is (from part a) about 0.006 mol/kg , so $I_m \approx 0.206 \text{ mol/kg}$. The Davies equation gives $\gamma_{\pm} = 0.74_5$. Use of this γ_{\pm} in the K_a equation gives $x = 0.0079 \text{ mol/kg}$. This gives a revised I_m of 0.2079 mol/kg , which gives $\gamma_{\pm} = 0.74_5$. We then obtain $x = 0.0079 \text{ mol/kg}$. (c) If x is the moles of HCOOH that ionize per kilogram, then $m(\text{H}^+) = x$ and $m(\text{HCOO}^-) = x + 0.400 \text{ mol/kg}$, since the KHCOO contributes 0.400 mol/kg of HCOO^- . So $1.80 \times 10^{-4} \text{ mol/kg} = \gamma_{\pm}^2 x(0.400 \text{ mol/kg} + x)/(0.200 \text{ mol/kg} - x)$. With the initial approximation $I_m \approx 0.400 \text{ mol/kg}$ (due to the salt), the Davies equation gives $\gamma_{\pm} = 0.73_0$. With x in the numerator and denominator neglected compared with 0.400 and 0.200 mol/kg , the K_a equation gives $x = 1.69 \times 10^{-4} \text{ mol/kg}$. This x is small enough to neglect its contribution to I_m and to neglect it compared with 0.200 mol/kg .

11.2 For $\text{H}_2\text{S}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{HS}^-(\text{aq})$, $\Delta G_{298}^\circ = [12.08 + 0 - (-27.83)] \text{ kJ/mol} = 39910 \text{ J/mol} = -(8.3145 \text{ J/mol-K}) \times (298.15 \text{ K}) \ln K^\circ$, so $K^\circ = 1.02 \times 10^{-7}$. For $\text{HS}^-(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{S}^{2-}(\text{aq})$, $\Delta G_{298}^\circ = (0 + 85.8 - 12.08) \text{ kJ/mol} = 73.72 \text{ kJ/mol} = -RT \ln K^\circ$ and $K^\circ = 1.2 \times 10^{-13}$.

11.3 For this very dilute solution of an extremely weak acid, we cannot neglect H^+ from the H_2O ionization. The last example in Sec. 11.3 gives $m(\text{H}^+) = (K_w + mK_a)^{1/2} = [1.00 \times 10^{-14} + (1.00 \times 10^{-5})(6.2 \times 10^{-10})]^{1/2} \text{ mol/kg} = 1.27 \times 10^{-7} \text{ mol/kg}$.

11.4 $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$. The only significant contribution to I_m is from the NaCl, so $I_m = 0.20 \text{ mol/kg}$. The Davies equation gives $\log \gamma_{\pm} = -0.127$ and $\gamma_{\pm} = 0.746$ for H_3O^+ and OH^- . Equation (11.12) gives $1.00 \times 10^{-14} = (0.746)^2 [m(\text{H}_3\text{O}^+)/m^\circ]^2$ and $m(\text{H}_3\text{O}^+) = 1.34 \times 10^{-7} \text{ mol/kg}$.

11.5 Substitution of $T/\text{K} = 310.15$ into the equation of Prob. 11.28 gives $\log K_w^\circ = -13.618$ and $K_w^\circ = 2.41 \times 10^{-14}$. We can take $I_m \approx 0$ and $\gamma_{\pm} \approx 1$. Equation (11.12) gives $2.41 \times 10^{-14} = [m(\text{H}_3\text{O}^+)/m^\circ]^2$ and $m(\text{H}_3\text{O}^+) = 1.55 \times 10^{-7} \text{ mol/kg}$.

11.6 In this extremely dilute HCl solution, the ionization of H_2O cannot be neglected. $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$. $K_w^\circ = m(\text{H}_3\text{O}^+)m(\text{OH}^-)/m^{\circ 2}$, since $\gamma_{\pm} \approx 1$ in this very dilute solution. If y moles of H_2O ionize per kilogram, then $m(\text{OH}^-) = y \text{ mol/kg}$ and, since HCl is a strong acid, $m(\text{H}_3\text{O}^+) =$

$(y + 1.00 \times 10^{-8})$ mol/kg. Therefore $K_w^\circ = 1.00 \times 10^{-14} = (y + 1.00 \times 10^{-8})y$ and $y^2 + (1.00 \times 10^{-8})y - 1.00 \times 10^{-14} = 0$. The quadratic formula gives the positive root as $y = 9.51 \times 10^{-8}$. So $m(\text{H}_3\text{O}^+) = (y + 1.00 \times 10^{-8})\text{mol/kg} = 1.05 \times 10^{-7}$ mol/kg.

11.7 $\text{HX} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{X}^-$. $K_a = \gamma_{\pm}^2 m(\text{H}_3\text{O}^+)m(\text{X}^-)/m(\text{HX})$. $m(\text{H}_3\text{O}^+) = m(\text{X}^-) = 0.0100$ mol/kg, since the H_3O^+ from the ionization of water is negligible. $I_m = 0.0100$ mol/kg.

The Davies equation gives $\log \gamma_{\pm} = -0.0448$ and $\gamma_{\pm} = 0.902$. Hence $K_a = (0.902)^2 (0.0100 \text{ mol/kg})^2 / (0.200 - 0.010) \text{ mol/kg} = 4.28 \times 10^{-4}$ mol/kg.

11.8 $a(\text{H}_2\text{O}) = \gamma(\text{H}_2\text{O})x(\text{H}_2\text{O}) \approx x(\text{H}_2\text{O})$, since H_2O is an uncharged species and its γ should be close to 1 in this fairly dilute solution. In 1 kg of H_2O there are 55.5 mol of H_2O . There is no significant ion pairing, so $n(\text{Na}^+) = n(\text{Cl}^-) = 0.50$ mol in 1 kg of water. Therefore, $x(\text{H}_2\text{O}) = (55.5 \text{ mol}) / (55.5 \text{ mol} + 0.50 \text{ mol} + 0.50 \text{ mol}) = 0.982 \approx a(\text{H}_2\text{O})$.

11.9 $\text{C}_2\text{H}_3\text{O}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HC}_2\text{H}_3\text{O}_2 + \text{OH}^-$

$$K_b^\circ = \frac{a(\text{HC}_2\text{H}_3\text{O}_2)a(\text{OH}^-)}{a(\text{C}_2\text{H}_3\text{O}_2^-)a(\text{H}_2\text{O})} = \frac{K_w^\circ}{K_a^\circ} = \frac{1.00 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.71 \times 10^{-10}$$

where $K_a^\circ = a(\text{H}_3\text{O}^+)a(\text{C}_2\text{H}_3\text{O}_2^-)/a(\text{HC}_2\text{H}_3\text{O}_2)a(\text{H}_2\text{O})$ and Eq.

(11.11) were used. If we neglect the OH^- from the ionization of water, then $m(\text{HC}_2\text{H}_3\text{O}_2) = m(\text{OH}^-)$. The solution is

reasonably dilute and the OH^- and $\text{C}_2\text{H}_3\text{O}_2^-$ ions have the same charge, so the Debye-Hückel (or Davies) equation gives $\gamma(\text{OH}^-) = \gamma(\text{C}_2\text{H}_3\text{O}_2^-)$; these activity coefficients cancel in K_b° . We take $a(\text{H}_2\text{O}) = 1$ and $\gamma(\text{HC}_2\text{H}_3\text{O}_2) = 1$. Let $y = m(\text{OH}^-)/m^\circ$. Then $5.7_1 \times 10^{-10} = y^2/(0.10 - y) \approx y^2/0.10$ and $y = 7.6 \times 10^{-6}$, so $m(\text{OH}^-) = 7.6 \times 10^{-6} \text{ mol/kg}$. Equation (11.12) gives $1.00 \times 10^{-14} = \gamma_{\pm}^2 m(\text{H}_3\text{O}^+)m(\text{OH}^-)/m^{\circ 2}$. We have $I_m \approx 0.10 \text{ mol/kg}$ and the Davies equation gives $\log \gamma_{\pm} = -0.107$ and $\gamma_{\pm} = 0.78$. We find $m(\text{H}_3\text{O}^+) = 2.2 \times 10^{-9} \text{ mol/kg}$.

11.10 (a) $\text{H}_2\text{S} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HS}^-$; $\text{HS}^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{S}^{2-}$. We neglect the H_3O^+ from water. Because K_a of HS^- is much less than K_a of H_2S , the H_3O^+ from the second ionization step is much less than that from the first step. Because of the smallness of K_a of HS^- , the ionization of HS^- does not change the HS^- molality to any significant extent. Hence we can take $m(\text{H}_3\text{O}^+) = m(\text{HS}^-)$. Let $y = m(\text{H}_3\text{O}^+)/m^\circ$.

Neglecting activity coefficients, we have $1.0 \times 10^{-7} = y^2/(0.10 - y) \approx y^2/0.10$ and $y = 1.0 \times 10^{-4}$; hence $m(\text{H}_3\text{O}^+) = 1.0 \times 10^{-4} \text{ mol/kg} = m(\text{HS}^-)$. Let $z = m(\text{S}^{2-})/m^\circ$. For the ionization of HS^- : $1 \times 10^{-17} = (1.0 \times 10^{-4})z/(0.00010 - z) \approx (0.00010)z/0.00010 = z$ and $m(\text{S}^{2-}) =$

$1 \times 10^{-17} \text{ mol/kg}$. (b) From part (a), $m(\text{H}_3\text{O}^+) \approx 1 \times 10^{-4} \text{ mol/kg} \approx m(\text{HS}^-)$, so $I_m = 1 \times 10^{-4} \text{ mol/kg}$. The Davies equation gives $\log \gamma_{\pm} = -0.0050$ and $\gamma_{\pm} = 0.988$ for H_3O^+ and HS^- . Hence $1.0 \times 10^{-7} = (0.988)^2 y^2/0.10$ and $y = 1.0_1 \times$

10^{-4} ; hence $m(\text{H}_3\text{O}^+) = m(\text{HS}^-) = 1.0_1 \times 10^{-4}$ mol/kg. The Davies equation gives $\log \gamma(\text{H}_3\text{O}^+) = -0.0050$ and $\gamma(\text{H}_3\text{O}^+) = 0.988$; also $\gamma(\text{HS}^-) = 0.988$; $\gamma(\text{S}^{2-}) = 0.954$. So $1 \times 10^{-17} = (0.988)(1.01 \times 10^{-4})(0.954)z/0.988(1.01 \times 10^{-4})$ and $m(\text{S}^{2-}) = 1 \times 10^{-17}$ mol/kg.

11.11 $\text{Cu}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{CuSO}_4(\text{aq})$. Neglecting ionic association, $I_m \approx 0.20$ mol/kg and the Davies equation gives $\log \gamma_{\pm} \approx -0.5080$ and $\gamma_{\pm} \approx 0.310$. Let $m[\text{CuSO}_4(\text{aq})]/m^\circ = z$. Use of the initial estimate of γ_{\pm} in K_m for the association reaction gives $230 \approx z/(0.310)^2(0.0500 - z)^2$ and $z^2 - 0.1452z + 0.0025 = 0$. The roots are found to be $z = 0.0200$ and 0.125 . Since z cannot exceed 0.05 , we have $m[\text{CuSO}_4(\text{aq})] \approx 0.0200$ mol/kg and $m(\text{Cu}^{2+}) \approx 0.0300$ mol/kg. This gives an improved estimate of $I_m \approx 0.12$ mol/kg; the Davies equation gives an improved estimate of $\gamma_{\pm} \approx 0.354$.

Then $230 \approx z/(0.354)^2(0.0500 - z)^2$ and $z^2 - 0.1347z + 0.0025 = 0$; we find $z = 0.0222$. Hence $m(\text{Cu}^{2+}) \approx 0.0278$ mol/kg and $I_m \approx 0.1112$ mol/kg. The Davies equation gives $\gamma_{\pm} \approx 0.361$ and this leads to $z = 0.0226$. Another repetition gives $\gamma_{\pm} \approx 0.363$ and $z = 0.0227$. Further repetition is clearly unnecessary and $\gamma_{\pm} = 0.363$ and $m(\text{Cu}^{2+}) = 0.0273$ mol/kg. We have $\alpha = 0.0273/0.0500 = 0.546$. Since $\nu_+ = \nu_- = 1$, Eq. (10.53) reduces to $\gamma_1 = \alpha\gamma_{\pm} = 0.546(0.363) = 0.198$. (The experimental γ_1 is 0.217 .)

11.12 (a) The equilibria are $\text{HX} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{X}^-$ and

$2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$. With activity coefficients taken as 1, we have: (1) $K_a = m(\text{X}^-)m(\text{H}_3\text{O}^+)/m(\text{HX})$ and (2) $K_w = m(\text{H}_3\text{O}^+)m(\text{OH}^-)$. Electroneutrality gives (3) $m(\text{H}_3\text{O}^+) = m(\text{OH}^-) + m(\text{X}^-)$. (b) Conservation of X gives (4) $m = m(\text{HX}) + m(\text{X}^-)$. (c) Using Eq. (2) to eliminate $m(\text{OH}^-)$ and Eq. (4) to eliminate $m(\text{X}^-)$, we find that Eqs. (1) and (3) become: (1)' $K_a = m(\text{H}_3\text{O}^+)m(\text{X}^-)/[m - m(\text{X}^-)]$ and (3)' $m(\text{H}_3\text{O}^+) = K_w/m(\text{H}_3\text{O}^+) + m(\text{X}^-)$. Let $y = m(\text{H}_3\text{O}^+)$. Solving (3)' for $m(\text{X}^-)$ and substituting into (1)', we get $y^3 + K_a y^2 - (K_w + mK_a)y - K_a K_w = 0$.

11.13 (a) For $\text{HX} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{X}^-$, $K_{m,a}$ is given by (11.14) with the m° 's omitted and where the γ 's are γ_m 's. Letting + and - indicate the H_3O^+ and X^- ions, we have

$$\frac{K_{c,a}}{K_{m,a}} = \frac{(\gamma_{c,+} c_+ / \gamma_{m,+} m_+)(\gamma_{c,-} c_- / \gamma_{m,-} m_-)}{\gamma_{c,\text{HX}}^c \text{HX} / \gamma_{m,\text{HX}}^m \text{HX}}$$

Substitution of $\gamma_{c,i} c_i / \gamma_{m,i} m_i = \rho_A$ for $i = +$, $i = -$, and $i = \text{HX}$ gives $K_{c,a}/K_{m,a} = (\rho_A)^2 / \rho_A = \rho_A$. (b) $c_i = n_i/V$ and $m_i = n_i/w_A$, so $c_i/m_i = w_A/V$. In a dilute solution, the solution's volume is approximately equal to the volume of pure solvent, so $c_i/m_i \approx w_A/V_A^* = \rho_A$. (c) Substituting $c_i/m_i = \rho_A$ into $\gamma_{c,i} c_i = \rho_A \gamma_{m,i} m_i$ gives $\gamma_{c,i} \approx \gamma_{m,i}$.

11.14 (a) From Sec. 10.6, $\epsilon_{r,A} = 78.4$ for water at 25°C ; for a 1:1 electrolyte:

$$b = \frac{(1)(1)(1.602 \times 10^{-19} \text{ C})^2}{4\pi(8.854 \times 10^{-12} \text{ C}^2/\text{N-m}^2)78.4(4.5 \times 10^{-10} \text{ m}) \times (1.381 \times 10^{-23} \text{ J/K})(298.1 \text{ K})} = 1.588$$

$$K_c = (4/3)\pi(4.5 \times 10^{-10} \text{ m})^3(6.022 \times 10^{23} \text{ mol}^{-1})e^{1.588} = 0.00112(10 \text{ dm})^3/\text{mol} = 1.12 \text{ dm}^3/\text{mol}$$

(b) $z_+ = 2$ and $|z_-| = 1$, so $b = 2(1)(1.588) = 3.176$ and we find $K_c = 5.51 \text{ dm}^3/\text{mol}$. (c) $b = 6.352$ and $K_c = 132 \text{ dm}^3/\text{mol}$. (d) $b = 9.528$ and $K_c = 3160 \text{ dm}^3/\text{mol}$. The K_c 's have the correct magnitudes.

11.15 $\bar{V} = M/\rho = (58.44 \text{ g/mol})/(2.16 \text{ g/cm}^3) = 27.0_6 \text{ cm}^3/\text{mol}$. From (11.23), $\ln a_i \approx (P - P^\circ)\bar{V}_i/RT = (P - 1 \text{ bar}) \times (27.0_6 \text{ cm}^3/\text{mol})/(83.14 \text{ cm}^3\text{-bar/mol-K})(298.1 \text{ K}) = 0.00109_2 \text{ bar}^{-1}(P - 1 \text{ bar})$. At 1, 10, 100, and 1000 bar, we get $\ln a_i = 0, 0.0098, 0.108$, and 1.09 , and we get $a_i = 1, 1.01, 1.11$, and 2.98 , respectively,

11.16 $K_{sp} = 5.38 \times 10^{-5} \text{ mol}^2/\text{kg}^2 = \gamma_{\pm}^2 m(\text{Ag}^+)^2$. With the initial approximation $\gamma_{\pm} \approx 1$, we get $m(\text{Ag}^+) \approx 0.0073_3 \text{ mol/kg}$, which gives $I_m = 0.0073 \text{ mol/kg}$. The Davies equation gives $\gamma_{\pm} \approx 0.91_4$. This γ_{\pm} gives $m(\text{Ag}^+) = 0.00802 \text{ mol/kg}$, which gives $I_m = 0.00802 \text{ mol/kg}$ and $\gamma_{\pm} = 0.91_1$. This γ_{\pm} gives $m(\text{Ag}^+) = 0.00805 \text{ mol/kg}$ as the solubility.

11.17 $\text{CaF}_2(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2\text{F}^{-}(\text{aq})$. $m(\text{F}^{-}) = 2m(\text{Ca}^{2+})$ and $K_{sp} = 3.2 \times 10^{-11} \text{ mol}^3/\text{kg}^3 = \gamma_{+}m(\text{Ca}^{2+})\gamma_{-}^2[m(\text{F}^{-})]^2 = 4\gamma_{\pm}^3[m(\text{Ca}^{2+})]^3$. With $\gamma_{\pm} \approx 1$, we get $m(\text{Ca}^{2+}) = 2.0 \times 10^{-4} \text{ mol/kg}$. This gives $I_m = \frac{1}{2}[4(2.0 \times 10^{-4} \text{ mol/kg}) + 4.0 \times$

$10^{-4} \text{ mol/kg}] = 6.0 \times 10^{-4} \text{ mol/kg}$. The Davies equation gives $\gamma_{\pm} = 0.94_6$. With this γ_{\pm} we get $m(\text{Ca}^{2+}) = 2.1 \times 10^{-4} \text{ mol/kg}$.

11.18 For $\text{BaF}_2(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + 2\text{F}^{-}(\text{aq})$, $\Delta G_{298}^{\circ} = [-560.77 + 2(-278.79) - (-1156.8)] \text{ kJ/mol} = 38.4_5 \text{ kJ/mol} = -RT \ln K_{\text{sp}}^{\circ}$, and $K_{\text{sp}} = 1.8_4 \times 10^{-7} \text{ mol}^3/\text{kg}^3$.

11.19 (a) $\text{KCl}(\text{s}) \rightleftharpoons \text{K}^{+}(\text{aq}) + \text{Cl}^{-}(\text{aq})$. $\Delta G_{298}^{\circ} = (-283.27 - 131.228 + 409.14) \text{ kJ/mol} = -5.36 \text{ kJ/mol} = -RT \ln K_{\text{sp}}^{\circ}$. $\ln K_{\text{sp}}^{\circ} = (5360 \text{ J/mol}) / (8.3145 \text{ J/mol-K})(298 \text{ K}) = 2.16$. $K_{\text{sp}}^{\circ} = 8.7$ and $K_{\text{sp}} = 8.7 \text{ mol}^2/\text{kg}^2$. (b) $K_{\text{sp}} = \gamma_{\pm}^2 m(\text{K}^{+})m(\text{Cl}^{-}) = \gamma_{\pm}^2 (\alpha m_1)(\alpha m_1) = \gamma_{\pm}^2 \alpha^2 m_1^2 = \gamma_1^2 m_1^2$. $\gamma_1^2 = K_{\text{sp}} / m_1^2 = 8.7 / (4.82)^2$ and $\gamma_1 = 0.61$.

11.20 $\text{CaCO}_3(\text{calcite}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$. $\Delta G_{298}^{\circ} = (-604.03 - 394.359 + 1128.79) \text{ kJ/mol} = 130.40 \text{ kJ/mol} = -RT \ln K^{\circ}$. $\ln K^{\circ} = -(130400 \text{ J/mol}) / (8.3145 \text{ J/mol-K}) \times (298.15 \text{ K}) = -52.60$. $K^{\circ} = 1.4 \times 10^{-23} = P(\text{CO}_2) / P^{\circ}$, where we took the solid's activities to be 1 and assumed ideal vapor. Therefore $P(\text{CO}_2) = 1.4 \times 10^{-23} \text{ bar}$.

11.21 Taking the activities of the solids as 1 and assuming ideal gases, we have $K^{\circ} = P(\text{CO}_2) / P(\text{CO}) = 1.15 = n(\text{CO}_2) / n(\text{CO})$. Since the initial $n(\text{CO}_2) / n(\text{CO})$ value exceeds 1.15, the equilibrium position lies to the left. Let z moles of CO_2 react to reach equilibrium. Then $1.15 = (5 - z) / (3 + z)$ and $z = 0.72 \text{ mol}$. The equilibrium amounts are $n(\text{Fe}_3\text{O}_4) = 2.72 \text{ mol}$, $n(\text{CO}) = 3.72 \text{ mol}$, $n(\text{FeO}) = 1.84$

mol, $n(\text{CO}_2) = 4.28 \text{ mol}$.

11.22 $\text{Ca}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{CaSO}_4(\text{aq})$. The 2.08 g is 0.0152_8 mol of CaSO_4 . Let $z \text{ mol/kg}$ of CaSO_4 ion pairs be formed. Then $190 = z/\gamma_{\pm}^2(0.0152_8 - z)^2$ or $z^2 - (0.0305_6 + 1/190\gamma_{\pm}^2)z + 0.000233_5 = 0$. The quadratic formula gives

$$z = 0.0152_8 + 1/380\gamma_{\pm}^2 \pm \frac{1}{2}(0.000322/\gamma_{\pm}^2 + 0.0000277/\gamma_{\pm}^4)^{\frac{1}{2}}$$

Initially we take $\gamma_{\pm} = 1$ and get $z \approx 0.00856$ (where the minus sign is used, since z can't exceed 0.015). Thus, our initial estimates are $m(\text{Ca}^{2+}) \approx 0.0067_2 \approx m(\text{SO}_4^{2-})$; these give $I_m \approx 0.0269 \text{ mol/kg}$. The Davies equation then gives $\log \gamma_{\pm} \approx -0.271$ and $\gamma_{\pm} \approx 0.536$. Use of this γ_{\pm} in the above equation for z gives $z \approx 0.00536$ and $m(\text{Ca}^{2+}) \approx 0.0099_2 \text{ mol/kg}$. Then $I_m \approx 0.0397 \text{ mol/kg}$, $\log \gamma_{\pm} \approx -0.315$, $\gamma_{\pm} \approx 0.485$. This γ_{\pm} gives $z \approx 0.00485$ and $m(\text{Ca}^{2+}) \approx 0.0104_3 \text{ mol/kg}$. Then $I_m \approx 0.0417 \text{ mol/kg}$, $\log \gamma_{\pm} \approx -0.320$, $\gamma_{\pm} \approx 0.478$. This gives $z \approx 0.00478$, $I_m \approx 0.0420 \text{ mol/kg}$, $\gamma_{\pm} \approx 0.477$. This gives $z = 0.00477$, which is the converged value. Thus $m(\text{Ca}^{2+}) = m(\text{SO}_4^{2-}) = 0.0105_1 \text{ mol/kg}$ and $K_{\text{sp}} = \gamma_{\pm}^2 m(\text{Ca}^{2+})m(\text{SO}_4^{2-}) = (0.477)^2(0.0105_1 \text{ mol/kg})^2 = 2.5_1 \times 10^{-5} \text{ mol}^2/\text{kg}^2$.

11.23 $K^\circ = P(\text{CO}_2)/P^\circ = (183 \text{ torr})/(750 \text{ torr}) = 0.244$.

(a) $(5.0 \text{ g})/(100.1 \text{ g/mol}) = 0.050 \text{ mol CaCO}_3$. We have $n_{\text{CO}_2} = (0.244 \text{ bar})(4000 \text{ cm}^3)/(83.14 \text{ cm}^3\text{-bar/mol-K})(1073 \text{ K}) = 0.0109 \text{ mol}$. Hence the equilibrium composition is 0.039

mol of CaCO_3 , 0.0109 mol of CaO , and 0.0109 mol of CO_2 .

(b) The 0.0050 mol of CaCO_3 is not enough to give 0.0109 mol of CO_2 ; therefore all the CaCO_3 dissociates to give 0 mol of CaCO_3 , 0.0050 mol of CaO , and 0.0050 mol of CO_2 .

11.24 Eq. (11.4) holds: $\Delta G^\circ = -RT \ln K^\circ = 0 + 0 -$

$2(-95.299 \text{ kJ/mol}) = 190.598 \text{ kJ/mol}$. So $K_{298}^\circ = 4.1 \times 10^{-34}$.

11.25 The Lewis-Randall rule gives $\phi_i = \phi_i^*(450^\circ\text{C}, 300 \text{ bar})$.

$\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$. Let $2z$ mol of NH_3 react to reach equilibrium. At equilibrium, $n_{\text{NH}_3} = 1 - 2z$, $n_{\text{H}_2} = 3 + 3z$, and $n_{\text{N}_2} = z$. $P_i = x_i P$ and $P_{\text{NH}_3} = [(1 - 2z)/(4 + 2z)]P$, $P_{\text{H}_2} = [(3 + 3z)/(4 + 2z)]P$, $P_{\text{N}_2} = [z/(4 + 2z)]P$. The left side of (11.30) is $(4.6 \times 10^{-5})[(0.91)^2/(1.14)(1.09)^3]^{-1} = 8.2 \times 10^{-5}$. The right side is $(P_{\text{NH}_3}/P^\circ)^2/(P_{\text{N}_2}/P^\circ)(P_{\text{H}_2}/P^\circ)^3 = (P/P^\circ)^{-2}(1 - 2z)^2(4 + 2z)^2/z(3 + 3z)^3 = 8.2 \times 10^{-5}$. Since $P/P^\circ = 300$, we must solve $(1 - 2z)^2(4 + 2z)^2/z(3 + 3z)^3 = 7.38$. z must lie between 0 and 0.5 and trial and error gives $z = 0.0566$. A BASIC program to calculate the left side of the equation is

```
10 INPUT Z                      30 PRINT F
20 F = (1 - 2*Z)^2*(4 + 2*Z)^2/(Z*(3 + 3*Z)^3)  40 GOTO 10
                                           50 END
```

At equilibrium, $n_{\text{NH}_3} = 1 - 2z = 0.887$, $n_{\text{H}_2} = 3.170$, $n_{\text{N}_2} = 0.0566$.

11.26 $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$. $\Delta G_{700}^\circ = 2(6.49 \text{ kcal/mol}) = 12.98 \text{ kcal/mol} = -RT \ln K^\circ$. $\ln K^\circ = -(12980 \text{ cal/mol})/(1.987 \text{ cal/mol-K})(700 \text{ K}) = -9.332$. $K^\circ = 8.85 \times 10^{-5}$. The

Lewis rule is: $\phi_i \approx \phi_i^*(T, P)$. For NH_3 , $P_r = (500 \text{ atm})/(111.3 \text{ atm}) = 4.49$ and $T_r = (700 \text{ K})/(405.6 \text{ K}) = 1.73$. For N_2 , $P_r = 500/33.5 = 14.9$ and $T_r = 700/126.2 = 5.55$. For H_2 , $P_r = 500/(12.8 + 8) = 24.0$ and $T_r = 700/(33.8 + 8) = 16.7$. The **Newton** graphs of ϕ (the full reference is in Sec. 10.9) give $\phi_{\text{NH}_3} \approx 0.86$, $\phi_{\text{N}_2} \approx 1.26$, and $\phi_{\text{H}_2} \approx 1.16$. The left side of Eq. (11.30) equals

$$(8.85 \times 10^{-5})/[(0.86)^2(1.26)^{-1}(1.16)^{-3}] = 2.35 \times 10^{-4}.$$

Let $2w$ moles of NH_3 decompose. The equilibrium amounts are $n(\text{NH}_3)/\text{mol} = 1 - 2w$, $n(\text{N}_2)/\text{mol} = w$, and $n(\text{H}_2)/\text{mol} = 3w$. $n_{\text{tot}}/\text{mol} = 1 + 2w$. Use of $P_i = x_i P$ gives for Eq. (11.30):

$$2.35 \times 10^{-4} = \frac{[(1 - 2w)/(1 + 2w)]^2(507)^2}{[w/(1 + 2w)][3w/(1 + 2w)]^3(507)^4}$$

$1631w^4 = (1 - 2w)^2(1 + 2w)^2 = [(1 - 2w)(1 + 2w)]^2 = (1 - 4w^2)^2$. Let $z = w^2$. Then $1631z^2 = (1 - 4z)^2 = 1 - 8z + 16z^2$ and $1615z^2 + 8z - 1 = 0$. We find $z = 0.0225$. Then $w = z^{1/2} = 0.150$ and $n(\text{NH}_3) = 0.700 \text{ mol}$, $n(\text{N}_2) = 0.150 \text{ mol}$, and $n(\text{H}_2) = 0.450 \text{ mol}$.

11.27 (a) Assuming ideal vapor and taking the solid's activities as 1, we have $K^\circ = P(\text{CO}_2)/P^\circ$. Equation (11.32) gives $[\partial \ln K^\circ / \partial (1/T)]_P = -\Delta H^\circ/R$. We plot $\ln K^\circ$ vs. $1/T$. The data are:

$\ln K^\circ$	-3.485	-2.372	-1.411	-0.677	-0.046
$10^4/T$	10.27	9.79	9.32	8.89	8.57
					K^{-1}

The measured slope is $-2.03 \times 10^4 \text{ K} = -\Delta H^\circ/R$ and $\Delta H^\circ =$

169 kJ/mol. At 1073 K, $\Delta G^\circ = -RT \ln K^\circ =$

$-(8.3145 \text{ J/mol-K})(1073 \text{ K}) \ln (183/750) = 12.6 \text{ kJ/mol}$

We have $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$ and $\Delta S^\circ_{1073} =$

$[(169000 - 12600) \text{ J/mol}]/(1073 \text{ K}) = 146 \text{ J/mol-K}.$

(b) From the extrapolated graph, we read $\ln K^\circ = 1.5$ at $10^4/T = 7.855$, so $K^\circ = 4.5$ and $P(\text{CO}_2) = 4.5P^\circ = 4.5 \text{ bar}.$

11.28 Substitution of $T/\text{K} = 298.15$ into the equation gives

$\log K^\circ_w = -13.998$ and $K^\circ_w = 1.003 \times 10^{-14}$. We have $\Delta G^\circ =$

$-RT \ln K^\circ = -(8.3145 \text{ J/mol-K})(298.15 \text{ K}) \ln (1.003 \times 10^{-14})$

$= 79.91 \text{ kJ/mol}.$ (Cf. Prob. 10.30.) We have $(\partial \ln K^\circ/\partial T)_P$

$= \Delta H^\circ/RT^2 = 2.302585(\partial \log K^\circ/\partial T)_P$. Differentiation of the

K°_w equation in the text (which is for $P = 1 \text{ bar}$) gives

$(\partial \log K^\circ_w/\partial T)_P = (24746.26 \text{ K})/T^2 - 405.8639/2.302585T +$

$0.48796/\text{K} - 0.0002371(2T/\text{K}^2) = 0.03376 \text{ K}^{-1}$ at $25^\circ\text{C}.$ Hence

$\Delta H^\circ = 2.302585RT^2(0.03376 \text{ K}^{-1}) = 57.45 \text{ kJ/mol}$ at $25^\circ\text{C}.$

$\Delta S^\circ_{298} = (\Delta H^\circ - \Delta G^\circ)/T = [(57450 - 79910) \text{ J/mol}]/(298 \text{ K})$

$= -75.3 \text{ J/mol-K}.$

11.29 $\Delta V^\circ = -5.4 \text{ cm}^3/\text{mol} + 1.4 \text{ cm}^3/\text{mol} - (18.015 \text{ g/mol})/($
 $0.997 \text{ g/cm}^3) = -22.1 \text{ cm}^3/\text{mol}.$ $(\partial \ln K^\circ/\partial P)_T = -\Delta V^\circ/RT$

and $\int_1^2 d \ln K^\circ = -\int_1^2 (\Delta V^\circ/RT) dP$ at constant T . Neglect-

ing the pressure dependence of ΔV° , we have $\ln (K^\circ_2/K^\circ_1) =$

$-(\Delta V^\circ/RT)(P_2 - P_1)$ and $\ln [K^\circ_{200 \text{ bar}}/(1.00 \times 10^{-14})] =$

$(22.1 \text{ cm}^3/\text{mol})(83.14 \text{ cm}^3\text{-bar/mol-K})^{-1}(298 \text{ K})^{-1}(199 \text{ bar})$

$= 0.178 = \ln K^\circ_{200 \text{ bar}} + 32.236$ and $K^\circ_{200 \text{ bar}} = 1.19 \times 10^{-14}.$

11.30 (a) As in Prob. 11.29, with the P dependence of ΔV° neglected, we have $-(\Delta V^\circ/RT)(P_2 - P_1) = \ln(K_2^\circ/K_1^\circ) = \ln 1.191 = 0.1748$ and $\Delta V^\circ = -0.1748(83.14 \text{ cm}^3\text{-bar/mol-K}) \times (298.1 \text{ K})/(399 \text{ bar}) = -10.9 \text{ cm}^3/\text{mol}$. (b) $\ln 2 = 0.693 = (10.9 \text{ cm}^3/\text{mol})(83.14 \text{ cm}^3\text{-bar/mol-K})^{-1}(298 \text{ K})^{-1}(P_2 - P_1)$ and $P_2 - P_1 = 1.58 \text{ kbar}$, so $P_2 = 1.58 \text{ kbar}$.

11.31 (a) Since $\mu_A^\circ = \mu_A^*$, we have $\bar{H}_A^\circ = \bar{H}_A^*$. Equation (10.26) gives $\bar{H}_{m,i}^\circ = \bar{H}_i^\circ$. Hence $\Delta H_m^\circ = \nu_A \bar{H}_A^* + \sum_{i \neq A} \nu_i \bar{H}_i^\circ$ and substitution in (11.32) gives the desired result. (b) $K_c/K_m =$

$$(\gamma_{x,A} x_A)^{\nu_A} \prod_{i \neq A} (\gamma_{c,i} c_i)^{\nu_i} / (\gamma_{x,A} x_A)^{\nu_A} \prod_{i \neq A} (\gamma_{m,i} m_i)^{\nu_i} = \prod_{i \neq A} (\gamma_{c,i} c_i / \gamma_{m,i} m_i)^{\nu_i} = \prod_{i \neq A} (\rho_A)^{\nu_i} = \rho_A^b, \text{ where } b = \sum_{i \neq A} \nu_i. \text{ (c) From (b), } K_m = K_c \rho_A^{-b} \text{ and } \ln K_m^\circ = \ln K_c^\circ - b \ln \rho_A + \ln(\text{const}), \text{ where const involves } c^\circ \text{ and } m^\circ.$$

Hence $(\partial \ln K_m^\circ / \partial T)_P = (\partial \ln K_c^\circ / \partial T)_P - b(\partial \ln \rho_A / \partial T)_P = (\partial \ln K_c^\circ / \partial T)_P + b\alpha_A = \Delta H^\circ / RT^2$, where we used the result of part (a). Thus $(\partial \ln K_c^\circ / \partial T)_P = \Delta H^\circ / RT^2 - b\alpha_A = \Delta H^\circ / RT^2$

$- \alpha_A \sum_{i \neq A} \nu_i$. (d) From (11.32) with the concentration scale used, $\Delta H_c^\circ / RT^2 = \Delta H^\circ / RT^2 - \alpha_A \sum_{i \neq A} \nu_i = \nu_A \bar{H}_A^* / RT^2 + \sum_{i \neq A} (\nu_i \bar{H}_i^\circ / RT^2 - \nu_i \alpha_A)$. Since $\Delta H_c^\circ = \nu_A \bar{H}_A^* + \sum_{i \neq A} \nu_i \bar{H}_{c,i}^\circ$, it

follows that $\bar{H}_{c,i}^\circ = \bar{H}_i^\circ - RT^2 \alpha_A$ for $i \neq A$.

11.32 $\Delta G^\circ - \Delta G^\circ = \sum_{i \neq H^+} \nu_i \mu_i^\circ + \nu(H^+) \mu[H^+ \text{ at } a(H^+) = 10^{-7}] - [\sum_{i \neq H^+} \nu_i \mu_i^\circ + \nu(H^+) \mu^\circ(H^+)] = \nu(H^+) \{\mu[H^+ \text{ at } a(H^+) = 10^{-7}] - \mu^\circ(H^+)\}$. We have $\mu_i = \mu_i^\circ + RT \ln a_i$, so $\mu[H^+ \text{ at } a(H^+) = 10^{-7}] = \mu^\circ(H^+) + RT \ln 10^{-7}$

$$= \mu^\circ(\text{H}^+) - 16.118RT. \quad \Delta G^\circ - \Delta G = -16.118\nu(\text{H}^+)RT.$$

11.33 $\Delta G^\circ = 2(4.83 \text{ kJ/mol}) = 9.66 \text{ kJ/mol}.$ $Q =$

$$(P_{\text{NH}_3}/P^\circ)^2/(P_{\text{N}_2}/P^\circ)(P_{\text{H}_2}/P^\circ)^3 \text{ and use of } P_i = x_i P \text{ gives}$$

$$Q = [(1/7)3]^2/[(2/7)3][(4/7)3]^3 = 0.0425. \quad (\partial G/\partial \xi)_{T,P} =$$

$$\Delta G^\circ + RT \ln Q = 9660 \text{ J/mol} + (8.3145 \text{ J/mol-K})(500 \text{ K}) \times$$

$$\ln 0.0425 = -3.47 \text{ kJ/mol. Since } (\partial G/\partial \xi)_{T,P} < 0, \text{ the re-}$$

action proceeds to the right.

11.34 Equations (11.35) and (11.2) give $(\partial G/\partial \xi)_{T,P} =$

$$\sum_i \nu_i \mu_i = \sum_i \nu_i (\mu_i^\circ + RT \ln a_i) = \sum_i \nu_i \mu_i^\circ + RT \sum_i \nu_i \ln a_i$$

$$= \Delta G^\circ + RT \sum_i \ln (a_i)^{\nu_i} = \Delta G^\circ + RT \ln [\prod_i (a_i)^{\nu_i}] =$$

$$\Delta G^\circ + RT \ln Q.$$

11.35 As found in Prob. 6.27, constant T and P addition of j will produce more j when $x_j > \nu_j/\Delta|\nu|$ where ν_j and $\Delta|\nu|$ have the same sign. ν_j and $\Delta|\nu|$ are small integers and typical values of $\nu_j/\Delta|\nu|$ are $1/2, 2/1, 1/3, 2/3$, etc. Since the solution is dilute and j is a solute, we have $x_j \ll 1$, and x_j will not exceed $\nu_j/\Delta|\nu|$. Hence the answer is no.

11.36 (a) False. Intermolecular interactions between He and the gases in the reaction may change the gases' fugacity coefficients and so shift the equilibrium. (b) True. See Fig. 4.6. (c) False. See Eq. (11.19). (d) False. $\Delta G^\circ \neq \Delta G$ in the reaction mixture. (e) False. The molality-scale standard state is a state in solution. (f) False. See (e).

CHAPTER 12

12.1 The contribution of sucrose to the vapor pressure can be neglected. $P = P_A = a_A P_A^*$. Since the solution is reasonably dilute, we can take $a_A \approx x_A$ and $P = x_A P_A^*$. In 100 g of solution, there are $98.00 \text{ g}/18.015 \text{ g/mol} = 5.440 \text{ mol}$ of water and $2.00 \text{ g}/342.3 \text{ g/mol} = 0.00584 \text{ mol}$ of sucrose. Then $x_A = 0.99893$ and $P_A = 0.99893(1074.6 \text{ torr}) = 1073.4 \text{ torr}$.

12.2 $n_{\text{C}_5\text{H}_{12}} = (0.226 \text{ g})(1 \text{ mol}/72.15 \text{ g}) = 0.00313_2 \text{ mol}$.
 $m_{\text{C}_5\text{H}_{12}} = (0.00313_2 \text{ mol})/(0.01645 \text{ kg}) = 0.190_4 \text{ mol/kg}$.
 $k_f = M_A R T_f^{*2} / \Delta \bar{H}_{\text{fus},A} = (84.16 \text{ g/mol})(1.9872 \text{ cal/mol-K}) \times (279.62 \text{ K})^2 / (7.47 \text{ cal/g})(84.16 \text{ g/mol}) = 2.08_0 \times 10^4 \text{ K g/mol}$
 $= 20.8_0 \text{ K kg/mol}$. $\Delta T_f = -k_f m = -(20.8_0 \text{ K kg/mol}) \times (0.190_4 \text{ mol/kg}) = -3.96 \text{ K}$. $T_f = 6.47^\circ\text{C} - 3.96^\circ\text{C} = 2.51^\circ\text{C}$.
 We assumed an ideally dilute solution and that only pure cyclohexane freezes out.

12.3 $k_b = M_A R T_b^{*2} / \Delta \bar{H}_{\text{vap},A} = (18.0153 \text{ g/mol}) \times (8.3145 \text{ J/mol-K})(373.15 \text{ K})^2 / (40660 \text{ J/mol}) = 512.9_5 \text{ K g/mol}$
 $= 0.5129_5 \text{ K kg/mol}$.

12.4 $m = -\Delta T_f / k_f = (0.112 \text{ K}) / (1.860 \text{ K kg/mol}) = 0.0602 \text{ mol/kg}$
 $= n_i / w_A = n_i / (0.0980 \text{ kg})$, so $n_i = 0.00590 \text{ mol}$ of maltose.
 $M_i = w_i / n_i = (2.00 \text{ g}) / (0.00590 \text{ mol}) = 339 \text{ g/mol}$ and $M_{r,i} = 339$.

12.5 (a) $\Delta T_f = -k_f m_B = -k_f n_B / w_A = -k_f w_B / M_B w_A$ and $M_B = -k_f w_B / \Delta T_f w_A$. (b) For 100 g of solution, the 3% solution has $w_B = 3.00$ g and $w_A = 97.00$ g; $M_B = -(1.86 \text{ K kg/mol}) \times (3.00 \text{ g}) / (-0.169 \text{ K})(97.0 \text{ g}) = 0.340_4 \text{ kg/mol} = 340._4 \text{ g/mol}$. For the 6, 9, 12, and 15% solutions, we find $M_B = 337._3$, $334._5$, $331._6$, and $328._2 \text{ g/mol}$. Plotting M_B vs. wt. % maltose, we get a nearly linear graph that extrapolates to $M_B = 343 \text{ g/mol}$ at 0 wt. %.

12.6 $1/T_f^* T_f = (1/T_f^*) [1/(T_f^* + \Delta T_f)] = (1/T_f^*) (1/T_f^*) \times [1/(1 + \Delta T_f/T_f^*)] = (1/T_f^*)^2 [1 - \Delta T_f/T_f^* + (\Delta T_f/T_f^*)^2 + \dots]$.

12.7 (a) $m_{\text{urea}} = [(1.00 \text{ g}) / (60.06 \text{ g/mol})] / (0.200 \text{ kg}) = 0.0833 \text{ mol/kg}$; $k_f = -\Delta T_f / m_{\text{urea}} = (0.250 \text{ K}) / (0.0833 \text{ mol/kg}) = 3.00 \text{ K kg/mol}$. $m_Y = -\Delta T_f / k_f = (0.200 \text{ K}) / (3.00 \text{ K kg/mol}) = 0.0666_7 \text{ mol/kg} = n_Y / (0.125 \text{ kg})$ and $n_Y = 0.00833 \text{ mol}$. $M_Y = w_Y / n_Y = (1.50 \text{ g}) / (0.00833 \text{ mol}) = 180 \text{ g/mol}$. $M_{r,Y} = 180$. (b) $\Delta \bar{H}_{\text{fus},A} = M_A R T_f^{*2} / k_f = (200 \text{ g/mol}) \times (1.987 \text{ cal/mol-K})(285 \text{ K})^2 / (3000 \text{ g K/mol}) = 10.8 \text{ kcal/mol} = 45.0 \text{ kJ/mol}$.

12.8 We have 0.00313_6 mol of $C_{10}H_8$ and $m_B = (0.00313_6 \text{ mol}) / (26.6 \text{ g}) = 1.18 \times 10^{-4} \text{ mol/g}$. Hence $k_b = (0.455 \text{ K}) / (1.18 \times 10^{-4} \text{ mol/g}) = 3860 \text{ K g/mol}$. Equation (12.20) gives $\Delta \bar{H}_{\text{vap}} = (119.4 \text{ g/mol})(8.314 \text{ J/mol-K}) \times (334.8 \text{ K})^2 / (3860 \text{ K g/mol}) = 28.8 \text{ kJ/mol} = 6.89 \text{ kcal/mol}$.

12.9 (a) We have $\gamma_A x_A = a_A$ and $\Delta T_f = [R(T_f^*)^2 / \Delta \bar{H}_{\text{fus},A}] \times$

$\ln a_A = (k_f/M_A)(-\phi M_A \nu m_i) = -k_f \phi \nu m_i$. (b) In 96.0 g of water we have 4.00 g (or 0.0229_5 mol) of K_2SO_4 . Hence $m_i = (0.0229_5 \text{ mol})/(0.0960 \text{ kg}) = 0.239 \text{ mol/kg}$. Then $\phi = -\Delta T_f/k_f \nu m_i = (0.950 \text{ K})/(1.86 \text{ K kg/mol}) 3 (0.239 \text{ mol/kg}) = 0.712$.

12.10 Equation (12.17) gives $\Sigma_{i \neq A} m_i = (2.37 \text{ K})/(14.1 \text{ K kg/mol}) = 0.168 \text{ mol/kg}$; in 100 g of bromoform, we have 0.0168 total moles of solutes. Let P and P_2 be phenol and its dimer. Then $2P \rightleftharpoons P_2$. The 2.58 g is 0.0274 mol of phenol. Let $2z$ mol of phenol react. At equilibrium, $n_P/\text{mol} = 0.0274 - 2z$, $n_{P_2} = z$, and $n_{\text{tot}} = 0.0274 - z$. Then $0.0168 = 0.0274 - z$ and $z = 0.0106$. So $n_P = 0.0062$ mol and $n_{P_2} = 0.0106$ mol. The molalities are $m_P = (0.0062 \text{ mol})/(0.100 \text{ kg}) = 0.062 \text{ mol/kg}$ and $m_{P_2} = 0.106 \text{ mol/kg}$. Thus $K_m = (0.106 \text{ mol/kg})/(0.062 \text{ mol/kg})^2 = 27.6 \text{ kg/mol}$.

12.11 $\Sigma_{i \neq A} m_i = -\Delta T_f/k_f = (0.70 \text{ K})/(5.1 \text{ K kg/mol}) = 0.137 \text{ mol/kg} = (n_{\text{nap}} + n_{\text{an}})/(0.300 \text{ kg})$; so $n_{\text{nap}} + n_{\text{an}} = 0.0412 \text{ mol}$. We have $6.0 \text{ g} = n_{\text{nap}}(128.2 \text{ g/mol}) + n_{\text{an}}(178.2 \text{ g/mol}) = n_{\text{nap}}(128.2 \text{ g/mol}) + (0.0412 \text{ mol} - n_{\text{nap}})(178.2 \text{ g/mol})$. We get $n_{\text{nap}} = 0.027 \text{ mol}$ and $n_{\text{an}} = 0.014 \text{ mol}$.

12.12 (a) In 100 g of solution, $n_B = (8.00 \text{ g})/(342.3 \text{ g/mol}) = 0.02337 \text{ mol}$ and $m_B = (0.02337 \text{ mol})/(0.092 \text{ kg}) = 0.254 \text{ mol/kg}$. $\Delta T_f = -(1.860 \text{ K kg/mol})(0.254 \text{ mol/kg}) = -0.472_5 \text{ K}$.

(b) $\ln a_A = (\Delta \bar{H}_{\text{fus},A}/R)(1/T_f^* - 1/T_f) =$
 $[(6007 \text{ J/mol})/(8.3145 \text{ J/mol-K})](1/273.15 - 1/272.66_5)/K =$
 -0.00470 and $a_A = 0.9953_1$. 100 g of solution has $n_A =$
 $(92.00 \text{ g})/(18.0153 \text{ g/mol}) = 5.1068 \text{ mol}$ of H_2O , so $x_A =$
 $5.1068/(5.1068 + 0.02337) = 0.99544$ and $\gamma_A = a_A/x_A =$
 $0.9953_1/0.99544 = 0.99987$. (c) $\phi = -(\ln a_A)/M_A m_i =$
 $0.00470/(0.018015 \text{ kg/mol})(0.254 \text{ mol/kg}) = 1.027$.

12.13 (a) $\Pi \approx cRT = (0.282 \text{ mol/L})(1 \text{ L}/10^3 \text{ cm}^3) \times$
 $(82.06 \text{ cm}^3\text{-atm/mol-K})(293.1 \text{ K}) = 6.78 \text{ atm}$. (b) $\bar{V}_{\text{H}_2\text{O}}^* =$
 $(18.015 \text{ g/mol})/(0.998 \text{ g/cm}^3) = 18.05 \text{ cm}^3/\text{mol}$. $\ln a_{\text{H}_2\text{O}} =$
 $-(\Pi \bar{V}_A^*/RT) = -[(7.61 \text{ atm})(18.05 \text{ cm}^3/\text{mol})/$
 $(82.06 \text{ cm}^3\text{-atm/mol-K})(293.1 \text{ K})] = -0.00571$; $a_{\text{H}_2\text{O}} =$
 0.99431 . $x_{\text{H}_2\text{O}} = 55.508/(55.508 + 0.300) = 0.99462$. $\gamma_{\text{H}_2\text{O}} =$
 $0.99431/0.99462 = 0.99969$.

12.14 $c_B = \Pi/RT = (6.1/760)\text{atm}/(82.06 \text{ cm}^3\text{-atm/mol-K})(273 \text{ K})$
 $= 3.5_8 \times 10^{-7} \text{ mol/cm}^3$. One cm^3 of solution contains $3.58 \times$
 10^{-7} mol of the protein and contains 0.0200 g of protein;
 so $M_B = (0.0200 \text{ g})/(3.5_8 \times 10^{-7} \text{ mol}) = 56000 \text{ g/mol}$; $M_{r,B} =$
 56000 . This is approximate because the solution is not
 actually ideally dilute.

12.15 We have 5.55 moles of water and 0.00292 moles of
 sucrose. Equation (12.26) gives

$\Pi = [(82.06 \text{ cm}^3\text{-atm/mol-K})(298.1 \text{ K})/(18.07 \text{ cm}^3/\text{mol})] \times$
 $(0.00292 \text{ mol})/(5.55 \text{ mol}) = 0.712 \text{ atm}$. We have $\Pi = \rho gh$
 and $h = \Pi/\rho g =$

$$\frac{0.712 \text{ atm}}{(1.00 \text{ g/cm}^3)(980.7 \text{ cm/s}^2)} \frac{8.314 \times 10^7 \text{ erg}}{82.06 \text{ cm}^3 \text{ atm}} = 736 \text{ cm}$$

12.16 $\Pi = \rho gh$. In the infinite-dilution limit, ρ of the solution goes to ρ of water, and we shall use ρ of water in the following calculations. For the first solution, $\Pi = (0.996 \text{ g/cm}^3)(980.7 \text{ cm/s}^2)(2.18 \text{ cm}) = 2129 \text{ erg/cm}^3$ and $\Pi/\rho_B = (2129 \text{ erg/cm}^3)/(0.00371 \text{ g/cm}^3) = 5.74 \times 10^5 \text{ erg/g}$. The other solutions give Π/ρ_B values of 6.29×10^5 , 7.18×10^5 , and $8.10 \times 10^5 \text{ erg/g}$. A plot of Π/ρ_B is nearly linear and extrapolates to $4.5_4 \times 10^5 \text{ erg/g}$ at $\rho_B = 0$. This intercept equals RT/M_B and $M_B = (8.314 \times 10^7 \text{ erg/mol-K})(303.1 \text{ K})/(4.5_4 \times 10^5 \text{ erg/g}) = 5.5_5 \times 10^4 \text{ g/mol}$; the number average molecular weight is 55500.

12.17 $\Pi/\rho_B \approx RT/M_B + A_2 RT \rho_B + A_3 RT \rho_B^2 = RT/M_B + A_2 RT \rho_B + A_2^2 M_B RT \rho_B^2/4 = [(RT/M_B)^{1/2} + A_2 (M_B RT)^{1/2} \rho_B/2]^2$ and taking the square root of both sides gives the desired result.

12.18 (a) $\Sigma_{i \neq A} c_i \approx \Pi/RT = (7 \text{ atm})/(82.06 \text{ cm}^3\text{-atm/mol-K}) \times (310 \text{ K}) = 0.000275 \text{ mol/cm}^3 = 0.275 \text{ mol/dm}^3 \approx c_{\text{Na}^+} + c_{\text{Cl}^-}$. Therefore $c_{\text{Na}^+} \approx 0.138 \text{ mol/dm}^3$ as compared to 0.15 mol/dm^3 .

(b) We shall approximate the concentrations by the molalities. Then $\Sigma_{i \neq A} c_i \approx [2(0.460) + 3(0.034) + 2(0.019) + 2(0.009)] \text{ mol/dm}^3 = 1.078 \text{ mol/dm}^3 = 0.001078 \text{ mol/cm}^3$. Then $\Pi \approx (82.06 \text{ cm}^3\text{-atm/mol-K})(293 \text{ K})(0.001078 \text{ mol/cm}^3) =$

26 atm.

12.19 We have $V_i = n_i RT/P$, so V_i is proportional to n_i and to x_i . Then $M_n = \sum_i x_i M_i$ and $M_{n,r} = (0.78)(28.01) + 0.21(32.00) + 0.01(39.95) = 29.0$.

$$\begin{aligned} \underline{12.20} \quad \Pi &= -(RT/\bar{V}_A^*) \ln a_A = -(RT/\bar{V}_A^*)(-\phi M_A \nu m_1) = \\ &(\phi RT/\bar{V}_A^*) M_A \nu n_1 / n_A M_A = \phi RT \nu n_1 / n_A \bar{V}_A^*. \end{aligned}$$

12.21 (a) $\mu_{A,1} = \mu_{A,2}$. Assuming ideally dilute solutions, we have $\mu_A^*(P_1, T) + RT \ln x_{A,1} = \mu_A^*(P_1 + \Pi, T) + RT \ln x_{A,2}$ and $\mu_A^*(P_1 + \Pi, T) - \mu_A^*(P_1, T) = RT \ln x_{A,1} - RT \ln x_{A,2} \approx -RTx_{B,1} + RTx_{B,2}$, where (12.11) was used. From (12.22), $\mu_A^*(P_1 + \Pi, T) - \mu_A^*(P_1, T) = \bar{V}_A^* \Pi$, where the pressure dependence of \bar{V}_A^* is neglected. Hence $\bar{V}_A^* \Pi = RT(x_{B,2} - x_{B,1})$. (b) $x_{B,2} = 0.100/(0.100 + 55.51) = 0.00180$ and $x_{B,1} = 0.0200/(0.0200 + 55.51) = 0.000360$. $\Pi = (82.06 \text{ cm}^3\text{-atm/mol-K})(298.1 \text{ K})(0.00144)/(18.07 \text{ cm}^3/\text{mol}) = 1.95 \text{ atm}$.

12.22 At equilibrium, the equality sign holds in (4.21) and $-P^\alpha dV^\alpha - P^\beta dV^\beta = dA^\alpha + dA^\beta = -P^\alpha dV^\alpha + \sum_i \mu_i^\alpha dn_i^\alpha - P^\beta dV^\beta + \sum_i \mu_i^\beta dn_i^\beta$, so $\sum_i \mu_i^\alpha dn_i^\alpha + \sum_i \mu_i^\beta dn_i^\beta = 0$. Let dn moles of substance j move from phase α to phase β . Then $dn_j^\beta = dn$ and $dn_j^\alpha = -dn$; we have $-\mu_j^\alpha dn + \mu_j^\beta dn = 0$ and $\mu_j^\alpha = \mu_j^\beta$.

12.23 $f = c_{\text{ind}} - p + 2 = 2 - p + 2 = 4 - p$ and $p = 4 - f$. The minimum f is 0, so the maximum p is 4 in a binary system.

12.24 As noted in Sec. 12.6, the upper curve is the P-vs.- $x_{A,liq}$ curve and the lower curve is the P-vs.- $x_{A,vap}$ curve. We take A as acetone. Table 10.1 gives P and the $x_{A,liq}$ and $x_{A,vap}$ values that correspond to each P value. Plotting these points, we get a phase diagram with a minimum in P at $x_{acetone} = 0.4$.

12.25 The width between the vertical axes is 60 mm and $x_A = 0.3$ lies at 18 mm. We draw a vertical line at 18 mm, and then a horizontal line that goes from the liquid line at 18 mm to the vapor line; the intersection with the vapor line is at 45 mm (corresponding to $x_A = 0.75$) and gives the result of the first distillation step; drawing a horizontal line from the liquid line at 45 mm, we find it intersects the vapor line at 58.2 mm, corresponding to $x_A = 0.97$.

12.26 $P = P_{ben} + P_{tol} = x_{ben}P_{ben}^* + x_{tol}P_{tol}^* = x_{ben}P_{ben}^* + (1 - x_{ben})P_{tol}^* = P_{tol}^* + (P_{ben}^* - P_{tol}^*)x_{ben}$. The graph is linear, so we need only two points to plot it: $P = P_{tol}^* = 22.3$ torr at $x_{ben} = 0$ and $P = P_{ben}^* = 74.7$ torr at $x_{ben} = 1$.

12.27 (a) As found in the Prob. 12.25 solution, the first vapor has $x_{A,vap} = 0.75$. (b) A horizontal line starting from $x_{A,vap} = 0.30$ intersects the liquid line at $x_{A,liq} = 0.04$. (c) When $n_{liq} = n_{vap}$, the horizontal tie line is bisected by the vertical line at $x_A = 0.30$. By trial and error, we find that the tie line with equal halves is the

one that joins $x_{A,liq} = 0.11$ with $x_{A,vap} = 0.50$.

12.28 A horizontal line at 80°C in Fig. 12.11b intersects the curve at w_{nic} values of 0.07_6 for phase α and 0.69 for phase β . We have $10\text{ g} = 0.07_6 m_{\alpha} + 0.69(20\text{ g} - m_{\alpha})$ and $m_{\alpha} = 6.2\text{ g}$; then $m_{\beta} = 20\text{ g} - 6.2\text{ g} = 13.8\text{ g}$. (Alternatively, the lever rule could be used.) The α phase therefore has $0.07_6(6.2\text{ g}) = 0.5\text{ g}$ of nicotine and 5.7 g of water. The β phase has $0.69(13.8\text{ g}) = 9.5\text{ g}$ of nicotine and 4.3 g of water.

12.29 Drawing a horizontal tie line at 80°C , we find it intersects the water-poor portion of the curve at $w_{nic} = 0.69$. Drawing the vertical line at weight fraction $w_{nic} = 0.5$ and using the lever rule (12.44), we find $(20\text{ g})(17\frac{1}{2}\text{ mm}) = m_{wp}(7\frac{3}{4}\text{ mm})$ and the mass of the water-poor phase is $m_{wp} = 45\text{ g}$. The mass of nicotine in the water-poor phase is $0.69(45\text{ g}) = 31\text{ g}$ and the mass of water in this phase is $45\text{ g} - 31\text{ g} = 14\text{ g}$.

12.30 (a) Let α be the water-poor phase and β the water-rich phase. $(0.400 - 0.375)m_{\alpha} = (0.89 - 0.40)m_{\beta} = (0.89 - 0.40)(10.0\text{ g} - m_{\alpha})$; $0.025m_{\alpha} = 4.90\text{ g} - 0.49m_{\alpha}$ and $m_{\alpha} = 9.5_1\text{ g}$, $m_{\beta} = 0.4_9\text{ g}$. Then $m_{H_2O}^{\alpha} = 0.375(9.5_1\text{ g}) = 3.6\text{ g}$, $m_{phenol}^{\alpha} = (9.5 - 3.6)\text{ g} = 5.9\text{ g}$; $m_{H_2O}^{\beta} = 0.89(0.4_9\text{ g}) = 0.4_4\text{ g}$; $m_{phenol}^{\beta} = 0.05\text{ g}$. (b) $0.375 = m_{H_2O}^{\alpha}/m^{\alpha}$, $0.89 = m_{H_2O}^{\beta}/m^{\beta} = (4.00\text{ g} - m_{H_2O}^{\alpha})/(10.0\text{ g} - m^{\alpha})$. The first equation gives $m_{H_2O}^{\alpha} = 0.375m^{\alpha}$ and substitution in the second

equation gives $0.89 = (4.00 \text{ g} - 0.375m^{\alpha})/(10.00 \text{ g} - m^{\alpha})$. Solving, we get $m^{\alpha} = 9.5 \text{ g}$, and the problem is completed as in (a).

12.31 Let B = benzene and A = cyclohexane. Equation (12.47) becomes

$T_{\ell} \approx T_B^*/[1 - RT_B^*(\Delta\bar{H}_{\text{fus},B})^{-1} \ln x_B] =$
 $(278.6 \text{ K})/(1 - 0.233 \ln x_B)$ and $T_r \approx$
 $(279.7 \text{ K})/(1 - 0.884 \ln x_A)$, where T_{ℓ} and T_r are the left- and right-hand curves in Fig. 12.12. We get

x_A	0	0.1	0.2	0.3	0.4	0.5	0.6
T_{ℓ}	278.6	271.9	264.8	257.2	249.0	239.9	229.6
T_r							192.7
x_A	0.7	0.8	0.9	1			
T_{ℓ}	217.6	202.6	181.3				
T_r	212.7	233.6	255.9	279.7			

Plotting the curves, we find they intersect at $71\frac{1}{2}$ mole percent cyclohexane and -58°C .

12.32 The halt at 84.3 wt. % Zn must correspond to a compound with melting point 595°C . (It could not be a eutectic halt since its temperature is too high for this.) The compound's empirical formula is found as follows:

$$(84.3 \text{ g})/(65.38 \text{ g/mol}) = 1.289 \text{ mol Zn};$$

$(15.7 \text{ g})/(24.305 \text{ g/mol}) = 0.646 \text{ mol Mg}$; the Zn:Mg mole ratio is 2:1 and the compound's empirical formula is MgZn_2 . The phase diagram is of the type shown in Fig.

12.18. The eutectic temperatures are 345°C and 368°C . One eutectic composition is 97 wt. % Zn (corresponding to 368°C). It is difficult to tell which curve the reading at 50% belongs to, so all that can be said is that the second eutectic composition is close to 50 wt. % Zn.

12.33 (a) The phase diagram is the same type as Fig.

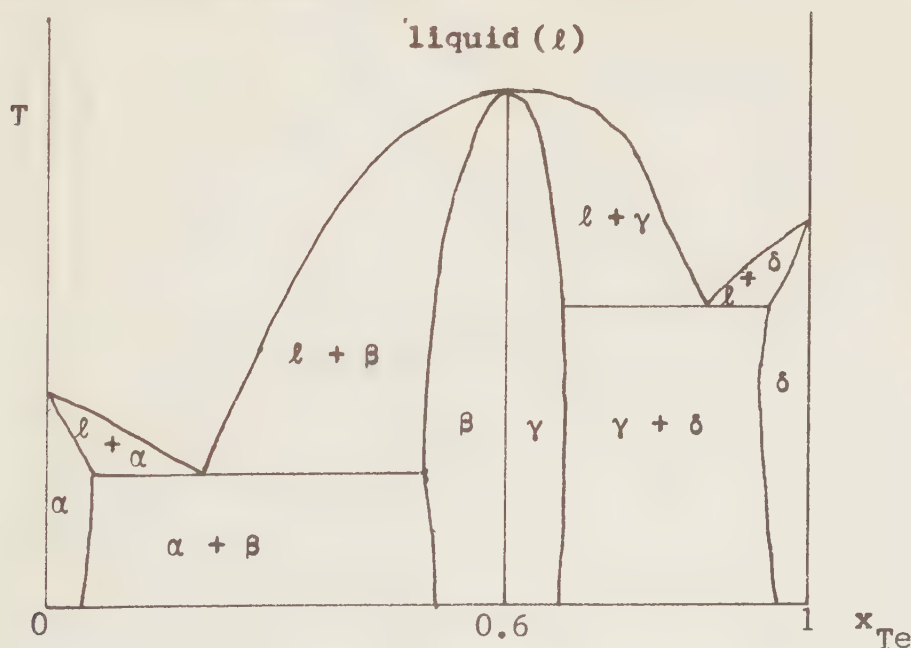
12.19c, with line PM lying at 0.1°C . The Liquid (ℓ) is a solution of salt in water, B is H_2O , the compound is $\text{NaCl}\cdot 2\text{H}_2\text{O}$, and A is NaCl. Since the diagram goes up to only 100°C , the right-hand melting-point curve (which is almost vertical below 100°C) does not reach the NaCl axis. The compound lies at 62 wt. % NaCl. (b) 20°C lies above the peritectic temperature of 0.1°C . As the solution evaporates, we move horizontally to the right on the diagram, eventually reaching the $\ell + \text{A}$ (solution + solid NaCl) region; eventually, pure NaCl is obtained. (c) This system lies initially in the $\ell + \text{A}$ (solution + solid NaCl) region. When the peritectic temperature of 0.1°C is reached, solid $\text{NaCl}\cdot 2\text{H}_2\text{O}$ begins to form. The 80 wt. % composition lies to the right of MN in Fig. 12.19c, and the system stays at 0.1°C until all the liquid disappears, leaving a mixture of the two solids NaCl and $\text{NaCl}\cdot 2\text{H}_2\text{O}$. Then this mixture is cooled to -10°C . No solid H_2O (ice) is present at -10°C .

12.34 A cooling curve that corresponds to l.s. \rightarrow

l.s. + $\alpha \rightarrow \alpha \rightarrow \alpha + \beta$ shows three breaks. A cooling curve that corresponds to l.s. \rightarrow l.s. + $\alpha \rightarrow$ l.s. + $\alpha + \beta \rightarrow \alpha + \beta$ shows a break followed by a eutectic halt. A cooling curve at the eutectic composition shows no break and one halt. Similarly for curves to the right of the eutectic composition.

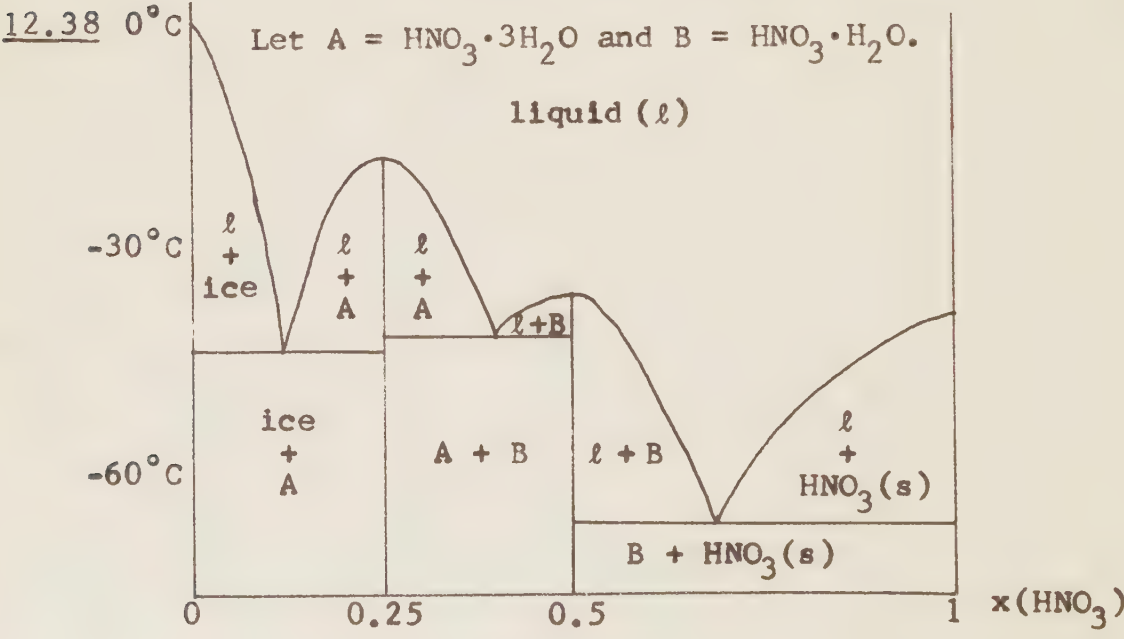
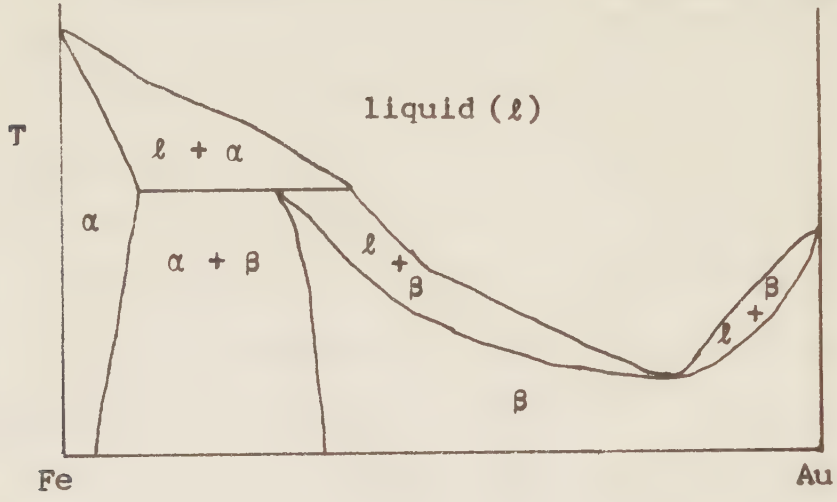
12.35 For $l \rightarrow l + B \rightarrow B + A_2B + l \rightarrow B + A_2B$, a break followed by a (eutectic) halt. For cooling a liquid with the eutectic composition, a halt. For $l \rightarrow l + A_2B \rightarrow l + B + A_2B \rightarrow B + A_2B$, a break and then a halt. For $l \rightarrow l + A \rightarrow l + A + A_2B \rightarrow l + A_2B \rightarrow l + B + A_2B \rightarrow B + A_2B$, break, halt, halt. For $l \rightarrow l + A \rightarrow l + A_2B + A \rightarrow A_2B$, break, halt. For $l \rightarrow l + A \rightarrow l + A + A_2B \rightarrow A + A_2B$, break, halt.

12.36 Just as Fig. 12.18 resembles two Fig. 12.12 diagrams placed side by side, the Bi-Te diagram resembles two Fig. 12.15 diagrams placed side by side:



α is a solid solution of Bi_2Te_3 in Bi. β is a solid solution of Bi in Bi_2Te_3 . γ is a solid solution of Te in Bi_2Te_3 . δ is a solid solution of Bi_2Te_3 in Te.

12.37 The intersection of the miscibility gap with the phase transition loop does not include the composition corresponding to the minimum, so we get a combination of Figs. 12.17 and 12.14. Phase α is a solution of Au in Fe. Phase β is a solution of Fe in Au. The phase diagram is:



12.39 (a) Equation (12.48) gives $\ln x_B =$

$$[(35.1 \text{ cal/g})(128.2 \text{ g/mol})/(1.987 \text{ cal/mol-K})] \times$$

$$[1/(353 \text{ K}) - 1/(298 \text{ K})] = -1.184 \text{ and } x_B = 0.306. \quad (\underline{b}) \text{ The}$$

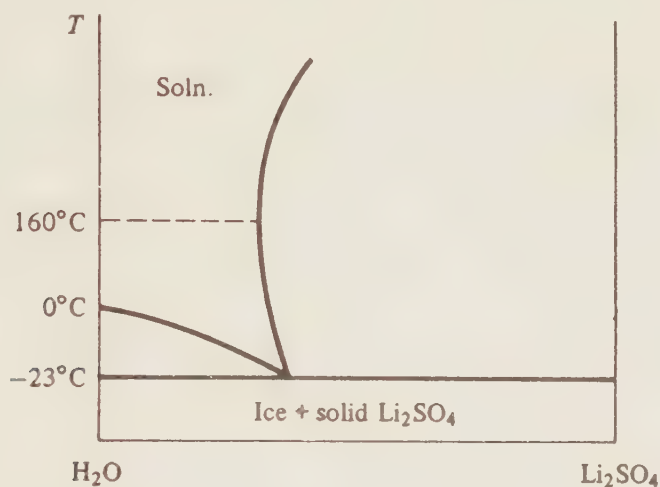
same as (a); $x_B = 0.306. \quad (\underline{c}) \ln x_B =$

$$[(38.7 \text{ cal/g})(178.2 \text{ g/mol})/(1.987 \text{ cal/mol-K})] \times$$

$$[1/(489 \text{ K}) - 1/(333 \text{ K})] = -3.325 \text{ and } x_B = 0.036.$$

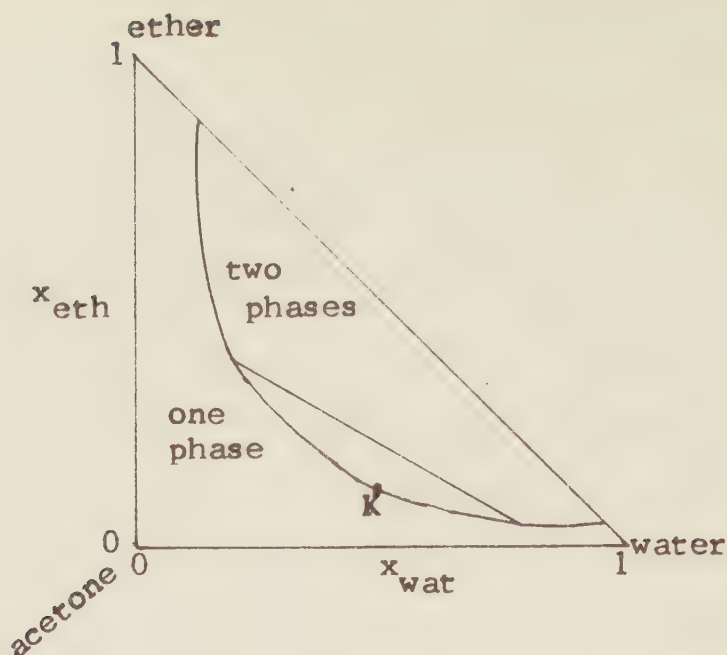
12.40 $(1000 \text{ g})(1 \text{ mol}/78.1 \text{ g}) = 12.8 \text{ mol}$. The $52\frac{1}{2}^\circ\text{C}$ point on the solubility curve CE is at $x_{\text{ben}} = 0.47 = (12.8 \text{ mol})/(12.8 \text{ mol} + n_{\text{tol}})$. We get $n_{\text{tol}} = 14 \text{ mol}$.

12.41



12.42 Pure water (wat) lies at the point $x_{\text{wat}} = 1, x_{\text{eth}} = 0$; pure ether (eth) lies at $x_{\text{wat}} = 0, x_{\text{eth}} = 1$; pure acetone (ac) lies at $x_{\text{wat}} = 0, x_{\text{eth}} = 0$. States with $x_{\text{ac}} = 0$ correspond to the line $x_{\text{wat}} + x_{\text{eth}} = 1$ or $x_{\text{eth}} = 1 - x_{\text{wat}}$; this is a line with intercept 1 and slope -1; the two-phase region is bounded on one side by part of this line. The plait point K is richer in water than in ether.

The phase diagram is



12.43 Draw \overline{DA} , \overline{DB} , and \overline{DC} in Fig. 12.23a. Let $\text{Ar}(\text{ABC})$ be the area of triangle ABC and let h be the altitude of this triangle. We have $\frac{1}{2}h\overline{BC} = \text{Ar}(\text{ABC}) = \text{Ar}(\text{ABD}) + \text{Ar}(\text{BDC}) + \text{Ar}(\text{CDA}) = \frac{1}{2}(\overline{AB} \cdot \overline{DG}) + \frac{1}{2}(\overline{BC} \cdot \overline{DE}) + \frac{1}{2}(\overline{CA} \cdot \overline{DF}) = \frac{1}{2}\overline{BC}(\overline{DG} + \overline{DE} + \overline{DF})$. Hence $h = \overline{DG} + \overline{DE} + \overline{DF}$.

12.44 (a) We drop perpendiculars from point F to each of the three sides of the triangle and take the ratio of each perpendicular distance to the triangle's height. We get for phase F: $x_{\text{ac}} = 0.05_5$, $x_{\text{wat}} = 0.91_9$, $x_{\text{eth}} = 0.02_6$.

Dropping perpendiculars from point H, we get the phase H composition as: $x_{\text{ac}} = 0.22_1$, $x_{\text{wat}} = 0.07_4$, $x_{\text{eth}} = 0.70_3$.

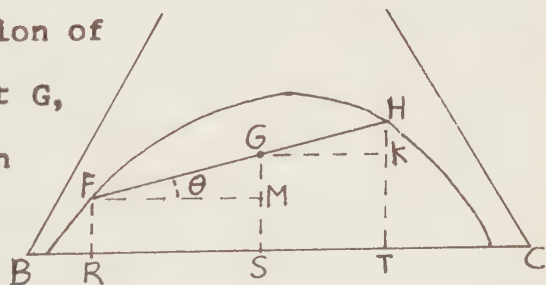
(b) $\overline{FG} = 31.2$ mm and $\overline{GH} = 19.6$ mm. The lever rule gives $31.2 n_F = 19.6 n_H = 19.6(40 \text{ mol} - n_F)$; then $n_F = 15.4$ mol and $n_H = 24.6$ mol. Phase F has $0.05_5(15.4 \text{ mol}) = 0.8_5$ mol of acetone, $0.91_9(15.4 \text{ mol}) = 14.2$ mol of water, and

$0.02_6(15.4 \text{ mol}) = 0.4 \text{ mol}$ of ether. Phase H has 5.4 mol of acetone, 1.8 mol of water, and 17.3 mol of ether.

12.45 (a) The diagram resembles Fig. 12.24 with ether replaced by ethyl acetate. (b) The overall composition is $x_{ac} = 0.20$, $x_{ethyl} = 0.40$, $x_{wat} = 0.40$. This point lies in the two-phase region and is just a shade below one of the tie lines graphed in (a). Drawing in a tie line through this point, we find it intersects the binodal curve at points corresponding to the following compositions. Phase α : $x_{wat}^\alpha = 0.91_5$, $x_{ac}^\alpha = 0.06_2$, $x_{ethyl}^\alpha = 0.02_3$. Phase β : $x_{wat}^\beta = 0.26_0$, $x_{ac}^\beta = 0.23_8$, $x_{ethyl}^\beta = 0.50_2$. We have $0.91_5 n^\alpha + 0.26_0(0.50 \text{ mol} - n^\alpha) = 0.20 \text{ mol}$; so $n^\alpha = 0.107 \text{ mol}$ and $n^\beta = 0.393 \text{ mol}$. (Alternatively, the lever rule could be used.) Then $n_{wat}^\alpha = 0.91_5(0.107 \text{ mol}) = 0.098 \text{ mol}$, $n_{ac}^\alpha = 0.0066 \text{ mol}$, $n_{ethyl}^\alpha = 0.0025 \text{ mol}$; $n_{wat}^\beta = 0.102 \text{ mol}$, $n_{ac}^\beta = 0.093_5 \text{ mol}$, $n_{ethyl}^\beta = 0.197 \text{ mol}$. Multiplication by the molar masses gives:

$$\begin{aligned} m_{wat}^\alpha &= 1.76 \text{ g}, & m_{ac}^\alpha &= 0.38 \text{ g}, & m_{ethyl}^\alpha &= 0.22 \text{ g}; \\ m_{wat}^\beta &= 1.84 \text{ g}, & m_{ac}^\beta &= 5.43 \text{ g}, & m_{ethyl}^\beta &= 17.4 \text{ g}. \end{aligned}$$

12.46 The overall composition of the system is given by point G, so the overall mole fraction x_A of A equals the distance \overline{GS} to the side opposite



vertex A. Points F and H give the compositions of the two

phases F and H in equilibrium, and $x_{A,F} = \overline{FR}$, $x_{A,H} = \overline{HT}$. Equation (12.49) with $\alpha = F$, $\beta = H$ becomes $n_F(\overline{GS} - \overline{FR}) = n_H(\overline{HT} - \overline{GS})$ and $\boxed{n_F/n_H = \overline{HK}/\overline{GM}}$. The figure gives $\sin \theta = \overline{HK}/\overline{GH} = \overline{GM}/\overline{FG}$. So $\overline{HK}/\overline{GM} = \overline{GH}/\overline{FG}$ and the boxed equation becomes $n_F/n_H = \overline{GH}/\overline{FG}$ or $\overline{FG}n_F = \overline{GH}n_H$.

12.47 (a) Since the solution in beaker B has a lower vapor pressure than that in A, the evaporation rate from the A solution exceeds that from the B solution and the equilibrium state will have beaker A empty, its liquid having vaporized from A and condensed in B. The vapor pressure in the box will be that of the diluted salt solution in B.

(b) The vapor pressure of the B solution is lower than that of the A solution. Liquid will evaporate from A and condense in B until the sucrose molalities are equalized. Let a mass z of H_2O vaporize from A. Equating molalities, we have $(0.01 \text{ mol})/(100 \text{ g} - z) = (0.03 \text{ mol})/(100 \text{ g} + z)$ and $z = 50 \text{ g}$. Beaker A ends up with 50 g of water and 0.01 mol of sucrose; beaker B ends up with 150 g of water and 0.03 mol of sucrose.

12.48 The diagram has the same appearance as Fig. 12.15. With x_A going from 0 to 1 on the horizontal axis, the areas are relabeled as follows: l.s. becomes vapor, l.s. + α becomes vapor + α (where α is a dilute solution of liquid A in the solvent liquid B), l.s. + β becomes vapor + β (where β is a dilute solution of liquid B in

liquid A). The horizontal line is a mixture of phase α , vapor, and phase β . The region $\alpha + \beta$ is a mixture of the two immiscible liquids α and β .

12.49 Yes. For example, an endothermic chemical reaction might occur. Another example is adding a salt to a mixture of water and ice at 0°C (see Sec 12.10).

12.50 (a) $c = 2$, $p = 1$; $f = c - p + 2 - r - a = 2 - 1 + 2 - 0 - 0 = 3$, but since P is held fixed, there are two degrees of freedom (temperature and x_A). (b) $c = 2$, $p = 2$; $f = 2 - 2 + 2 - 0 - 0 = 2$, but since P is held fixed, there is one degree of freedom. Once T is fixed, the mole-fraction composition of each phase is fixed. (c) $c = 2$, $p = 3$; $f = 2 - 3 + 2 - 0 - 0 = 1$, but since P is held fixed, there are no degrees of freedom. All intensive variables (T , P , mole fractions) are fixed.

12.51 Assuming ideal vapor, we have $P_i \equiv x_{i,\text{vap}} P = \gamma_{I,i} x_i P_i^*$. But for an azeotrope, $x_{i,\text{vap}} = x_i$, so $x_i P = \gamma_{I,i} x_i P_i^*$ and $\gamma_{I,i} = P/P_i^*$. $\gamma_{I,\text{ethanol}} = (760 \text{ torr})/(581 \text{ torr}) = 1.31$ and $\gamma_{I,\text{ethyl acetate}} = (760 \text{ torr})/(631 \text{ torr}) = 1.20$.

12.52 (a) For each substance, $\mu_i^\alpha = \mu_i^\beta$ and $\mu_i^* + RT \ln \gamma_{I,i}^\alpha x_i^\alpha = \mu_i^* + RT \ln \gamma_{I,i}^\beta x_i^\beta$, so $\gamma_{I,i}^\alpha x_i^\alpha = \gamma_{I,i}^\beta x_i^\beta$. For phase α , x_w is very close to 1 and $\gamma_{I,w}^\alpha \approx 1$. Hence (1) $x_w^\alpha = \gamma_{I,w}^\beta x_w^\beta$ and $\gamma_{I,w}^\beta = x_w^\alpha/x_w^\beta = 0.999595/0.00300 = 333$. For phase β , $\gamma_{I,\text{ben}}^\beta \approx 1$ and $\gamma_{I,\text{ben}}^\alpha x_{\text{ben}}^\alpha = (1) x_{\text{ben}}^\beta$, so

$\gamma_{I,ben}^{\alpha} = x_{ben}^{\beta} / x_{ben}^{\alpha} = 0.99700 / 0.000405 = 2460$. (b) This solution is phase β . With ideal vapor assumed, $P_i = \gamma_{I,i} x_i P_i^*$, so $P_{ben} = 1(0.997)(95.2 \text{ torr}) = 94.9 \text{ torr}$ and $P_w = 333(0.00300)(23.8 \text{ torr}) = 23.8 \text{ torr}$. $P = P_{ben} + P_w = 118.7 \text{ torr}$. (c) This solution is phase α . $P_{ben} = 2460 \times (0.000405)(95.2 \text{ torr}) = 94.8 \text{ torr}$; $P_w = 1(0.999595) \times (23.8 \text{ torr}) = 23.8 \text{ torr}$. $P = 118.6 \text{ torr}$.

12.53 Let b stand for benzene and α and β be the two liquid phases. $\mu_b^{\alpha} = \mu_b^{\beta}$ and $\mu_b^* + RT \ln \gamma_{I,b}^{\alpha} x_b^{\alpha} = \mu_b^* + RT \ln \gamma_{I,b}^{\beta} x_b^{\beta}$, so $\gamma_{I,b}^{\alpha} x_b^{\alpha} = \gamma_{I,b}^{\beta} x_b^{\beta}$. Above solution α , $P_b^{\alpha} = \gamma_{I,b}^{\alpha} x_b^{\alpha} P_b^*$. Above solution β , $P_b^{\beta} = \gamma_{I,b}^{\beta} x_b^{\beta} P_b^*$. Use of $\gamma_{I,b}^{\alpha} x_b^{\alpha} = \gamma_{I,b}^{\beta} x_b^{\beta}$ gives $P_b^{\alpha} = P_b^{\beta}$.

12.54 Assuming an ideally dilute solution, we have $-0.64^{\circ}\text{C} \approx -k_f m_B$ and $m_B \approx (0.64 \text{ K}) / (1.86 \text{ K kg/mol}) = 0.34_4 \text{ mol/kg}$. (a) $\Delta T_b \approx k_b m_b = (0.513 \text{ K kg/mol}) \times (0.34_4 \text{ mol/kg}) = 0.17_6 \text{ K}$. The normal boiling point of water is 99.975°C (Sec. 1.5 and Fig. 7.1), so $T_b \approx 100.15^{\circ}\text{C}$. (b) $P = P_A \approx x_A P_A^*$. We have $m_B = n_B / w_A = n_B / n_A M_A \approx x_B / M_A$ since the solution is dilute. Then $x_B \approx m_B M_A = (0.34_4 \text{ mol/kg})(0.01801 \text{ kg/mol}) = 0.0062$. So $P \approx 0.9938(23.76 \text{ torr}) = 23.61 \text{ torr}$. (c) $\Pi \approx x_B RT / \bar{V}_A^* = 0.0062(82.06 \text{ cm}^3 \text{ atm/mol-K})(293 \text{ K}) / (18.0 \text{ cm}^3/\text{mol}) = 8.3 \text{ atm}$.

12.55 (a) False. See Fig. 12.13. (b) True. See Fig. 12.1.

(c) False. See line FHK in Fig. 12.12. (d) False. The eutectic solution in Fig. 12.12 freezes entirely at one temperature. (e) True. As x_A increases in the solution, μ_A in the solution must increase [Eq. (4.90)], so $\mu_{A,v}$ of the vapor in equilibrium with the solution must increase. Since $\mu_{A,v} = \mu_A^{\circ,v}(T) + RT \ln (P_A/P^\circ)$, if $\mu_{A,v}$ increases at constant T , P_A must increase.

Reminder: Use this manual to check your own work, and not to avoid working problems.

CHAPTER 13

13.1 (a) $V = (4/3)\pi r^3$ and $r = (3V/4\pi)^{1/3} = [3(1.0 \text{ cm}^3)/4\pi]^{1/3} = 0.62 \text{ cm}$. $A = 4\pi r^2 = 4\pi(0.62 \text{ cm})^2 = 4.8 \text{ cm}^2$. (b) The volume of one particle is $(4/3)\pi \times (300 \times 10^{-8} \text{ cm})^3 = 1.13 \times 10^{-16} \text{ cm}^3$. The number of particles is $(1.0 \text{ cm}^3)/(1.13 \times 10^{-16} \text{ cm}^3) = 8.8_4 \times 10^{15}$. The area of one particle is $4\pi(300 \times 10^{-8} \text{ cm})^2 = 1.13 \times 10^{-10} \text{ cm}^2$. The total area of the particles is $(8.8_4 \times 10^{15}) \times (1.13 \times 10^{-10} \text{ cm}^2) = 1.0 \times 10^6 \text{ cm}^2$.

13.2 $dw_{\text{rev}} = \gamma dA$ and $w_{\text{rev}} = \gamma \Delta A = (73 \text{ dyn/cm}) \times (3.0 \text{ cm}^2) = 220 \text{ ergs}$.

13.3 $\gamma = \gamma_0(1 - T/T_c)^{11/9}$. At 0°C , $26.5 \text{ mN/m} = \gamma_0[1 - (273.1 \text{ K})/(523.2 \text{ K})]^{11/9} = 0.4057 \gamma_0$ and $\gamma_0 = 65.3 \text{ mN/m}$. At 50°C , $\gamma = (65.3 \text{ mN/m})[1 - (323.1 \text{ K})/(523.2 \text{ K})]^{11/9} = 20.2 \text{ mN/m}$.

13.4 $\gamma_0 = (37.8)^{2/3}(523.2)^{1/3}(0.432/0.252 - 0.951) \text{ dyn/cm} = 69.3 \text{ dyn/cm}$. $\gamma = \gamma_0(1 - T/T_c)^{11/9} = (69.3 \text{ dyn/cm}) \times [1 - (273.1 \text{ K})/(523.2 \text{ K})]^{11/9} = 28.1 \text{ dyn/cm}$. The percent error is $100(28.1 - 26.5)/26.5 = 6.0 \%$.

13.5 $\gamma/1_z = [(50 \text{ dyn/cm})/(10 \text{ cm})](82.06 \text{ cm}^3 \text{ atm})/(8.314 \times 10^7 \text{ ergs}) = 4.9 \times 10^{-6} \text{ atm}$.

13.6 (a) Substitution of numerical values of z/L into the equation gives $\rho/\rho_{\text{liq}} = 0.9997, 0.982, 0.953, 0.881,$

0.500, 0.12, 0.05, 0.02, and 0.0003 for $z/L = -2, -1, -0.75, -0.5, 0, 0.5, 0.75, 1,$ and 2 , respectively. (b)

The planes at $z = -0.75L$ and $z = 0.75L$ include 90% of the change in density, so the thickness is $1.5L$. (c) The thickness of the interphase region is $1.5L = 1.5(5\frac{1}{2} \text{ \AA}) = 8\frac{1}{2} \text{ \AA}$, which is about 3 atomic diameters thick for Hg.

$$\begin{aligned} \underline{13.7} \quad P^\alpha - P^\beta &= 2\gamma/R = 2(73 \text{ dyn/cm})/(0.040 \text{ cm}) = 3650 \text{ erg/cm}^3 \\ &= (3650 \text{ erg/cm}^3)(82.06 \text{ cm}^3 \text{ atm})/(8.314 \times 10^7 \text{ ergs}) = \\ &0.0036 \text{ atm} = 2.7 \text{ torr.} \quad P^\alpha = P^\beta + 2.7 \text{ torr} = 762.7 \text{ torr.} \end{aligned}$$

$$\begin{aligned} \underline{13.8} \quad \text{From (13.12), } \gamma &= \\ &\frac{1}{2}(0.7914 - 0.0012)(\text{g/cm}^3)(980.7 \text{ cm/s}^2)(3.33 \text{ cm})(0.0175 \text{ cm}) \\ &= 22.6 \text{ dyn/cm.} \end{aligned}$$

$$\begin{aligned} \underline{13.9} \quad h &= 2\gamma \cos \theta / (\rho_\beta - \rho_\alpha)gr = 2(490 \text{ dyn/cm}) \cos 140^\circ / \\ &(13.59 - 0.001)(\text{g/cm}^3)(980.7 \text{ cm/s}^2)(0.0175 \text{ cm}) = -3.22 \text{ cm.} \end{aligned}$$

$$\begin{aligned} \underline{13.10} \quad h &= 2\gamma / (\rho_\beta - \rho_\alpha)gr = \\ &2(52.2 \text{ dyn/cm}) / (0.3383 \text{ g/cm}^3)(980.7 \text{ cm/s}^2)(0.0175 \text{ cm}) = \\ &18.0 \text{ cm.} \end{aligned}$$

13.11 (a) For $\theta = 0$, we have a hemispherical interface (as in Fig. 13.8b). The volume of the liquid above the meniscus is the difference in volume between a cylinder and a hemisphere and equals $(\pi r^2)r - \frac{1}{2}(4/3)\pi r^3 = \pi r^3/3 = (\pi r^2)(r/3)$. Hence, this extra liquid has volume and mass equal to those of a cylindrical column of liquid of height $r/3$, and we must replace h by $h + r/3$ in the equation for

γ . (b) $h + r/3 = 3.33 \text{ cm} + (0.0175 \text{ cm})/3 = 3.33_6 \text{ cm}$. Replacing 3.33 cm by 3.33_6 cm , we get $\gamma = 22.6 \text{ dyn/cm}$.

13.12 $\gamma = \frac{1}{2}(\rho_\beta - \rho_\alpha)gh_1r_1$ and $\gamma = \frac{1}{2}(\rho_\beta - \rho_\alpha)gh_2r_2$.
 $h_1 - h_2 = [2\gamma/(\rho_\beta - \rho_\alpha)g](1/r_1 - 1/r_2)$ and $\gamma =$
 $\frac{1}{2}(\rho_\beta - \rho_\alpha)g(h_1 - h_2)r_1r_2/(r_2 - r_1) = \frac{1}{2}(0.900 \text{ g/cm}^3) \times$
 $(980.7 \text{ cm/s}^2)(1.00 \text{ cm})(0.0600 \text{ cm})(0.0400 \text{ cm})/(0.0200 \text{ cm}) =$
 53.0 dyn/cm .

13.13 $c_2 = c = (\gamma^* - \gamma)/b$ and $(\partial \ln c_2/\partial \gamma)_T =$
 $(1/c_2)(\partial c_2/\partial \gamma)_T = (1/c_2)(-1/b) = -1/bc_2$. $(\partial \gamma/\partial \ln c_2)_T =$
 $-bc_2$ and Eq. (13.34) gives $\Gamma_{2(1)} = bc_2/RT = (\gamma^* - \gamma)/RT$.

13.14 $\Gamma_{2(1)} = -(1/RT)(\partial \gamma/\partial \ln m/m^\circ)_T$. We plot γ vs.
 $\ln m/m^\circ$. The data are

$\gamma/(\text{dyn/cm})$	61.3	59.2	56.1	52.5	47.2
$\ln (m/m^\circ)$	-4.452	-4.157	-3.913	-3.597	-3.199

For $m = 0.020 \text{ mol/kg}$, $\ln (m/m^\circ) = -3.912$. Drawing the tangent line at this point, we find its slope to be -11.8 dyn/cm . Hence $\Gamma_{2(1)} =$
 $(11.8 \text{ dyn/cm})/(8.314 \times 10^7 \text{ ergs/mol-K})(294 \text{ K}) =$
 $4.8 \times 10^{-10} \text{ mol/cm}^2$.

13.15 Equations (10.4) and (10.52) give $u_1 = u_1^\circ +$
 $RT \ln a_1 = u_1^\circ + vRT \ln (v_\pm \gamma_1 m_1/m^\circ)$. We therefore have
 $\ln a_1 = v \ln (v_\pm \gamma_1 m_1/m^\circ)$. So $d \ln a_2 = v d \ln (v_\pm \gamma_2 m_2/m^\circ)$
 $= v d[\ln v_\pm + \ln (\gamma_2 m_2/m^\circ)] = v d \ln (\gamma_2 m_2/m^\circ)$ and
 $(\partial \gamma/\partial \ln a_2)_T = v^{-1}[\partial \gamma/\partial \ln (\gamma_2 m_2/m^\circ)]_T$ and substitution

In Eq. (13.33) gives the desired result.

13.16 Equation (13.31) and $n_1^\alpha/n_1^\beta = x_1^\alpha/x_1^\beta$ give

$$\Gamma_{1(1)} = \frac{45 \times 10^{-8} \text{ mol}}{100 \text{ cm}^2} \left[\frac{2.0 \times 10^{-8} \text{ mol}}{45 \times 10^{-8} \text{ mol}} - \frac{0.10}{0.90} \right]$$

$$= -3.0 \times 10^{-10} \text{ mol/cm}^2$$

13.17 $A = U - TS$ and $dA = dU - T dS - S dT = T dS - P dV$

$$+ \gamma d\mathcal{A} + \sum_i \mu_i dn_i - T dS - S dT = -S dT - P dV +$$

$$\gamma d\mathcal{A} + \sum_i \mu_i dn_i. \text{ At constant } T, V, \text{ and } n_i, \quad dA = \gamma d\mathcal{A}$$

$$\text{and } (\partial A / \partial \mathcal{A})_{T, V, n_i} = \gamma.$$

13.18 (a) From Fig. 13.10, $V^\alpha = \mathcal{A}z_0$ and $V^\beta = \mathcal{A}(b - z_0)$.

$$\text{Equation (13.19) with } i \text{ replaced by } 1 \text{ reads } n_1^\sigma = n_1 - c_1^\alpha \mathcal{A}z_0 - c_1^\beta \mathcal{A}(b - z_0) = n_1 + z_0 \mathcal{A}(c_1^\beta - c_1^\alpha) - c_1^\beta V, \text{ since}$$

$$\mathcal{A}b = V. \text{ Setting } n_1^\sigma = 0 \text{ and solving for } z_0, \text{ we get } z_0 = (c_1^\beta V - n_1) / (c_1^\beta - c_1^\alpha) \mathcal{A}. \text{ (b) Substitution of } V^\alpha = \mathcal{A}z_0$$

$$\text{and } V^\beta = \mathcal{A}(b - z_0) \text{ into (13.19) gives } n_1^\sigma = n_1 + \mathcal{A}z_0(c_1^\beta - c_1^\alpha) - c_1^\beta V. \text{ Substituting the } z_0 \text{ equation of part}$$

$$(a), \text{ dividing by } \mathcal{A}, \text{ and using } \Gamma_{1(1)} \equiv n_1^\sigma / \mathcal{A}, \text{ we get the equation in the text.}$$

$$\underline{13.19} \text{ (a) } n_i = n_{i, \text{bulk}}^\alpha + n_{i, \text{bulk}}^\beta + n_i^s = c_i^\alpha V_{\text{bulk}}^\alpha + c_i^\beta V_{\text{bulk}}^\beta + n_i^s. \text{ Since the volume of the interphase region}$$

$$\text{is very small, we can take } V = V_{\text{bulk}}^\alpha + V_{\text{bulk}}^\beta. \text{ Then } n_i = c_i^\alpha V_{\text{bulk}}^\alpha + c_i^\beta (V - V_{\text{bulk}}^\alpha) + n_i^s = V_{\text{bulk}}^\alpha (c_i^\alpha - c_i^\beta) + c_i^\beta V + n_i^s.$$

$$\text{Since } c_i^\beta \ll c_i^\alpha, \text{ we have } n_i = V_{\text{bulk}}^\alpha c_i^\alpha + c_i^\beta V + n_i^s =$$

$n_{i,bulk}^{\alpha} + c_i^{\beta} V + n_i^s$. Q.E.D. Replacing i by 1 , we get the second equation. (b) In the Prob. 13.18b equation we have $(c_1^{\beta} - c_1^{\alpha}) / (c_1^{\beta} - c_1^{\alpha}) \approx (-c_1^{\alpha}) / (-c_1^{\alpha}) = c_1^{\alpha} / c_1^{\alpha} = (n_{i,bulk}^{\alpha} / V_{bulk}^{\alpha}) / (n_{1,bulk}^{\alpha} / V_{bulk}^{\alpha}) = n_{i,bulk}^{\alpha} / n_{1,bulk}^{\alpha}$. Use of this relation and the results of (a) gives $\Gamma_{i(1)} = A^{-1} [n_{i,bulk}^{\alpha} + n_i^s - (n_{1,bulk}^{\alpha} + n_1^s)(n_{i,bulk}^{\alpha} / n_{1,bulk}^{\alpha})] = A^{-1} [n_i^s - n_1^s (n_{i,bulk}^{\alpha} / n_{1,bulk}^{\alpha})]$.

13.20 $\bar{V} = M/\rho = (284.5 \text{ g/mol}) / (0.94 \text{ g/cm}^3) = 303 \text{ cm}^3/\text{mol}$. The volume per molecule is $(303 \text{ cm}^3/\text{mol}) / (6.02 \times 10^{23}/\text{mol}) = 5.03 \times 10^{-22} \text{ cm}^3$. The cross-sectional area of a molecule is 20 \AA^2 . Let ℓ be the molecule's length. Then $5.03 \times 10^{-22} \text{ cm}^3 = (20 \times 10^{-16} \text{ cm}^2)\ell$ and $\ell = 2.5 \times 10^{-7} \text{ cm} = 25 \text{ \AA}$.

13.21 (a) $\frac{1}{2}[4057 (10^2 \text{ cm})^2]t = 4.8 \text{ cm}^3$ and $t = 2.3_7 \times 10^{-7} \text{ cm} = 24 \text{ \AA}$. (b) $\bar{V} = M/\rho = (885.4 \text{ g/mol}) / (0.90 \text{ g/cm}^3) = 984 \text{ cm}^3/\text{mol} = (6.02 \times 10^{23} \text{ mol}^{-1})A(2.3_7 \times 10^{-7} \text{ cm})$ and $A = 6.9 \times 10^{-15} \text{ cm}^2$. (c) There is one molecule, which is $(6.02 \times 10^{23})^{-1}$ moles, per each $6.9 \times 10^{-15} \text{ cm}^2$ area, so $\Gamma_{2(1)} = n_1/A = (6.02 \times 10^{23}/\text{mol})^{-1} / (6.9 \times 10^{-15} \text{ cm}^2) = 2.4 \times 10^{-10} \text{ mol/cm}^2$.

13.22 (a) We plot $1/v$ vs. $1/P$. The data are

$10^3 v^{-1} / (\text{g/cm}^3)$	9.90	7.35	6.54	6.17	6.06	6.02
$10^2 P^{-1} / \text{atm}^{-1}$	28.6	10.0	5.99	3.89	2.99	2.55

The straight-line fit is only fair. The intercept is

$0.0056 \text{ g/cm}^3 = 1/v_m$, and $v_m = 179 \text{ cm}^3/\text{g}$. The slope is

$0.0155 \text{ atm g/cm}^3 = 1/v_m b$, and $b =$

$1/(179 \text{ cm}^3/\text{g})(0.0155 \text{ atm g/cm}^3) = 0.36 \text{ atm}^{-1}$. (b) To

keep the units simple, we rewrite the Freundlich isotherm

as $v = k(P/P^\#)^a$, where $P^\# = 1 \text{ atm}$. We plot $\log v$ vs.

$\log (P/P^\#)$. The data are

$\log v$	2.004	2.134	2.185	2.210	2.217	2.220
----------	-------	-------	-------	-------	-------	-------

$\log (P/P^\#)$	0.544	1.000	1.223	1.410	1.525	1.593
-----------------	-------	-------	-------	-------	-------	-------

The straight-line fit is rather poor in that the points

show a pronounced curvature at high P . (Recall from the

text that the Freundlich isotherm doesn't work at high P .)

Ignoring the three points at high P , we draw a straight

line through the remaining points. The intercept is 1.86_3

$= \log k$, and $k = 73 \text{ cm}^3/\text{g}$. The slope is $0.264 = a$.

(c) For the Langmuir isotherm, $v_m b = c = 64.5 \text{ cm}^3/(\text{g atm})$

and $v = (64.5 \text{ cm}^3/\text{g})(P/P^\#)/(1 + 0.36P/P^\#)$; with $P/P^\# =$

7.0 , one gets $v = 128 \text{ cm}^3/\text{g}$. For the Freundlich isotherm,

$v = (73 \text{ cm}^3/\text{g})(7)^{0.264} = 122 \text{ cm}^3/\text{g}$.

13.23 (a) $v = r \ln (sP^\#) + r \ln (P/P^\#)$, where $P^\# = 1 \text{ atm}$.

A plot of v vs. $\ln (P/P^\#)$ is linear with slope r and in-

tercept $r \ln (sP^\#)$. (b) The data are

$v/(\text{cm}^3/\text{g})$	101	136	153	162	165	166
----------------------------	-----	-----	-----	-----	-----	-----

$\ln (P/P^\#)$	1.253	2.303	2.815	3.246	3.512	3.669
----------------	-------	-------	-------	-------	-------	-------

As with the Freundlich isotherm in Prob. 13.22b, the

points at high pressures show a strong curvature, indicating that the Temkin isotherm doesn't apply at high P . (Note that it predicts $v \rightarrow \infty$ as $P \rightarrow \infty$.) We ignore the three high-pressure points and draw a straight line through the remaining points. The slope is $33.4 \text{ cm}^3/\text{g} = r$. The intercept is $59 \text{ cm}^3/\text{g} = (33.4 \text{ cm}^3/\text{g}) \ln (sP^\#)$ and $s = 5.85 \text{ atm}^{-1}$.

13.24 We have $1 + bP = cP/v$, so a plot of P/v vs. P is linear.

13.25 (a) The curve resembles Fig. 13.15b, indicating formation of more than a monolayer. We have a type II isotherm and the BET equation is appropriate. (b) We plot $P/v(P^* - P)$ vs. P/P^* , where (since 77 K is the normal boiling point) $P^* = 760 \text{ torr}$. The data are

$10^2 [P/v(P^* - P)] / (\text{g}/\text{cm}^3)$	9.97	16.4	24.1	29.9	35.8
$10^2 P/P^*$	7.37	12.5	19.1	24.1	29.3

$10^2 [P/v(P^* - P)] / (\text{g}/\text{cm}^3)$	45.6	81.3	112.9	162.6
$10^2 P/P^*$	37.8	58.2	70.1	80.1

The low- and medium-pressure points fit a straight line well, but the three points at high pressure deviate greatly from this line (it is common for the BET isotherm to work poorly at high pressures) and will be ignored. Using a generous scale to plot the points, we draw a straight line of slope m and intercept b through the first six

points. We find $m = 1.17 \text{ g/cm}^3$ and $b = 1.6 \times 10^{-2} \text{ g/cm}^3$. We have $m = 1/v_m - 1/v_m c$ and $b = 1/v_m c$, so $v_m = (m + b)^{-1} = 0.843 \text{ cm}^3/\text{g}$; also, $c = (1 - mv_m)^{-1} = 73$. (c) $n = (1 \text{ atm})(0.843 \text{ cm}^3)/(82.06 \text{ cm}^3\text{-atm/mol-K})(273.15 \text{ K}) = 3.76 \times 10^{-5}$ moles of N_2 adsorbed per gram of sample. This is 2.26×10^{19} molecules, so the surface area of the powder is $(2.26 \times 10^{19})(16 \times 10^{-16} \text{ cm}^2) = 36000 \text{ cm}^2 = 3.6 \text{ m}^2$.

13.26 For $\theta \ll 1$ in Eq. (13.35), we have $1/\theta \gg 1$ and $1/bP + 1 \gg 1$, so that $1/bP \gg 0$ and hence $1/bP \gg 1$ and $bP \ll 1$. Therefore bP can be neglected in the denominator of (13.36) to give $v = cP$.

13.27 Let N be the number of adsorption sites. The rate of desorption of A is proportional to the number $\theta_A N$ of adsorbed A molecules and equals $k_{d,A} \theta_A N$. The A adsorption rate is proportional to the gas A partial pressure P_A and to the number $(1 - \theta_A - \theta_B)N$ of unoccupied sites. Hence $k_{d,A} \theta_A N = k_{a,A} P_A (1 - \theta_A - \theta_B)N$ and

$\theta_A = (k_{a,A}/k_{d,A})P_A(1 - \theta_A - \theta_B) = b_A P_A(1 - \theta_A - \theta_B)$, where $b_A = k_{a,A}/k_{d,A}$. Similarly, $\theta_B = b_B P_B(1 - \theta_A - \theta_B)$.

Division gives $\theta_B/\theta_A = b_B P_B/b_A P_A$. Hence, $\theta_A = b_A P_A \times (1 - \theta_A - b_B P_B \theta_A/b_A P_A)$ and $\theta_A = b_A P_A/(1 + b_A P_A + b_B P_B)$. Similarly, $\theta_B = b_B P_B/(1 + b_A P_A + b_B P_B)$. The fraction of occupied sites is $\theta_A + \theta_B$ and equals v/v_m , so $v/v_m =$

$$\theta_A + \theta_B = (b_A P_A + b_B P_B)/(1 + b_A P_A + b_B P_B).$$

13.28 (a) From (13.41), $d \ln P = -(\Delta \bar{H}_a / RT^2) dT$ at constant θ ; integration gives $\ln (P_2/P_1) = (\langle \Delta \bar{H}_a \rangle / R)(1/T_2 - 1/T_1)$, where $\langle \Delta \bar{H}_a \rangle$ is an average $\Delta \bar{H}_a$ over the temperature range. $\ln (0.03/0.0007) = [\langle \Delta \bar{H}_a \rangle / (8.314 \text{ J/mol-K})] \times [(873 \text{ K})^{-1} - (773 \text{ K})^{-1}]$ and $\langle \Delta \bar{H}_a \rangle = -210 \text{ kJ/mol}$. (b) For $\theta = 0.10$ and 500 to 600°C, $\langle \Delta \bar{H}_a \rangle = R[(873 \text{ K})^{-1} - (773 \text{ K})^{-1}]^{-1} \ln (23/8) = -59 \text{ kJ/mol}$. For 600 to 700°C, $\langle \Delta \bar{H}_a \rangle = R[(973 \text{ K})^{-1} - (873 \text{ K})^{-1}]^{-1} \ln (50/23) = -55 \text{ kJ/mol}$.

13.29 (a) Multiplication of (13.40) by vc gives $Pc/(P^* - P) = (v/v_m)[1 + (c - 1)P/P^*]$ and $v/v_m = PP^*c/(P^* - P)(P^* + Pc - P)$. (b) For $P \ll P^*$, we have $P^* - P \approx P^*$ and $v/v_m = PP^*c/P^*(P^* + Pc) = Pc/(P^* + cP) = (P^*)^{-1}cP/[1 + c(P^*)^{-1}P]$, which is the form of the Langmuir isotherm (13.35).

13.30 This suggests that the CO is chemisorbed in two different forms, as shown in Fig. 13.14.

13.31 (a) Taking activity coefficients as 1, we have $K_c = [L_n]/[L]^n$. Conservation of matter gives $c = [L] + n[L_n]$, so $K_c = [L_n]/(c - n[L_n])^n = x/(c - nx)^n$, where $x = [L_n]$; $(c - nx)^n = x/K_c$ and $c = nx + (x/K_c)^{1/n}$. (b) $f = [L]/c = (c - n[L_n])/c = 1 - nx/c$. (c) With $K_c^\circ = 10^{200}$, we have $K_c = 10^{200}/(c^\circ)^{49}$, where $c^\circ = 1 \text{ mol/dm}^3$. The equations of (a) and (b) give $c = 50x + c^\circ(x/c^\circ)^{0.02}/10^4$, $f = 1 - 50x/c$, and $[L] = fc$. For various assumed values of $x \equiv [L_n]$, we

calculate c , etc., as

x/c°	0	10^{-18}	10^{-10}	10^{-8}	10^{-7}	10^{-6}
$10^5 c/c^\circ$	0	4.37	6.31	6.97	7.74	12.6
$10^5 n[L_n]/c^\circ$	0	5×10^{-12}	0.00050	0.050	0.500	5.00
$10^5 [L]/c^\circ$	0	4.37	6.31	6.92	7.24	7.60
f	1	1.000000	0.99992	0.993	0.935	0.603

x/c°	$10^{-5.5}$	10^{-5}	$10^{-4.5}$	10^{-4}
$10^5 c/c^\circ$	23.6	57.9	166	508
$10^5 n[L_n]/c^\circ$	15.8	50.0	158	500
$10^5 [L]/c^\circ$	7.76	7.94	8.13	8.32
f	0.329	0.137	0.049	0.016

The plots of $[L]$ and $n[L_n]$ have the form of Fig. 13.17b.

(d) From the graph of f , we find that $c = 0.00015 \text{ mol/dm}^3$ at $f = 0.5$.

13.32 (a) $\log z = 0.4343 \ln z$ and $\gamma =$

$[73.0 - 12.99 \ln(ac + 1)] \text{ dyn/cm}$. We have $d \ln c =$

$c^{-1}dc$ and $(\partial \gamma / \partial \ln c) = c(\partial \gamma / \partial c) =$

$-(12.99 \text{ dyn/cm})ac/(ac + 1)$; Eq. (13.34) with $R = 8.314 \times$

10^7 ergs/mol-K gives $\Gamma_{2(1)} = (5.37 \times 10^{-10} \text{ mol/cm}^2) \times$

$ac/(ac + 1)$. (b) This resembles the Langmuir isotherm;

c corresponds to P and $\Gamma_{2(1)}$ corresponds to v . (c) With

$a = 19.64 \text{ dm}^3/\text{mol}$, we get

$10^{10} \Gamma_{2(1)}/(\text{mol/cm}^2)$	0	2.66	3.56	4.28	4.76	5.01	5.11
$c/(\text{mol/dm}^3)$	0	0.05	0.1	0.2	0.4	0.7	1.0

13.33 (a) $dP_A/P_A = (\bar{V}_A^l/RT) dP$ at constant T . Integration gives $\ln (P_{A,2}/P_{A,1}) = (\bar{V}_A^l/RT)(P_2 - P_1)$, where we neglected the pressure dependence of \bar{V}_A^l . Let state 1 be the bulk state and state 2 be a drop of liquid with radius r .

Equation (13.9) gives the extra pressure experienced by the drop due to its curvature as $P_2 - P_1 = 2\gamma/r$. Hence

$$\ln (P_r/P_{\text{bulk}}) = (\bar{V}^l/RT)(2\gamma/r) \text{ and}$$

$P_r = P_{\text{bulk}} \exp (2\gamma\bar{V}^l/rRT)$. (b) $\bar{V}^l = M/\rho = (18.015 \text{ g/mol})/(0.998 \text{ g/cm}^3) = 18.05 \text{ cm}^3/\text{mol}$. The result of part (a) gives $P_r/(17.535 \text{ torr}) =$

$$\exp \left[\frac{2(73 \text{ dyn/cm})(18.05 \text{ cm}^3/\text{mol})}{(1.00 \times 10^{-5} \text{ cm})(8.314 \times 10^7 \text{ erg/mol-K})(293.1 \text{ K})} \right]$$

and $P_r = 17.726 \text{ torr}$.

CHAPTER 14

$$\begin{aligned} \underline{14.1} \quad F &= Q_1 Q_2 / 4\pi\epsilon_0 r^2 = \\ &= \frac{2(1.60 \times 10^{-19} \text{ C})(1.60 \times 10^{-19} \text{ C})}{4\pi(8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2})(1.0 \times 10^{-10} \text{ m})^2} = 4.6 \times 10^{-8} \text{ N} \end{aligned}$$

$$\begin{aligned} \underline{14.2} \quad (\underline{a}) \quad E &= Q/4\pi\epsilon_0 r^2 = \\ &= (8.988 \times 10^9 \text{ N m}^2 \text{ C}^{-2})(1.60 \times 10^{-19} \text{ C}) / (2.0 \times 10^{-10} \text{ m})^2 = \\ &= 3.6 \times 10^{10} \text{ V/m.} \quad (\underline{b}) \quad 0.90 \times 10^{10} \text{ V/m.} \end{aligned}$$

$$\begin{aligned} \underline{14.3} \quad \phi_2 - \phi_1 &= (Q/4\pi\epsilon_0)(1/r_2 - 1/r_1) = \\ &= \frac{1.60 \times 10^{-19} \text{ C}}{4\pi(8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2})} \left(\frac{1}{4.0 \times 10^{-10} \text{ m}} - \frac{1}{2.0 \times 10^{-10} \text{ m}} \right) \\ &= -3.60 \text{ V} \end{aligned}$$

$$\underline{14.4} \quad (\underline{a}) \quad (3.00 \text{ mol})(2 \times 96485 \text{ C/mol}) = 5.79 \times 10^5 \text{ C.}$$

$$(\underline{b}) \quad (0.600 \text{ mol})(-96485 \text{ C/mol}) = -5.79 \times 10^4 \text{ C.}$$

$$\begin{aligned} \underline{14.5} \quad \text{Equation (14.23) gives } \mu_1^{\text{Li}} - \mu_1^{\text{Rb}} &= \\ &= (-96500 \text{ C/mol})(-0.1 \text{ V}) = 10^4 \text{ J/mol.} \end{aligned}$$

$$\begin{aligned} \underline{14.6} \quad \mathcal{E} \equiv \phi_R - \phi_L &= \phi_{\text{Cu}} - \phi_{\text{Cu}'} = (\phi_{\text{Cu}} - \phi_{\text{CuSO}_4(\text{aq})}) + \\ &+ (\phi_{\text{CuSO}_4(\text{aq})} - \phi_{\text{ZnSO}_4(\text{aq})}) + (\phi_{\text{ZnSO}_4(\text{aq})} - \phi_{\text{Zn}}) + \\ &+ (\phi_{\text{Zn}} - \phi_{\text{Cu}'}) = 0.3 \text{ V} - 0.1 \text{ V} + 0 + 0.2 \text{ V} = 0.4 \text{ V.} \end{aligned}$$

$$\underline{14.7} \quad (\underline{a}) \quad 2; \quad (\underline{b}) \quad 1; \quad (\underline{c}) \quad 2; \quad (\underline{d}) \quad 6; \quad (\underline{e}) \quad 2.$$

$$\begin{aligned} \underline{14.8} \quad \Delta G_{298}^\circ / (\text{kJ/mol}) &= 0 + 4(0) + 2(-111.25) - 97.89 \\ &= -65.49 - 2(-237.129) = 88.38. \end{aligned}$$

$$\mathcal{E}^{\circ} = -\Delta G^{\circ}/n\mathcal{F} =$$

$$-(88380 \text{ J/mol})/2(96485 \text{ C/mol}) = -0.458 \text{ V.}$$

14.9 (a) The NaCl changes the ionic strength and hence changes the activity coefficients and the activities.

Therefore \mathcal{E} changes. (b) By definition, $\mathcal{E}^{\circ} \equiv -\Delta G^{\circ}/n\mathcal{F}$. The NaCl doesn't change ΔG° and so doesn't change \mathcal{E}° .

14.10 (a) Equation (14.49) applies. We plot the left side (l.s.) of (14.49) vs. $(m/m^{\circ})^{\frac{1}{2}}$. We have $\text{l.s.} = \mathcal{E} + [2(8.314 \text{ J/mol-K})(333.15 \text{ K})/(96485 \text{ C/mol})] \ln (m/m^{\circ}) = \mathcal{E} + (0.05741 \text{ V}) \ln (m/m^{\circ})$. The data are

l.s./V	0.1985	0.1993	0.2008	0.2104
$(m/m^{\circ})^{\frac{1}{2}}$	0.03162	0.04472	0.07071	0.31622

Plotting the three points at high dilution and drawing a straight line through them, we find the intercept to be $\mathcal{E}^{\circ} = 0.1966 \text{ V}$. (b) From Eq. (14.49), $(2RT/\mathcal{F}) \ln \gamma_{\pm} = \mathcal{E}^{\circ} - \text{l.s.}$ and $\ln \gamma_{\pm} = (17.417 \text{ V}^{-1})(0.1966 \text{ V} - \text{l.s.}) = 3.424 - 17.417(\text{l.s.}/\text{V})$. At 0.005 mol/kg , $\ln \gamma_{\pm} = 3.424 - 17.417(0.2008) = -0.073$ and $\gamma_{\pm} = 0.930$. At 0.1 mol/kg , $\ln \gamma_{\pm} = -0.240_5$ and $\gamma_{\pm} = 0.786$.

14.11 (a) $\ln \phi = B^{\dagger}P = BP/RT = (14.0 \text{ cm}^3/\text{mol}) \times (750/760) \text{ atm} / (82.06 \text{ cm}^3\text{-atm/mol-K})(298.1 \text{ K}) = 0.00056_5$ and $\phi = 1.00056_5$. $f = \phi P = 1.00056_5 \text{ bar}$. (b) The half-reaction is $\text{H}_2 \rightarrow 2\text{H}^{+} + 2\text{e}^{-}$ and the error in \mathcal{E} is

$$(RT/n\mathcal{F}) \ln f(\text{H}_2) - (RT/n\mathcal{F}) \ln P(\text{H}_2) = (RT/n\mathcal{F}) \ln (f/P) = \\ (RT/n\mathcal{F}) \ln \phi = [(8.3145 \text{ J/mol-K})(298.15 \text{ K})/(2(96485 \text{ C/mol}))] \times \\ 0.00056_5 = 0.0000073 \text{ V.}$$

14.12 Equation (14.39) shows that \mathcal{E} depends only on the chemical potentials μ_i of the species involved in the cell's chemical reaction, so \mathcal{E} must be independent of what metals are used for the terminals.

14.13 (a) Doubled; (b) squared; (c) doubled, since $\ln Q^2 = 2 \ln Q$; (d) unchanged.

14.14 (a) Equation (14.21) applied to $\text{Cu} \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + 2\text{e}^-(\text{Cu})$ gives $\tilde{\mu}_{\text{Cu}} = \tilde{\mu}_{\text{Cu}^{2+}(\text{aq})} + 2\tilde{\mu}_{\text{e}^-(\text{Cu})}$. Substitution of (14.19) for $\tilde{\mu}$ of each species gives $\mu_{\text{Cu}} = \mu_{\text{Cu}^{2+}(\text{aq})} + 2\mathcal{F}\phi(\text{aq. CuSO}_4) + 2[\mu_{\text{e}^-(\text{Cu})} - \mathcal{F}\phi(\text{Cu})]$ and $\phi(\text{Cu}) - \phi(\text{aq. CuSO}_4) = [\mu_{\text{Cu}^{2+}(\text{aq})} - \mu_{\text{Cu}} + 2\mu_{\text{e}^-(\text{Cu})}]/2\mathcal{F}$. (b) By analogy to the result of (a), we have $\phi(\text{Zn}) - \phi(\text{aq. ZnSO}_4) = [\mu_{\text{Zn}^{2+}(\text{aq})} - \mu_{\text{Zn}} + 2\mu_{\text{e}^-(\text{Zn})}]/2\mathcal{F}$. (c) For $\text{e}^-(\text{Cu}') \rightleftharpoons \text{e}^-(\text{Zn})$, Eqs. (14.21) and (14.19) give $\tilde{\mu}_{\text{e}^-(\text{Cu}')} = \tilde{\mu}_{\text{e}^-(\text{Zn})}$, $\mu_{\text{e}^-(\text{Cu}')} - \mathcal{F}\phi(\text{Cu}') = \mu_{\text{e}^-(\text{Zn})} - \mathcal{F}\phi(\text{Zn})$, and $\phi(\text{Cu}') - \phi(\text{Zn}) = [\mu_{\text{e}^-(\text{Cu}')} - \mu_{\text{e}^-(\text{Zn})}]/\mathcal{F}$. (d) Substitution in (14.25) and use of $\mathcal{E}_J \equiv \phi(\text{aq. CuSO}_4) - \phi(\text{aq. ZnSO}_4)$ gives $\mathcal{E} = [\mu_{\text{Cu}^{2+}(\text{aq})} - \mu_{\text{Cu}} + 2\mu_{\text{e}^-(\text{Cu})}]/2\mathcal{F} + \mathcal{E}_J - [\mu_{\text{Zn}^{2+}(\text{aq})} - \mu_{\text{Zn}} + 2\mu_{\text{e}^-(\text{Zn})}]/2\mathcal{F} + (\mu_{\text{e}^-(\text{Zn})} - \mu_{\text{e}^-(\text{Cu}')})/\mathcal{F} = \mathcal{E}_J + (\mu_{\text{Cu}^{2+}(\text{aq})} + \mu_{\text{Zn}} - \mu_{\text{Zn}^{2+}(\text{aq})} - \mu_{\text{Cu}})/2\mathcal{F}$, since $\mu_{\text{e}^-(\text{Cu})} = \mu_{\text{e}^-(\text{Cu}')} \text{ (Sec. 14.3)}$. Substitution of $\mu_i = \mu_i^\circ + RT \ln a_i$ for each species gives $\mathcal{E} = \mathcal{E}_J +$

$$(\mu_{\text{Cu}^{2+}(\text{aq})}^{\circ} + \mu_{\text{Zn}}^{\circ} - \mu_{\text{Zn}^{2+}(\text{aq})}^{\circ} - \mu_{\text{Cu}}^{\circ})/2\mathcal{F} + (RT/2\mathcal{F}) \times$$

$$(\ln a_{\text{Cu}^{2+}(\text{aq})} + \ln a_{\text{Zn}} - \ln a_{\text{Zn}^{2+}(\text{aq})} - \ln a_{\text{Cu}}) = \mathcal{E}_J$$

$$- \Delta G^{\circ}/2\mathcal{F} - (RT/2\mathcal{F}) \ln [a_{\text{Zn}^{2+}(\text{aq})} a_{\text{Cu}} / a_{\text{Cu}^{2+}(\text{aq})} a_{\text{Zn}}],$$

which is (14.51), since $\mathcal{E}^{\circ} = -\Delta G^{\circ}/2\mathcal{F}$.

14.15 (a) $\Delta G_{298}^{\circ}/(\text{kJ/mol}) = 2(-4.7) + 3(0) - 3(65.49)$
 $- 2(0) = -205.9$. $\Delta G^{\circ} =$
 $= -2.06 \times 10^5 \text{ J/mol}$. $\mathcal{E}^{\circ} = -\Delta G^{\circ}/n\mathcal{F} = (2.06 \times 10^5 \text{ J/mol})/$
 $6(96485 \text{ C/mol}) = 0.356 \text{ V}$. (b) The left half-reaction must
be an oxidation and is $\text{Fe} \rightarrow \text{Fe}^{3+} + 3\text{e}^{-}$; the right half-
reaction is $\text{Cu}^{2+} + 2\text{e}^{-} \rightarrow \text{Cu}$. Then $\mathcal{E}^{\circ} = \mathcal{E}_{\text{R}}^{\circ} - \mathcal{E}_{\text{L}}^{\circ} =$
 $0.34 \text{ V} - (-0.04 \text{ V}) = 0.38 \text{ V}$.

14.16 (a) At 25°C , $\mathcal{E}^{\circ} = -1.978 \text{ V} = \mathcal{E}_{\text{R}}^{\circ} - \mathcal{E}_{\text{L}}^{\circ} =$
 $\mathcal{E}_{\text{nonesuch}}^{\circ} - \mathcal{E}_{\text{calomel}}^{\circ} = \mathcal{E}_{\text{nonesuch}}^{\circ} - 0.268 \text{ V}$ and
 $\mathcal{E}_{\text{nonesuch}}^{\circ} = -1.710 \text{ V}$. (b) Use of $\mathcal{E}^{\circ} = \mathcal{E}_{\text{R}}^{\circ} - \mathcal{E}_{\text{L}}^{\circ}$ gives
at 43°C : $-0.80 \text{ V} = \mathcal{E}_{\text{nonpareil}}^{\circ} - \mathcal{E}_{\text{calomel}}^{\circ}$ and $1.70 \text{ V} =$
 $\mathcal{E}_{\text{calomel}}^{\circ} - \mathcal{E}_{\text{nonesuch}}^{\circ}$. Addition of these equations gives
 $0.90 \text{ V} = \mathcal{E}_{\text{nonpareil}}^{\circ} - \mathcal{E}_{\text{nonesuch}}^{\circ}$. For the cell
nonpareil | nonesuch, $\mathcal{E}^{\circ} = \mathcal{E}_{\text{nonesuch}}^{\circ} - \mathcal{E}_{\text{nonpareil}}^{\circ} =$
 -0.90 V

14.17 $\mathcal{E}^{\circ} = \mathcal{E}_{\text{R}}^{\circ} - \mathcal{E}_{\text{L}}^{\circ} = 0.222 \text{ V} - 0 = 0.222 \text{ V}$. We have
 $\mathcal{E} = \mathcal{E}^{\circ} - (RT/n\mathcal{F}) \ln Q$ so $\ln Q = (n\mathcal{F}/RT)(\mathcal{E}^{\circ} - \mathcal{E})$.
We shall write the cell reaction using the smallest inte-
gers as coefficients, as in Eq. (14.34). (a) $\ln Q =$
 $2(96485 \text{ C/mol})(0.222 \text{ V} + 1.00 \text{ V})/(8.314 \text{ J/mol-K})(298.1 \text{ K})$

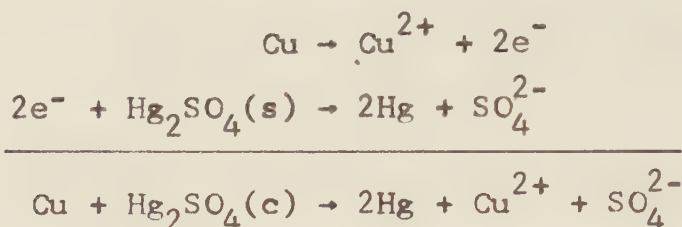
= 95.1 and $Q = 2 \times 10^{41}$. (b) With $\mathcal{E} = 1.00$ V, we get $\ln Q = -60.6$ and $Q = 5 \times 10^{-27}$.

14.18 The emf is given by Eq. (14.45) and the following paragraph as $\mathcal{E} = \mathcal{E}^\circ + (RT/2\mathcal{F}) \ln [P(\text{H}_2)/P^\circ]$, where $a(\text{H}^+)a(\text{Cl}^-) = a(\text{HCl}) = 1$. We have $\ln [P(\text{H}_2)/P^\circ] = (2\mathcal{F}/RT)(\mathcal{E} - \mathcal{E}^\circ) = (77.85 \text{ V}^{-1})(\mathcal{E} - 0.222 \text{ V})$. (a) $\ln [P(\text{H}_2)/P^\circ] = (77.85 \text{ V}^{-1})(-0.500 \text{ V} - 0.222 \text{ V}) = -56.2_1$ and $P(\text{H}_2) = 4 \times 10^{-25} \text{ atm}$. (b) $\ln [P(\text{H}_2)/P^\circ] = 21.6_4$ and $P(\text{H}_2) = 2.5 \times 10^9 \text{ atm}$. (This answer is only approximate, since at this high pressure we should use the fugacity, rather than the pressure, of H_2 .)

14.19 (a) The left half-reaction is an oxidation, so the half-reactions are $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^-$ and $\text{I}_2 + 2e^- \rightarrow 2\text{I}^-$. Multiplying the left half-reaction by 2 and adding it to the right one, we get as the cell reaction: $2\text{Fe}^{2+} + \text{I}_2 \rightarrow 2\text{Fe}^{3+} + 2\text{I}^-$. (b) $\mathcal{E}^\circ = \mathcal{E}_R^\circ - \mathcal{E}_L^\circ = 0.536 \text{ V} - 0.771 \text{ V} = -0.235 \text{ V}$. $\mathcal{E} = \mathcal{E}^\circ - (RT/n\mathcal{F}) \ln Q = -0.235 \text{ V} - [(8.314 \text{ J/mol-K})(298.1 \text{ K})/2(96485 \text{ C/mol})] \times \ln [(1.20)^2(0.100)^2/(2.00)^2 1] = -0.163 \text{ V}$. (c) $\mathcal{E} = \phi_R - \phi_L < 0$, so $\phi_R < \phi_L$ and the left-hand terminal is at the higher potential. (d) The negative value of \mathcal{E} indicates that the spontaneous cell reaction is in a direction opposite to that written in (a). Hence the half-reaction $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$ occurs spontaneously in the left half-cell. Electrons therefore flow into the left terminal from

the load.

14.20 (a) The left half-reaction is an oxidation, so



(b) $\mathcal{E}^\circ = \mathcal{E}_\text{R}^\circ - \mathcal{E}_\text{L}^\circ = 0.613 \text{ V} - 0.340 \text{ V} = 0.273 \text{ V}$. Equation (14.46) gives $a(\text{Cu}^{2+})a(\text{SO}_4^{2-}) = (\gamma_\text{i}m_\text{i}/m^\circ)^2 = [0.043(1.00)]^2 = 0.00185$. The activities of the solids are 1 and $\mathcal{E} = 0.273 \text{ V} - (RT/2\mathcal{F}) \ln 0.00185 = 0.354 \text{ V}$. (c) With $\gamma_\text{i} = 1$, we would get $\mathcal{E} = \mathcal{E}^\circ = 0.273 \text{ V}$.

14.21 The cell reaction is $\text{Zn} + 2\text{AgCl}(\text{c}) \rightleftharpoons \text{Zn}^{2+} + 2\text{Ag} + 2\text{Cl}^-$ and $\mathcal{E}^\circ = 0.222 \text{ V} - (-0.763 \text{ V}) = 0.985 \text{ V}$. Using Eq. (14.46), we have $\mathcal{E} = \mathcal{E}^\circ - (RT/2\mathcal{F}) \ln [a(\text{Zn}^{2+})a(\text{Cl}^-)^2] = \mathcal{E}^\circ - (RT/2\mathcal{F}) \ln [4(0.0100\gamma_\text{i})^3] = 0.985 \text{ V} - [(8.314 \text{ J/mol}\cdot\text{K})(298.15 \text{ K})/2(96485 \text{ C/mol})] \times \ln [4(0.0100)^3(0.708)^3] = 1.158 \text{ V}$.

14.22 Addition of (1) $\text{Cr}^{3+} + \text{e}^- \rightarrow \text{Cr}^{2+}$ and (2) $\text{Cr}^{2+} + 2\text{e}^- \rightarrow \text{Cr}$ gives (3) $\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr}$. Hence $\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$, which becomes $-n_3\mathcal{F}\mathcal{E}_3^\circ = -n_1\mathcal{F}\mathcal{E}_1^\circ - n_2\mathcal{F}\mathcal{E}_2^\circ$; so $\mathcal{E}_3^\circ = (n_1\mathcal{E}_1^\circ + n_2\mathcal{E}_2^\circ)/n_3 = [1(-0.424 \text{ V}) + 2(-0.90 \text{ V})]/3 = -0.74 \text{ V}$.

14.23 $\mathcal{E} = \mathcal{E}^\circ - (RT/n\mathcal{F}) \ln [a(\text{Zn}^{2+})/a(\text{Cu}^{2+})]$. The ZnSO_4 solution has $I_\text{m}/m^\circ = \frac{1}{2}[2^2(0.002) + 2^2(0.002)] = 0.00800$ and the Davies equation gives $\log \gamma(\text{Zn}^{2+}) = -0.163$, $\gamma(\text{Zn}^{2+})$

$= 0.68_8$. Also, $I_m/m^\circ = 0.00400$ for $\text{CuSO}_4(\text{aq})$; $\log \gamma(\text{Cu}^{2+}) = -0.119$; $\gamma(\text{Cu}^{2+}) = 0.76_0$. Use of $a_{m,i} = \gamma_i m_i/m^\circ$ gives $a(\text{Zn}^{2+}) = 0.68_8(0.00200) = 0.00138$ and $a(\text{Cu}^{2+}) = 0.00076_0$. So $\mathcal{E} = 0.340 \text{ V} - (-0.763 \text{ V}) - (RT/2\mathcal{F}) \ln(0.00138/0.00076_0) = 1.095 \text{ V}$.

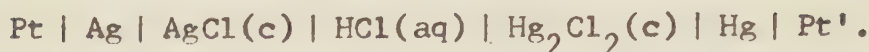
14.24 (a) The half-reactions are $\text{Ag} \rightarrow \text{Ag}^+(0.01m^\circ) + e^-$ and $\text{Ag}^+(0.05m^\circ) + e^- \rightarrow \text{Ag}$. The cell reaction is $\text{Ag}^+(0.05m^\circ) \rightarrow \text{Ag}^+(0.01m^\circ)$. We have $\mathcal{E}^\circ = \mathcal{E}_R^\circ - \mathcal{E}_L^\circ = 0$. Then $\mathcal{E} = 0 - (RT/\mathcal{F}) \ln [\gamma_{+,L}(0.01)/\gamma_{+,R}(0.05)] = -(0.02569 \text{ V})[-1.6094 + \ln(\gamma_{+,L}/\gamma_{+,R})] = 0.04135 \text{ V} - (0.02569 \text{ V}) \ln(\gamma_{+,L}/\gamma_{+,R})$. We have $I_{m,L} = 0.0100 \text{ mol/kg}$ and $I_{m,R} = 0.0500 \text{ mol/kg}$. The Davies equation for Ag^+ gives $\log \gamma_{+,L} = -0.0448$ and $\gamma_{+,L} = 0.902$; also, $\log \gamma_{+,R} = -0.0855_5$ and $\gamma_{+,R} = 0.821$. Hence $\mathcal{E} = 0.04135 \text{ V} - (0.02569 \text{ V}) \ln(0.902/0.821) = 0.0389 \text{ V}$. (b) $\mathcal{E} = \phi_R - \phi_L > 0$, so $\phi_R > \phi_L$. (c) The electrons flow from low to high potential and hence flow into the right terminal.

14.25 (a) $\text{Pt} \mid \text{Ag} \mid \text{AgCl}(\text{c}) \mid \text{KCl}(\text{aq}) \mid \text{Hg}_2\text{Cl}_2(\text{c}) \mid \text{Hg} \mid \text{Pt}'$.

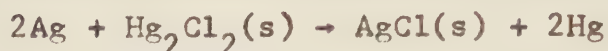
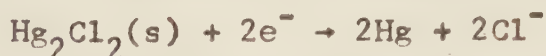
(b) $\text{Pt} \mid \text{H}_2 \mid \text{H}_2\text{SO}_4(\text{aq}) \mid \text{Hg}_2\text{SO}_4(\text{c}) \mid \text{Hg} \mid \text{Pt}'$ (or we can use a $\text{Pb} \mid \text{PbSO}_4$ half-cell).

14.26 Equation (14.60) gives $\mathcal{E} = -[(8.314 \text{ J/mol-K})(358.1 \text{ K})/2(96485 \text{ C/mol})] \ln(2521/666) = -0.0205 \text{ V}$.

14.27 $\text{Pt}' \mid \text{H}_2 \mid \text{HCl}(\text{aq}) \mid \text{Cl}_2 \mid \text{Pt}$,



$$\underline{14.28} \quad (\underline{a}) \quad [\text{Ag} + \text{Cl}^- \rightarrow \text{AgCl}(\text{s}) + \text{e}^-] \times 2$$



$$(\underline{b}) \quad \mathcal{E} = \mathcal{E}^\circ - (RT/2\mathcal{F}) \ln [a(\text{AgCl})a^2(\text{Hg})/a^2(\text{Ag})a(\text{Hg}_2\text{Cl}_2)]$$

$= \mathcal{E}^\circ$, since the activities of the solids can be taken as 1. So $\mathcal{E} = \mathcal{E}^\circ = \mathcal{E}_R^\circ - \mathcal{E}_L^\circ = 0.2680 \text{ V} - 0.2221 \text{ V} = 0.0459 \text{ V}$.

$$1. \text{ So } \mathcal{E} = \mathcal{E}^\circ = \mathcal{E}_R^\circ - \mathcal{E}_L^\circ = 0.2680 \text{ V} - 0.2221 \text{ V} = 0.0459 \text{ V}.$$

$$(\underline{c}) \quad \mathcal{E} = \mathcal{E}^\circ = 0.0459 \text{ V}. \quad (\underline{d}) \text{ Since } \mathcal{E} = \mathcal{E}^\circ, \text{ we have}$$

$$\partial \mathcal{E} / \partial T = \partial \mathcal{E}^\circ / \partial T. \text{ So } \Delta S^\circ = n\mathcal{F}(\partial \mathcal{E}^\circ / \partial T)_P =$$

$$2(96485 \text{ C/mol})(0.000338 \text{ V/K}) = 65.2 \text{ J/mol-K}. \quad \Delta G^\circ =$$

$$-n\mathcal{F}\mathcal{E}^\circ = -2(96485 \text{ C/mol})(0.0459 \text{ V}) = -8860 \text{ J/mol}. \quad \Delta H^\circ =$$

$$\Delta G^\circ + T \Delta S^\circ = -8860 \text{ J/mol} + (298.1 \text{ K})(65.2 \text{ J/mol-K}) =$$

$$10.6 \text{ kJ/mol}.$$

$$\underline{14.29} \quad \mathcal{E}^\circ = \mathcal{E}_R^\circ - \mathcal{E}_L^\circ = 0 - (-0.01 \text{ V}) = 0.01 \text{ V}. \quad \Delta G^\circ =$$

$$-n\mathcal{F}\mathcal{E}^\circ = -RT \ln K^\circ \text{ and } \ln K^\circ = n\mathcal{F}\mathcal{E}^\circ / RT =$$

$$2(96485 \text{ C/mol})(0.01 \text{ V}) / (8.314 \text{ J/mol-K})(298.1 \text{ K}) = 0.8.$$

$$K^\circ = 2.$$

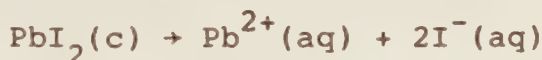
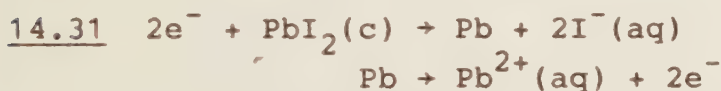
$$\underline{14.30} \quad (\underline{a}) \text{ For the reaction } 2\text{Na}^+ + \text{H}_2 \rightarrow 2\text{Na} + 2\text{H}^+, \text{ we have}$$

$$\mathcal{E}_{298}^\circ = \mathcal{E}_R^\circ - \mathcal{E}_L^\circ = -2.714 \text{ V} - 0 = -2.714 \text{ V}. \text{ Then } \Delta G_{298}^\circ =$$

$$-n\mathcal{F}\mathcal{E}^\circ = -2(96485 \text{ C/mol})(-2.714 \text{ V}) = 5.237 \times 10^5 \text{ J/mol} =$$

$$2(0) + 2(0) - 2\Delta G_{f,298}^\circ(\text{Na}^+) - 2(0) \text{ and } \Delta G_{f,298}^\circ(\text{Na}^+) =$$

$-2.619 \times 10^5 \text{ J/mol} = -261.9 \text{ kJ/mol}$. (b) For the reaction $2\text{Cl}^- + 2\text{H}^+ \rightarrow \text{Cl}_2 + \text{H}_2$, we have $\mathcal{E}_{298}^\circ = 0 - (1.358 \text{ V}) = -1.358 \text{ V}$. Then $\Delta G_{298}^\circ = -2(96485 \text{ C/mol})(-1.358 \text{ V}) = 2.621 \times 10^5 \text{ J/mol} = 0 + 0 - 2\Delta G_{f,298}^\circ(\text{Cl}^-) - 2(0)$ and $\Delta G_{f,298}^\circ(\text{Cl}^-) = -1.310 \times 10^5 \text{ J/mol} = -131.0 \text{ kJ/mol}$. (c) For the reaction $\text{Cu}^{2+} + \text{H}_2 \rightarrow \text{Cu} + 2\text{H}^+$, $\mathcal{E}_{298}^\circ = 0.340 \text{ V} - 0 = 0.340 \text{ V}$ and $\Delta G_{298}^\circ = -2(96485 \text{ C/mol})(0.340 \text{ V}) = -6.56 \times 10^4 \text{ J/mol} = 0 + 2(0) - \Delta G_{f,298}^\circ(\text{Cu}^{2+}) - 0$ and $\Delta G_{f,298}^\circ(\text{Cu}^{2+}) = 6.56 \times 10^4 \text{ J/mol} = 65.6 \text{ kJ/mol}$.



$\mathcal{E}^\circ = -0.365 \text{ V} - (-0.125 \text{ V}) = -0.240 \text{ V}$. $\Delta G^\circ = -n\mathcal{F}\mathcal{E}^\circ = -2(96485 \text{ C/mol})(-0.240 \text{ V}) = 4.63 \times 10^4 \text{ J/mol}$. $\ln K_{\text{sp}}^\circ = -\Delta G^\circ/RT = -(46300 \text{ J/mol})/(8.314 \text{ J/mol-K})(298.1 \text{ K}) = -18.68$ and $K_{\text{sp}}^\circ = 7.7 \times 10^{-9}$.

14.32 (a) The half-reactions are $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$ and $2(\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+})$. The cell reaction is $\text{Fe} + 2\text{Fe}^{3+} \rightarrow 3\text{Fe}^{2+}$. (b) $\Delta G^\circ = -n\mathcal{F}\mathcal{E}^\circ = -2(96485 \text{ C/mol}) \times [0.771 \text{ V} - (-0.440 \text{ V})] = -2.337 \times 10^5 \text{ J/mol}$. $\Delta S^\circ = n\mathcal{F}(\partial \mathcal{E}^\circ / \partial T)_P = 2(96485 \text{ C/mol})(0.00114 \text{ V/K}) = 220 \text{ J/mol-K}$. $\Delta H^\circ = \Delta G^\circ + T \Delta S^\circ = -2.337 \times 10^5 \text{ J/mol} + (298.1 \text{ K})(220 \text{ J/mol-K}) = -1.68 \times 10^5 \text{ J/mol}$.

14.33 (a) $\mathcal{E}^\circ = 1.358 \text{ V} - 1.065 \text{ V} = 0.293 \text{ V}$. $\Delta G^\circ = -2(96485 \text{ C/mol})(0.293 \text{ V}) = -56500 \text{ J/mol}$. $\ln K^\circ = -\Delta G^\circ/RT$

$= (56500 \text{ J/mol}) / (8.314 \text{ J/mol-K})(298.1 \text{ K}) = 22.8$ and $K^\circ = 8 \times 10^9$. (b) $\mathcal{E}^\circ = 0.293 \text{ V}$, $n = 1$, and $\Delta G^\circ = -28300 \text{ J/mol}$. $\ln K^\circ = 11.4_0$ and $K^\circ = 9.0 \times 10^4$. (c) The half-reactions are $2(\text{Ag} + \text{Cl}^- \rightarrow \text{AgCl} + \text{e}^-)$ and $\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$. $\mathcal{E}^\circ = 1.358 \text{ V} - 0.222 \text{ V} = 1.136 \text{ V}$. $\Delta G^\circ = -2(96485 \text{ C/mol})(1.136 \text{ V}) = -2.192 \times 10^5 \text{ J/mol}$. $\ln K^\circ = 88.4_3$ and $K^\circ = 2.5 \times 10^{38}$. (d) This is the reverse of (c), so $\Delta G^\circ = 2.19_2 \times 10^5 \text{ J/mol}$ and $K^\circ = (2.5 \times 10^{38})^{-1} = 4.0 \times 10^{-39}$. (e) The half-reactions are $2(\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-)$ and $\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$. $\mathcal{E}^\circ = -0.440 \text{ V} - 0.771 \text{ V} = -1.21 \text{ V}$. $\Delta G^\circ = 2.33_7 \times 10^5 \text{ J/mol}$, $\ln K^\circ = -94.2_7$ and $K^\circ = 1 \times 10^{-41}$.

14.34 Equations (14.65) and (14.66) give at 10°C : $\mathcal{E}^\circ = 0.23643 \text{ V} - (4.8621 \times 10^{-4} \text{ V/K})(10 \text{ K}) - (3.4205 \times 10^{-6} \text{ V/K}^2)(10 \text{ K})^2 + (5.869 \times 10^{-9} \text{ V/K}^3)(10 \text{ K})^3 = 0.23123 \text{ V}$. Then $\Delta G^\circ = -2(96485 \text{ C/mol})(0.23123 \text{ V}) = -4.4621 \times 10^4 \text{ J/mol}$. Equation (14.67) gives at 10°C : $\Delta S^\circ = 2(96485 \text{ C/mol})[-4.8621 \times 10^{-4} \text{ V/K} + 2(-3.4205 \times 10^{-6} \text{ V/K}^2)(10 \text{ K}) + 3(5.869 \times 10^{-9} \text{ V/K}^3)(10 \text{ K})^2] = -106.69 \text{ J/mol-K}$. Then $\Delta H^\circ = \Delta G^\circ + T \Delta S^\circ = -4.4621 \times 10^4 \text{ J/mol} + (283.15 \text{ K})(-106.69 \text{ J/mol-K}) = -7.4830 \times 10^4 \text{ J/mol}$. From (14.64) and (14.65), $\Delta C_p^\circ = 2\mathcal{F}T[2c + 6d(T - T_0)] = 2(96485 \text{ C/mol})(283.15 \text{ K}) \times [2(-3.4205 \times 10^{-6} \text{ V/K}^2) + 6(5.869 \times 10^{-9} \text{ V/K}^3)(10 \text{ K})] = -354.55 \text{ J/mol-K}$.

14.35 For the cell $\text{Ag}|\text{Ag}^+||\text{I}^-|\text{AgI(c)}|\text{Ag}$, we have the half-

reactions $\text{Ag} \rightarrow \text{Ag}^+ + \text{e}^-$ and $\text{AgI(c)} + \text{e}^- \rightarrow \text{Ag} + \text{I}^-$; the cell reaction is $\text{AgI(c)} \rightarrow \text{Ag}^+ + \text{I}^-$. Equation (14.68) gives $\mathcal{E}^\circ = RT \ln K_{\text{sp}}^\circ / n\mathcal{F} = (8.314 \text{ J/mol-K})(298.1 \text{ K}) \times \ln (8.2 \times 10^{-17}) / (96485 \text{ C/mol}) = -0.951 \text{ V} = \mathcal{E}_\text{R}^\circ - \mathcal{E}_\text{L}^\circ = \mathcal{E}_\text{R}^\circ - 0.799 \text{ V}$. Hence $\mathcal{E}_\text{R}^\circ = -0.152 \text{ V}$.

14.36 The half-reactions are $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$ and $2(\text{AgBr} + \text{e}^- \rightarrow \text{Ag} + \text{Br}^-)$. The cell reaction is $\text{H}_2 + 2\text{AgBr} \rightleftharpoons 2\text{H}^+ + 2\text{Br}^- + 2\text{Ag}$. $\mathcal{E}^\circ = 0.071 \text{ V}$. Equation (14.46) gives

$$\begin{aligned} \mathcal{E} &= \mathcal{E}^\circ - (RT/2\mathcal{F}) \ln \{a(\text{H}^+)^2 a(\text{Br}^-)^2 / [P(\text{H}_2)/P^\circ]\} = \\ &= \mathcal{E}^\circ - (RT/\mathcal{F}) \ln [a(\text{H}^+)a(\text{Br}^-)] = \mathcal{E}^\circ - (RT/\mathcal{F}) \times \\ &\ln (\gamma_1 m_1 / m^\circ)^2. \text{ Hence } 0.200 \text{ V} = 0.071 \text{ V} - \\ &[2(8.314 \text{ J/mol-K})(298.15 \text{ K}) / (96485 \text{ C/mol})] \ln (0.100\gamma_1). \end{aligned}$$

We get $\ln (0.100\gamma_1) = -2.51_1$ and $\gamma_1 = 0.81$.

14.37 As in Prob. 14.30b, we find $\Delta G_\text{f}^\circ(\text{Cl}^-) = -131.0 \text{ kJ/mol}$. Since $\mu^\circ(\text{HCl}) = \mu^\circ(\text{H}^+) + \mu^\circ(\text{Cl}^-)$ [see Eq. (10.44)] and $\Delta G_\text{f}^\circ(\text{H}^+) = 0$, we have $\Delta G_\text{f}^\circ[\text{HCl(aq)}] = -131.0 \text{ kJ/mol}$.

14.38 (a) The half-reactions are $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$ and $2[\text{AgCl(c)} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-]$. The cell reaction is $\text{H}_2 + 2\text{AgCl(c)} \rightarrow 2\text{H}^+ + 2\text{Cl}^- + 2\text{Ag}$. The solids' activities can be taken as 1, and $\mathcal{E} = \mathcal{E}^\circ - (RT/2\mathcal{F}) \times \ln \{[a(\text{H}^+)]^2 [a(\text{Cl}^-)]^2\} = \mathcal{E}^\circ - (RT/\mathcal{F}) \ln [a(\text{H}^+)a(\text{Cl}^-)]$. Since we are writing H^+ rather than H_3O^+ , we write the water ionization as $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$. Then $K_\text{w}^\circ = a(\text{H}^+)a(\text{OH}^-)/a(\text{H}_2\text{O})$ and $a(\text{H}^+) = K_\text{w}^\circ a(\text{H}_2\text{O})/a(\text{OH}^-)$. Hence $a(\text{H}^+)a(\text{Cl}^-) =$

$$K_w^\circ a(\text{H}_2\text{O})a(\text{Cl}^-)/a(\text{OH}^-) = K_w^\circ a(\text{H}_2\text{O})\gamma(\text{Cl}^-)m(\text{Cl}^-)/\gamma(\text{OH}^-)m(\text{OH}^-).$$

Substitution in the above equation for \mathcal{E} gives the desired result. (b) As $I_m \rightarrow 0$, the γ 's go to 1 and $a(\text{H}_2\text{O})$

goes to 1. Hence $\mathcal{E} \rightarrow \mathcal{E}^\circ - (RT/\mathcal{F}) \ln [K_w^\circ m(\text{Cl}^-)/m(\text{OH}^-)]$.

$$\begin{aligned} \text{So } \ln K_w^\circ &= (\mathcal{F}/RT) \{ \mathcal{E}^\circ - \mathcal{E} - (RT/\mathcal{F}) \ln [m(\text{Cl}^-)/m(\text{OH}^-)] \}^\infty \\ &= [(96485 \text{ C/mol}) / (8.314 \text{ J/mol-K})(298.15 \text{ K})] (-0.8279 \text{ V}) = \\ &= -32.22_5 \text{ and } K_w^\circ = 1.01 \times 10^{-14}. \end{aligned}$$

14.39 (a) The half-reactions are the same as in Prob.

14.38a and the cell reaction is $\text{H}_2 + 2\text{AgCl}(\text{c}) \rightarrow 2\text{H}^+ +$

$2\text{Cl}^- + 2\text{Ag}$. As in Prob. 14.38a, $\mathcal{E} = \mathcal{E}^\circ - (RT/\mathcal{F}) \times$
 $\ln [a(\text{H}^+)a(\text{Cl}^-)]$. For the ionization $\text{HX} \rightleftharpoons \text{H}^+ + \text{X}^-$, we have

$K_a^\circ = a(\text{H}^+)a(\text{X}^-)/a(\text{HX})$ and $a(\text{H}^+) = K_a^\circ a(\text{HX})/a(\text{X}^-)$. Hence

$$a(\text{H}^+)a(\text{Cl}^-) = K_a^\circ a(\text{HX})a(\text{Cl}^-)/a(\text{X}^-) =$$

$K_a^\circ \gamma(\text{HX})m(\text{HX})\gamma(\text{Cl}^-)m(\text{Cl}^-)/\gamma(\text{X}^-)m(\text{X}^-)m^\circ$. Substitution in the
 above equation for \mathcal{E} gives the desired result. (b) As

$I_m \rightarrow 0$, the γ 's $\rightarrow 1$ and we get $\ln K_a^\circ =$

$$(\mathcal{F}/RT) \{ \mathcal{E}^\circ - \mathcal{E} - (RT/\mathcal{F}) \ln [m(\text{Cl}^-)m(\text{HX})/m(\text{X}^-)m^\circ] \}^\infty =$$

$$[(96485 \text{ C/mol}) / (8.314 \text{ J/mol-K})(298.15 \text{ K})] (-0.2814 \text{ V}) =$$

$$-10.953 \text{ and } K_a^\circ = 1.75 \times 10^{-5}.$$

$$\underline{14.40} \quad \text{Sn} + \text{Pb}^{2+} \rightleftharpoons \text{Sn}^{2+} + \text{Pb}. \quad \mathcal{E}^\circ = -0.125 \text{ V} + 0.136 \text{ V} =$$

$$0.011 \text{ V}. \quad \ln K^\circ = n\mathcal{F}\mathcal{E}^\circ/RT = 2(96485 \text{ C/mol})(0.011 \text{ V})/$$

$$(8.314 \text{ J/mol-K})(298 \text{ K}) = 0.86 \quad \text{and } K^\circ = 2.4. \quad \text{The solids'}$$

activities can be taken as 1, so $2.4 = a(\text{Sn}^{2+})/a(\text{Pb}^{2+}) \approx$

$m(\text{Sn}^{2+})/m(\text{Pb}^{2+}) = z/(0.1 - z)$. We find $z = 0.070$. Hence

$m(\text{Sn}^{2+}) = 0.07 \text{ mol/kg}$ and $m(\text{Pb}^{2+}) = 0.03 \text{ mol/kg}$. The so-

lution is reasonably dilute, so we expect the activity coefficients to be determined mainly by the ionic strength. Hence $\gamma(\text{Pb}^{2+}) \approx \gamma(\text{Sn}^{2+})$ and the activity coefficients cancel in the expression for K° .

14.41 $\mathcal{G}_X = 612 \text{ mV}$ and $\mathcal{G}_S = 741 \text{ mV}$. Equation (14.73) gives $\text{pH}(X) = 6.86 + [(612 - 741)10^{-3} \text{ V}](96485 \text{ C/mol}) / (8.314 \text{ J/mol-K})(298.1 \text{ K})2.3026 = 4.68$.

14.42 In Eq. (14.78), we take $\gamma_{\text{Na}^+}^\alpha \approx \gamma_{\text{Na}^+}^\beta$, since the ionic strengths of the two solutions are equal. Then $\phi^\beta - \phi^\alpha = [(8.314 \text{ J/mol-K})(298.1 \text{ K}) / (96485 \text{ C/mol})] \ln 0.100/0.150 = -0.0104 \text{ V}$, where β is the $\text{NaNO}_3\text{-KNO}_3$ solution.

14.43 $p = \delta d$ and $\delta = p/d = (3.57 \times 10^{-30} \text{ C m}) / (1.30 \times 10^{-10} \text{ m}) = 2.75 \times 10^{-20} \text{ C}$. $\delta/e = (2.75 \times 10^{-20} \text{ C}) / (1.60 \times 10^{-19} \text{ C}) = 0.172$.

14.44 (a) $1/r_2 - 1/r_1 = (r_1 - r_2)/r_1 r_2 = (r_1 - r_2)(r_1 + r_2)/r_1 r_2 (r_1 + r_2) = (r_1^2 - r_2^2)/r_1 r_2 (r_1 + r_2)$.

(b) For $r \gg d$, we have $r_1 \approx r_2 \approx r$, and $1/r_2 - 1/r_1 \approx (r_1^2 - r_2^2)/2r^3$. The law of cosines for triangle PAC gives $r_2^2 = r_1^2 + d^2 - 2r_1 d \cos \theta$. (Because $r \gg d$, angle PAC is very nearly equal to angle PBC.) Then $r_1^2 - r_2^2 = 2r_1 d \cos \theta - d^2 = d(2r_1 \cos \theta - d) \approx 2rd \cos \theta$, since $d \ll r_1$. (c) $\phi = (Q/r_2 - Q/r_1)/4\pi\epsilon_0 = Q(2rd \cos \theta)/2r^3(4\pi\epsilon_0) = (p \cos \theta)/4\pi\epsilon_0 r^2$, since $p = Qd$.

$$\underline{14.45} \text{ (a) } w = \int_1^2 F \, dr = -(Q_1 Q_2 / 4\pi\epsilon_0) \int_1^2 r^{-2} \, dr = \\ -(Q_1 Q_2 / 4\pi\epsilon_0) (1/r_1 - 1/r_2) =$$

$$\frac{(1.602 \times 10^{-19} \text{ C})^2}{4\pi(8.854 \times 10^{-12} \text{ C}^2/\text{N}\cdot\text{m}^2)} \left(\frac{1}{10^{-9} \text{ m}} - \frac{1}{10^{-8} \text{ m}} \right) = 2.08 \times 10^{-19} \text{ J}$$

(b) From Eq. (14.89), we include a factor $1/\epsilon_r$, where (Sec. 10.6) $\epsilon_r = 78.40$; so $w = (2.08 \times 10^{-19} \text{ J})/78.40 = 2.65 \times 10^{-21} \text{ J}$.

14.46 $p = 0$ for CCl_4 and Eq. (14.87) gives

$$\frac{1.24}{4.24} \frac{153.8 \text{ g/mol}}{1.59 \text{ g/cm}^3} = \frac{6.022 \times 10^{23} \text{ mol}^{-1}}{3(8.854 \times 10^{-12} \text{ C}^2/\text{N}\cdot\text{m}^2)} \alpha$$

$$\text{and } \alpha = 1.25 \times 10^{-33} \text{ cm}^3 \cdot \text{C}^2/\text{N}\cdot\text{m}^2 = 1.25 \times 10^{-39} \text{ C}^2\cdot\text{m}/\text{N}. \\ \alpha/4\pi\epsilon_0 = (1.25 \times 10^{-39} \text{ C}^2\cdot\text{m}/\text{N})/4\pi(8.854 \times 10^{-12} \text{ C}^2/\text{N}\cdot\text{m}^2) \\ = 1.12 \times 10^{-29} \text{ m}^3 = 11.2 \text{ \AA}^3.$$

14.47 (a) $p = 0$ for CH_4 . Also, $PV = (m/M)RT$ and $M/\rho = RT/P$. Equation (14.87) gives

$$\frac{0.00094}{3.001} \frac{(82.06 \times 10^{-6} \text{ m}^3\cdot\text{atm}/\text{mol}\cdot\text{K})(273.1 \text{ K})}{1.00 \text{ atm}} = \\ \frac{6.022 \times 10^{23} \text{ mol}^{-1}}{3(8.854 \times 10^{-12} \text{ C}^2/\text{N}\cdot\text{m}^2)} \alpha$$

$$\alpha = 3.10 \times 10^{-40} \text{ C}^2 \text{ N}^{-1} \text{ m}. \text{ Also, } \alpha/4\pi\epsilon_0 = \\ (3.10 \times 10^{-40} \text{ C}^2\cdot\text{m}/\text{N})/4\pi(8.854 \times 10^{-12} \text{ C}^2/\text{N}\cdot\text{m}^2) = \\ 2.78 \times 10^{-30} \text{ m}^3 = 2.78 \text{ \AA}^3. \text{ (b) } \epsilon_r + 2 \approx 3. \text{ } M/\rho = RT/P.$$

$p = 0$. Equation (14.87) gives $\epsilon_r - 1 = PN_A \alpha / RT \epsilon_0 = 4\pi PN_A (\alpha / 4\pi \epsilon_0) / RT = 4\pi (10.0 \text{ atm}) (6.022 \times 10^{23} \text{ mol}^{-1}) \times (2.78 \times 10^{-30} \text{ m}^3) / (82.06 \times 10^{-6} \text{ m}^3 \text{-atm/mol-K}) (373.1 \text{ K}) = 0.00687$ and $\epsilon_r = 1.00687$.

14.48 Equation (14.87) applies. We plot

$M\rho^{-1}(\epsilon_r - 1)/(\epsilon_r + 2)$ vs. $1/T$. Noting that $M/\rho = RT/P$ for a gas, we have

$10^5 M\rho^{-1}(\epsilon_r - 1)/(\epsilon_r + 2)$	5.73	5.35	5.00 ₅	4.67	4.31
$10^3/(T/K)$	2.602	2.380	2.249	2.066	1.916

where the units of the first line are m^3/mol . The plot is reasonably linear with slope $0.0210 \text{ m}^3\text{-K/mol} = N_A p^2 / 9 \epsilon_0 k$.

So $p^2 = (0.0210 \text{ m}^3\text{-K/mol}) 9 (8.854 \times 10^{-12} \text{ C}^2/\text{N-m}^2) \times (1.381 \times 10^{-23} \text{ J/K}) / (6.022 \times 10^{23} \text{ mol}^{-1}) = 3.84 \times 10^{-59} \text{ C}^2 \text{ m}^2$ and $p = 6.19 \times 10^{-30} \text{ C m}$. The intercept is

$3.2 \times 10^{-6} \text{ m}^3/\text{mol} = N_A \alpha / 3 \epsilon_0$, and

$$\alpha = \frac{3(8.854 \times 10^{-12} \text{ C}^2/\text{N-m}^2)(3.2 \times 10^{-6} \text{ m}^3/\text{mol})}{6.022 \times 10^{23} \text{ mol}^{-1}}$$

$$\alpha = 1.4 \times 10^{-40} \text{ C}^2\text{-m/N}$$

[Using Eqs. (20.2) and (20.3), one finds that the dipole moment is 1.86 D. Also, one finds $\alpha / 4\pi \epsilon_0 = 1.3 \times 10^{-30} \text{ m}^3 = 1.3 \text{ \AA}^3$.]

14.49 (a) CSe_2 , because of a greater α ; (b) $n\text{-C}_{10}\text{H}_{22}$; (c) o-dichlorobenzene, because of a greater p .

14.50 (a) Let $f \equiv (\epsilon_r - 1)/(\epsilon_r + 2)$. $df/d\epsilon_r = 1/(\epsilon_r + 2) - (\epsilon_r - 1)/(\epsilon_r + 2)^2 = [(\epsilon_r + 2) - (\epsilon_r - 1)]/(\epsilon_r + 2)^2 = 3/(\epsilon_r + 2)^2 > 0$. (b) We have $1 \leq \epsilon_r \leq \infty$. Since $df/d\epsilon_r > 0$ for all ϵ_r , the minimum value of f is at the minimum value of ϵ_r ; at $\epsilon_r = 1$, $f_{\min} = 0$. As $\epsilon_r \rightarrow \infty$, f approaches its maximum possible value, which is 1.

14.51 Let $P(K^+) = P_K$. Then $\phi^{\text{int}} - \phi^{\text{ext}} =$

$$0.02569 \text{ V} \ln \frac{P_K^{10} + 0.04P_K^{460} + 0.5P_K^{40}}{P_K^{410} + 0.04P_K^{49} + 0.5P_K^{540}}$$

$$= (0.02569 \text{ V}) \ln (48.4/682) = -0.068 \text{ V} = -68 \text{ mV}$$

14.52 The half-reactions are $\text{Ag} + \text{Cl}^-(0.0100\text{m}^\circ) \rightarrow \text{AgCl} + e^-$ and $\text{AgCl} + e^- \rightarrow \text{Ag} + \text{Cl}^-(0.100\text{m}^\circ)$. Equation (14.51) gives $\mathcal{E} = \mathcal{E}_J + 0 - (RT/\mathcal{F}) \ln (0.100\gamma_{-,R}/0.0100\gamma_{-,L})$. We have $I_{m,R} = 0.100 \text{ mol/kg}$ and the Davies equation for Cl^- gives $\log \gamma_{-,R} = -0.107_2$ and $\gamma_{-,R} = 0.781$. Similarly, $\gamma_{-,L} = 0.902$. Then $\mathcal{E} = -0.038 \text{ V}$
 $- [(8.314 \text{ J/mol-K})(298.15 \text{ K})/(96485 \text{ C/mol})] \ln 8.66 =$
 $-0.093 \text{ V}.$

14.53 $I_m = 0.100 \text{ mol/kg}$. The Davies equation for H^+ gives $\log \gamma_+ = -0.107_2$ and $\gamma_+ = 0.781$. Then $a(\text{H}^+) = (0.781)(0.100) = 0.0781$ and $-\log a(\text{H}^+) = 1.10_7$.

14.54 $K_C^\circ/K_m^\circ = ([a_C(\text{Ag}^+)]^2/a_C(\text{Cu}^{2+}))/([a_m(\text{Ag}^+)]^2/a_m(\text{Cu}^{2+}))$
 $= (0.997)^2/0.997 = 0.997$. $\Delta G^\circ = -RT \ln K^\circ = -n\mathcal{F}\mathcal{E}^\circ$ and
 $\mathcal{E}^\circ = (RT/n\mathcal{F}) \ln K^\circ$, so $\mathcal{E}_m^\circ - \mathcal{E}_C^\circ = (RT/n\mathcal{F})(\ln K_m^\circ -$

$$\ln K_C^\circ = -(RT/n\mathcal{F}) \ln (K_C^\circ/K_m^\circ) = -(RT/2\mathcal{F}) \ln 0.997 =$$

0.000039 V = 0.039 mV, which is insignificant.

14.55 (a) C; (b) m; (c) N/C = V/m; (d) V; (e) V; (f) C m;
(g) dimensionless; (h) J/mol.

14.56 If the left and right electrodes are at different temperatures, the emf is nonzero.

CHAPTER 15

15.1 (a) $E_{\text{tr}} = \frac{3}{2}nRT = 1.5(1.00 \text{ mol})(8.314 \text{ J/mol-K})(298 \text{ K})$
 $= 3720 \text{ J} = 889 \text{ cal.}$ (b) 3720 J. (c) $(0.470 \text{ g})/$
 $(16.0 \text{ g/mol}) = 0.0293 \text{ mol}$ and $\frac{3}{2}nRT = 109 \text{ J.}$

15.2 (a) $\langle \epsilon_{\text{tr}} \rangle = \frac{3}{2}kT = 1.5(1.381 \times 10^{-23} \text{ J/K})(571.1 \text{ K}) =$
 $1.18 \times 10^{-20} \text{ J.}$ (b) $1.18 \times 10^{-20} \text{ J.}$

15.3 $\langle \epsilon_{\text{tr}}(T_2) \rangle / \langle \epsilon_{\text{tr}}(T_1) \rangle = (3kT_2/2) / (3kT_1/2) = T_2/T_1 =$
 $(373.1 \text{ K}) / (273.1 \text{ K}) = 1.366.$

15.4 $\gamma = C_P/C_V = (5nR/2) / (3nR/2) = 5/3 = 1.6667.$

15.5 $v_{\text{rms}} = (3RT/M)^{1/2}$, so $v_{\text{rms}}(\text{Ne})/v_{\text{rms}}(\text{He}) = (M_{\text{He}}/M_{\text{Ne}})^{1/2}$
 $= (4.0026/20.179)^{1/2} = 0.4454.$

15.6 $v_{\text{rms}} = (3RT_{\text{H}_2}/M_{\text{H}_2})^{1/2} = (3RT_{\text{O}_2}/M_{\text{O}_2})^{1/2}$ and $T_{\text{H}_2} =$
 $(M_{\text{H}_2}/M_{\text{O}_2})T_{\text{O}_2} = (2.016/32.00)(293.1 \text{ K}) = 18.5 \text{ K.}$

15.7 $E_{\text{tr}} = \frac{3}{2}nRT = \frac{3}{2}PV = 1.5(1.00 \text{ atm})(90 \times 10^6 \text{ cm}^3) \times$
 $(8.314 \text{ J}) / (82.06 \text{ cm}^3 \text{ atm}) = 1.37 \times 10^7 \text{ J.}$ The answer is
the same for $40^\circ\text{C}.$

15.8 (a) $m/k = N_A m / N_A k = M/R.$ The interval is small
enough to be considered "infinitesimal" and Eq. (15.44)
gives $dN_V = 4\pi N(M/2\pi RT)^{3/2} e^{-Mv^2/2RT} v^2 dv =$

$$4\pi(6.02 \times 10^{23}) \left[\frac{0.0320 \text{ kg/mol}}{2\pi(8.314 \text{ J/mol-K})(300 \text{ K})} \right]^{3/2} \times$$

$$\exp \left[- \frac{(0.0320 \text{ kg/mol})(500 \text{ m/s})^2}{2(8.314 \text{ J/mol-K})(300 \text{ K})} \right] (500 \text{ m/s})^2 (0.001 \text{ m/s})$$

$= 1.1 \times 10^{18}$ (b) Considering the interval as infinitesimal and using (15.42) with x replaced by z , we have dN_{v_z}

$$= N(M/2\pi RT)^{\frac{1}{2}} \exp(-Mv_z^2/2RT) dv_z =$$

$$(6.02 \times 10^{23}) [0.0320 \text{ kg/mol} / 2\pi(8.314 \text{ J/mol-K})(300 \text{ K})]^{1/2} \times \exp[-(0.0320 \text{ kg/mol})(150 \text{ m/s})^2 / 2(8.314 \text{ J/mol-K})(300 \text{ K})] \times (0.001 \text{ m/s}) = 7.45 \times 10^{17}.$$

The fraction of molecules with x and z velocity components simultaneously in the ranges v_x to $v_x + dv_x$ and v_z to $v_z + dv_z$ is $g(v_x)g(v_z) \times dv_x dv_z = (dN_{v_x}/N)(dN_{v_z}/N)$ and the number of such molecules is $(dN_{v_x}/N)(dN_{v_z}/N)N = dN_{v_x} dN_{v_z} / N$. From part (b), $dN_{v_x} = dN_{v_z} = 7.45 \times 10^{17}$ and $dN_{v_x} dN_{v_z} / N = (7.45 \times 10^{17})^2 / (6.022 \times 10^{23}) = 9.22 \times 10^{11}$.

15.9 This probability equals $dN_v/N = 4\pi(M/2\pi RT)^{3/2} \times e^{-Mv^2/2RT} dv = 4\pi[(0.0160 \text{ kg/mol})/2\pi(8.314 \text{ J/mol-K})(300 \text{ K})]^{3/2} \times \exp[-(0.0160 \text{ kg/mol})(400 \text{ m/s})^2 / 2(8.314 \text{ J/mol-K})(300 \text{ K})] \times (400 \text{ m/s})^2 (0.001 \text{ m/s}) = 1.24 \times 10^{-6}$.

15.10(a) Equation (15.44) gives $(dN_{v_2}/N)/(dN_{v_1}/N) =$

$$\frac{v_2^2 e^{-mv_2^2/2kT}}{v_1^2 e^{-mv_1^2/2kT}} = (v_2^2/v_1^2) \exp [M(v_1^2 - v_2^2)/2RT] = \frac{500^2}{1500^2} \exp \left[\frac{(0.0320 \text{ kg/mol})(1500^2 - 500^2) \text{ m}^2/\text{s}^2}{2(8.314 \text{ J/mol-K})(298.1 \text{ K})} \right] = 45000$$

(b) From (15.44), $(m/2\pi kT)^{3/2} \exp(-mv_1^2/2kT) 4\pi v_1^2 = (m/2\pi kT)^{3/2} \exp(-mv_2^2/2kT) 4\pi v_2^2$ and $\exp[m(v_2^2 - v_1^2)/2kT] = v_2^2/v_1^2$. Taking logs, we have $m(v_2^2 - v_1^2)/2kT = 2 \ln(v_2/v_1)$ and $T = M(v_2^2 - v_1^2)/4R \ln(v_2/v_1) = (0.0320 \text{ kg/mol}) \times (1500^2 - 500^2)(\text{m/s})^2 / 4(8.314 \text{ J/mol-K}) \ln 3.00 = 1750 \text{ K}$.

$$\begin{aligned} 15.11 \quad \langle f_1(w) + f_2(w) \rangle &= \int_{w_{\min}}^{w_{\max}} [f_1(w) + f_2(w)] g(w) dw = \\ &= \int_{w_{\min}}^{w_{\max}} f_1(w) g(w) dw + \int_{w_{\min}}^{w_{\max}} f_2(w) g(w) dw = \langle f_1(w) \rangle + \\ &\langle f_2(w) \rangle. \end{aligned}$$

15.12 The fraction of molecules with x and y velocity components simultaneously in the ranges v_x to $v_x + dv_x$ and v_y to $v_y + dv_y$ is $g(v_x)g(v_y) dv_x dv_y = (m/2\pi kT) \exp(-mv^2/2kT) dv_x dv_y$, where $v^2 = v_x^2 + v_y^2$. Molecules with speeds lying between v and $v + dv$ have their velocity vectors lying within a thin annulus (ring) of inner radius v and outer radius $v + dv$. The area of this annulus is $\pi(v + dv)^2 - \pi v^2 = 2\pi v dv$, where the $\pi(dv)^2$ term is negligible. The probability that \vec{v} lies in this annulus is the following sum over the annulus:
 $\Sigma (m/2\pi kT) e^{-mv^2/2kT} dv_x dv_y = (m/2\pi kT) e^{-mv^2/2kT} (2\pi v dv) = (m/kT) e^{-mv^2/2kT} v dv$, and this is the desired probability.

15.13 (a) Since the integrand has the same value at $-x$ as at $+x$, the areas on each side of the origin are equal, and the integral from $-\infty$ to 0 equals the integral from 0 to ∞ .
 (b) For very small x , $e^{-ax^2} \approx 1$ and the graph resembles

that of $y = x$. For large x , the exponential factor dominates the factor x and the function goes to 0. The graph resembles the $v = 1$ graph in Fig. 18.12. The area on the left side of the origin is negative and exactly cancels the area on the right side of the origin.

15.14 (a) Let $z = ax^2$. Then $dz = 2ax \, dx$ and $\int_0^\infty xe^{-ax^2} dx = (1/2a) \int_0^\infty e^{-z} dz = -(1/2a)e^{-z} \Big|_0^\infty = -(1/2a)(0 - 1) = 1/2a$.

(b) $(\partial/\partial a) \int_0^\infty xe^{-ax^2} dx = \int_0^\infty (\partial/\partial a)xe^{-ax^2} dx = -\int_0^\infty x^3 e^{-ax^2} dx = (\partial/\partial a)(1/2a) = -1/2a^2$ and $\int_0^\infty x^3 e^{-ax^2} dx = 1/2a^2$. Similarly, $(\partial/\partial a) \int_0^\infty x^3 e^{-ax^2} dx = -\int_0^\infty x^5 e^{-ax^2} dx = (\partial/\partial a)(1/2a^2) = -1/a^3$ and $\int_0^\infty x^5 e^{-ax^2} dx = 1/a^3$.

15.15 (a) $v_{\text{rms}} = (3RT/M)^{1/2} =$

$[3(8.314 \times 10^7 \text{ ergs/mol-K})(500 \text{ K})/(44.01 \text{ g/mol})]^{1/2} =$

$5.32 \times 10^4 \text{ cm/s}$. (b) $\langle v \rangle = (8/3\pi)^{1/2} v_{\text{rms}} = 4.90 \times 10^4 \text{ cm/s}$.

(c) $v_{\text{mp}} = (2/3)^{1/2} v_{\text{rms}} = 4.35 \times 10^4 \text{ cm/s}$.

15.16 $dG(v)/dv = (m/2\pi kT)^{3/2} \times$

$[8\pi v e^{-mv^2/2kT} - 4\pi v^2 (mv/kT) e^{-mv^2/2kT}]$. The equation

$dG(v)/dv = 0$ gives $8\pi v_{\text{mp}} = 4\pi m v_{\text{mp}}^3 / kT$ and $v_{\text{mp}} = (2kT/m)^{1/2} = (2RT/M)^{1/2}$. ($v = 0$ and $v = \infty$ also satisfy $G' = 0$ but these

are minima.)

15.17 $\langle v^2 \rangle = \int_0^\infty v^2 G(v) dv = 4\pi (m/2\pi kT)^{3/2} \int_0^\infty v^4 e^{-mv^2/2kT} dv = 4\pi (m/2\pi kT)^{3/2} (24\pi^{1/2}/2^{5/2})(2kT/m)^{5/2} = 3kT/m = 3RT/M,$

where integral 3 (with $n = 2$) of Table 15.1 was used.

15.18 $\langle v^3 \rangle = \int_0^\infty v^3 G(v) dv = 4\pi(m/2\pi kT)^{\frac{3}{2}} \int_0^\infty v^5 e^{-mv^2/2kT} dv$
 $= 4\pi(m/2\pi kT)^{3/2} (2/2)(2kT/m)^3 = 2^{7/2} (kT/m)^{3/2} / \pi^{\frac{1}{2}} =$
 $2^{7/2} (RT/M)^{3/2} / \pi^{\frac{1}{2}}$. We have $\langle v \rangle \langle v^2 \rangle = (8RT/\pi M)^{\frac{1}{2}} (3RT/M) =$
 $3(2^{3/2})(RT/M)^{3/2} / \pi^{\frac{1}{2}} \neq \langle v^3 \rangle$.

15.19 (a) $\langle v_x \rangle = \int_{-\infty}^\infty v_x g(v_x) dv_x = (m/2\pi kT)^{\frac{1}{2}} \times$
 $\int_{-\infty}^\infty v_x e^{-mv_x^2/2kT} dv_x = 0$, where integral 4 of Table 15.1
 was used. From Fig. 15.5, v_x is as likely to be negative
 as positive, so $\langle v_x \rangle = 0$. (b) In calculating $\langle v_x \rangle$, we
 average positive and negative values of v_x and get zero.
 In calculating $\langle v_x^2 \rangle$, all the v_x^2 values are nonnegative,
 and we must get $\langle v_x^2 \rangle$ to be positive.

15.20 $\langle v_x^4 \rangle = \int_{-\infty}^\infty v_x^4 g(v_x) dv_x =$
 $2(m/2\pi kT)^{\frac{1}{2}} \int_0^\infty v_x^4 e^{-mv_x^2/2kT} dv_x$. Integral 3 with $n = 2$ in
 Table 15.1 gives $\langle v_x^4 \rangle = 2(m/2\pi kT)^{\frac{1}{2}} (24\pi^{\frac{1}{2}}/2^5 \cdot 2)(2kT/m)^{5/2} =$
 $3(kT/m)^2 = 3(RT/M)^2$.

15.21 Differentiation of the distribution function in Eq.
 (15.52) with respect to ϵ_{tr} gives
 $2\pi(\pi kT)^{-3/2} [\frac{1}{2} \epsilon_{tr}^{-\frac{1}{2}} e^{-\epsilon_{tr}/kT} - (1/kT) \epsilon_{tr}^{\frac{1}{2}} e^{-\epsilon_{tr}/kT}] = 0$ and
 $\epsilon_{tr,mp} = \frac{1}{2} kT = \langle \epsilon_{tr} \rangle / 3$.

15.22 (a) $(2\pi)^{\frac{1}{2}} I(u) = \int_0^u e^{-s^2/2} ds =$
 $\int_0^u [1 - s^2/2 + (1/2!)s^4/4 - (1/3!)s^6/8 + \dots] ds =$
 $u - u^3/6 + u^5/40 - u^7/336 + \dots$. (b) $(2\pi)^{\frac{1}{2}} I(0.30) =$
 $0.30 - (0.30)^3/6 + (0.30)^5/40 - (0.30)^7/336 + \dots =$
 0.2956 and $I(0.30) = 0.118$.

15.23 (a) The desired probability is $\int_0^{v'} G(v) dv =$
 $(m/2\pi kT)^{3/2} \int_0^{v'} e^{-mv^2/2kT} 4\pi v^2 dv = (4/\pi^{1/2} v_{mp}^3) \times$
 $\int_0^{v'} e^{-(v/v_{mp})^2} v^2 dv = (4/\pi^{1/2} v_{mp}^3) B$, where $v_{mp} = (2kT/m)^{1/2}$ and
 $B = \int_0^{v'} e^{-(v/v_{mp})^2} v^2 dv$. The integration-by-parts formula
is $\int x dy = xy - \int y dx$. Let $x = v$ and $dy = e^{-(v/v_{mp})^2} v dv$.
Then $y = -\frac{1}{2} v_{mp}^2 e^{-(v/v_{mp})^2}$ and $B = -\frac{1}{2} v_{mp}^2 v e^{-(v/v_{mp})^2} \Big|_0^{v'} +$
 $\frac{1}{2} v_{mp}^2 \int_0^{v'} e^{-(v/v_{mp})^2} dv$. Let $s = 2^{1/2} v/v_{mp}$. Then $B =$
 $-\frac{1}{2} v_{mp}^2 v' e^{-(v'/v_{mp})^2} + \frac{1}{2} v_{mp}^2 \int_0^{2^{1/2} v'/v_{mp}} e^{-s^2/2} v_{mp}^2 2^{-1/2} ds =$
 $-\frac{1}{2} v_{mp}^2 v' e^{-(v'/v_{mp})^2} + v_{mp}^3 2^{-3/2} (2\pi)^{1/2} I(2^{1/2} v'/v_{mp})$ and
 $\int_0^{v'} G(v) dv = 2I(2^{1/2} v'/v_{mp}) - 2\pi^{-1/2} (v'/v_{mp}) e^{-(v'/v_{mp})^2}$.

(b) The fraction with speed in the range from 0 to $4.243 v_{mp}$ is $2I(2^{1/2} \cdot 4.243) - 2\pi^{-1/2} (4.243) e^{-(4.243)^2} =$
 $2I(6.000) - (7.27 \times 10^{-8}) = 2(0.4999999990) - (7.27 \times 10^{-8})$
 $= 0.9999999253$, where the table following Eq. (15.51) was
used. The fraction with speeds exceeding $4.243 v_{mp}$ is
 $1 - 0.9999999253 = 7.5 \times 10^{-8}$.

15.24 From Eq. (15.58), $0.872 = (M_0/M)^{1/2} =$
 $[(32.0 \text{ g/mol})/M]^{1/2}$ and $M = 42.1 \text{ g/mol}$. The only hydrocarbon
with this molar mass is C_3H_6 .

15.25 (a) Equation (15.58) applies. We have $dN/dt =$
 $N_A (dn/dt) = N_A (\Delta n / \Delta t)$ and $P = (\Delta n / \Delta t) (2\pi MRT)^{1/2} / A =$
 $\frac{[2\pi(44.96 \text{ g/mol})(8.314 \times 10^7 \text{ ergs/mol-K})(1690 \text{ K})]^{1/2}}{\pi(0.1763/2)^2 \text{ cm}^2} \times$

$$\times \frac{(10.5 \times 10^{-3} \text{ g})/(44.96 \text{ g/mol})}{(49.5 \times 60) \text{ s}}$$

$$P = (20.29 \text{ dyn/cm}^2) \frac{82.06 \text{ cm}^3 \text{ atm}}{8.314 \times 10^7 \text{ ergs}} \frac{760 \text{ torr}}{1 \text{ atm}} = 0.0152 \text{ torr}$$

(b) Equation (15.67) applies. The order of magnitude of d is a couple of angstroms. The order of magnitude of λ is

$$\frac{(82 \text{ cm}^3\text{-atm/mol-K})(1690 \text{ K})}{2^{\frac{1}{2}}\pi(2 \times 10^{-8} \text{ cm})^2(0.015/760) \text{ atm}(6 \times 10^{23}/\text{mol})} = 7 \text{ cm}$$

Since $d_{\text{hole}} = 0.2 \text{ cm}$, the condition $\lambda \gg d_{\text{hole}}$ is met.

15.26 The CO_2 partial pressure is 0.00033 atm and Eq. (15.56) gives $dN_w/dt =$

$$\frac{(1.0 \text{ cm}^2)(0.00033 \text{ atm})(6.02 \times 10^{23}/\text{mol})}{4(82.06 \text{ cm}^3\text{-atm/mol-K})(298 \text{ K})} \times \left[\frac{8(8.314 \times 10^7 \text{ erg/mol-K})(298 \text{ K})}{\pi(44.0 \text{ g/mol})} \right]^{\frac{1}{2}} =$$

$= 7.7 \times 10^{19} \text{ s}^{-1}$. The mass striking the leaf in 1 sec is $[(7.7 \times 10^{19})/(6.0 \times 10^{23} \text{ mol}^{-1})](44 \text{ g/mol}) = 5.6 \text{ mg}$.

15.27 $P = (0.010/760) \text{ atm}(101325 \text{ Pa/atm}) =$

$= 1.33 \text{ N/m}^2$. As discussed in the text, we can take the evaporation rate as essentially equal to the rate at which molecules of vapor in equilibrium with the liquid strike the liquid. Equation (15.58) gives

$$\frac{dN}{dt} = \frac{(1.33 \text{ N/m}^2)(6.02 \times 10^{23}/\text{mol})(10^{-4} \text{ m}^2)}{[2\pi (0.3906 \text{ kg/mol}) (8,3145 \text{ J/mol-K})(393 \text{ K})]^{\frac{1}{2}}}$$

$$= 8.9 \times 10^{17} \text{ s}^{-1}$$

$$\frac{(8.9 \times 10^{17} \text{ molecules})}{0.58 \text{ mg}} \times \frac{1 \text{ mole}}{6.02 \times 10^{23} \text{ molecules}} \times \frac{390.6 \text{ g}}{1 \text{ mole}} =$$

15.28 (a) $z_{(b)b} = (2 + 2) \text{ collns./s} = 4 \text{ s}^{-1}$. (b) $z_{bb} = [(2 + 2 + 2) \text{ s}^{-1}] / (1 \times 10^{-5} \text{ cm}^3) = 6 \times 10^5 \text{ s}^{-1} \text{ cm}^{-3}$.

$$N_b z_{(b)b} / V = 3(4 \text{ s}^{-1}) / (1 \times 10^{-5} \text{ cm}^3) = 12 \times 10^5 \text{ s}^{-1} \text{ cm}^{-3} \neq z_{bb}$$

$$z_{bb} \cdot \frac{1}{2} N_b z_{(b)b} / V = \frac{1}{2} (12 \times 10^5 \text{ s}^{-1} \text{ cm}^{-3}) = 6 \times 10^5 \text{ s}^{-1} \text{ cm}^{-3} = z_{bb}$$

15.29 (a) $z_{(b)b} = 2^{\frac{1}{2}} \pi d_b^2 (8RT/\pi M_b)^{\frac{1}{2}} P_b N_A / RT = 2^{\frac{1}{2}} \pi \times (3.7 \times 10^{-10} \text{ m})^2 [8(8.3145 \text{ J/mol-K})(298 \text{ K})/\pi(0.0280 \text{ kg/mol})]^{\frac{1}{2}} \times (1.00 \text{ atm})(6.02 \times 10^{23}/\text{mol}) / (82.06 \times 10^{-6} \text{ m}^3\text{-atm/mol-K})(298 \text{ K}) = 7.1 \times 10^9 \text{ s}^{-1}$. (b) $z_{bb} = \frac{1}{2} N_b z_{(b)b} / V = \frac{1}{2} z_{(b)b} (P N_A / RT) = \frac{1}{2} (7.1 \times 10^9 \text{ s}^{-1})(1.00 \text{ atm})(6.02 \times 10^{23}/\text{mol}) / (82.06 \text{ cm}^3\text{-atm/mol-K})(298 \text{ K}) = 8.7 \times 10^{28} \text{ s}^{-1} \text{ cm}^{-3}$. (c) $1.0 \times 10^{-6} \text{ t}_{\text{crr}} = 1.3 \times 10^{-9} \text{ atm}$. $z_{(b)b}$ is proportional to P and z_{bb} is proportional to P^2 , so $z_{(b)b} = (7.1 \times 10^9 \text{ s}^{-1})(1.3 \times 10^{-9} \text{ atm}/1 \text{ atm}) = 9.3 \text{ s}^{-1}$ and $z_{bb} = (8.7 \times 10^{28} \text{ s}^{-1} \text{ cm}^{-3})(1.3 \times 10^{-9}/1)^2 = 1.5 \times 10^{11} \text{ s}^{-1} \text{ cm}^{-3}$.

15.30 Let $b = \text{CO}_2$ and $c = \text{N}_2$. $P_b = 0.97(4.7 \text{ torr}) \times (1 \text{ atm}/760 \text{ torr}) = 0.0060 \text{ atm}$ and $P_c = 0.00019 \text{ atm}$. (a) From (15.61), $z_{(b)b} = 4\pi^{\frac{1}{2}} d_b^2 (RT/M_b)^{\frac{1}{2}} P_b N_A / RT = 4\pi^{\frac{1}{2}} \times (4.6 \times 10^{-10} \text{ m})^2 [(8.3145 \text{ J/mol-K})(220 \text{ K})/(0.044 \text{ kg/mol})]^{\frac{1}{2}} \times (0.0060 \text{ atm})(6.02 \times 10^{23}/\text{mol}) / (82.06 \times 10^{-6} \text{ m}^3\text{-atm/mol-K})(220 \text{ K}) =$

$$6.1 \times 10^7 \text{ s}^{-1}. \text{ (b) } z_{(c)b} = (8\pi)^{\frac{1}{2}}(r_b + r_c)^2 [RT(M_b^{-1} + M_c^{-1})]^{\frac{1}{2}} \times \\ P_b N_A / RT = (8\pi)^{\frac{1}{2}}(4.15 \times 10^{-10} \text{ m})^2 (RT)^{\frac{1}{2}} \times$$

$$[(0.044 \text{ kg/mol})^{-1} + (0.028 \text{ kg/mol})^{-1}]^{\frac{1}{2}}(0.0060 \text{ atm})N_A / RT \\ = 5.65 \times 10^7 \text{ s}^{-1}. \text{ (c) } z_{(c)c} = 4\pi^{\frac{1}{2}}(3.7 \times 10^{-10} \text{ m})^2 \times \\ [RT/(0.028 \text{ kg/mol})]^{\frac{1}{2}}(0.00019 \text{ atm})N_A / RT = 1.6 \times 10^6 \text{ s}^{-1}.$$

$$z_{(c)c} + z_{(c)b} = 1.6 \times 10^6 \text{ s}^{-1} + 5.65 \times 10^7 \text{ s}^{-1} = 5.81 \times \\ 10^7 \text{ s}^{-1}. \text{ (d) } z_{bc} = N_b z_{(b)c} / V = N_c z_{(c)b} / V = z_{(c)b} P_c N_A / RT = \\ (5.65 \times 10^7 \text{ s}^{-1})(0.00019 \text{ atm})N_A / RT = 3.6 \times 10^{23} \text{ s}^{-1} \text{ cm}^{-3}.$$

$$\text{ (e) } z_{bb} = \frac{1}{2}N_b z_{(b)b} / V = \frac{1}{2}z_{(b)b} P_b N_A / RT = \frac{1}{2}(6.1 \times 10^7 \text{ s}^{-1}) \times \\ (0.0060 \text{ atm})N_A / RT = 6.1 \times 10^{24} \text{ s}^{-1} \text{ cm}^{-3}. z_{cc} = \frac{1}{2}z_{(c)c} \times \\ P_c N_A / RT = 5.1 \times 10^{21} \text{ s}^{-1} \text{ cm}^{-3}. z_{bb} + z_{cc} + z_{bc} = \\ (6.1 \times 10^{24} + 5 \times 10^{21} + 3.6 \times 10^{23}) \text{ s}^{-1} \text{ cm}^{-3} = 6.5 \times 10^{24} \\ \text{ s}^{-1} \text{ cm}^{-3}.$$

$$\underline{15.31} \text{ (a) } \lambda = RT/2^{\frac{1}{2}}\pi d^2 P N_A = (82.06 \text{ cm}^3\text{-atm/mol-K})(300 \text{ K})/ \\ 2^{\frac{1}{2}}\pi(3.7 \times 10^{-8} \text{ cm})^2(750/760)\text{atm}(6.02 \times 10^{23}/\text{mol}) = 6.8 \times \\ 10^{-6} \text{ cm. (b) } \lambda = (6.8 \times 10^{-6} \text{ cm})(750/1) = 5.1 \times 10^{-3} \text{ cm.} \\ \text{ (c) } 5.1 \times 10^3 \text{ cm.}$$

$$\underline{15.32} \quad 14100 \text{ ft} = (14100 \text{ ft})(12 \text{ in./1 ft})(2.54 \text{ cm/1 in.}) \times \\ (0.01 \text{ m/1 cm}) = 4298 \text{ m. } P = P_0 e^{-Mgz/RT} = (760 \text{ torr}) \times \\ \exp[-(0.029 \text{ kg/mol})(9.81 \text{ m/s}^2)(4298 \text{ m})/(8.3145 \text{ J/mol-K}) \times \\ (290 \text{ K})] = 458 \text{ torr.}$$

$$\underline{15.33} \quad \text{The last equation in the Sec. 15.8 example gives} \\ P_{\text{bot}} - P_{\text{top}} = P_{\text{bot}} Mgz/RT = (1 \text{ atm})(0.029 \text{ kg/mol}) \times \\ (9.81 \text{ m/s}^2)(30 \times 12 \times 2.54 \times 10^{-2} \text{ m})/(8.314 \text{ J/mol-K})(298 \text{ K}) \\ = 1.05 \times 10^{-3} \text{ atm} = 0.80 \text{ torr.}$$

$$\underline{15.34} \quad P/P_0 = e^{-Mgz/RT} = 0.5 \text{ and } z = -(RT/Mg) \ln 0.5 = \\ -[(8.3145 \text{ J/mol-K})(250 \text{ K})/(0.029 \text{ kg/mol})(9.81 \text{ m/s}^2)] \ln 0.5 \\ = 5060 \text{ m.}$$

$$\underline{15.35} \quad M_n = 0.97(44) + 0.03(28) = 43.5. \quad P = P_0 e^{-Mgz/RT} = \\ (4.7 \text{ torr}) \exp [-(0.0435 \text{ kg/mol})(3.7 \text{ m/s}^2)(40000 \text{ m})/ \\ (8.314 \text{ J/mol-K})(180 \text{ K})] = 0.064 \text{ torr.}$$

15.36 (a) For \bar{C}_V the translational contribution is $3R/2$, the rotational contribution is $3R/2$, and the vibrational contribution is $2[3(5) - 6]R/2 = 9R$, so \bar{C}_V is predicted to be $12R$. $\bar{C}_P = \bar{C}_V + R$ and \bar{C}_P is predicted to be $13R$. (b) No; the actual \bar{C}_P is less than $13R$ at 400 K . (c) \bar{C}_P will reach $13R$ at high temperatures.

$$\underline{15.37} \quad \langle p_x^2/2m \rangle = \frac{1}{2}m \langle v_x^2 \rangle = \frac{1}{2}m \int_{-\infty}^{\infty} v_x^2 g(v_x) dv_x = \\ \frac{1}{2}m(m/2\pi kT)^{\frac{1}{2}} \int_{-\infty}^{\infty} \exp(-mv_x^2/2kT) v_x^2 dv_x = \frac{1}{2}m(m/2\pi kT)^{\frac{1}{2}} \times \\ 2(2!\pi^{\frac{1}{2}}/2^3 1!)(2kT/m)^{3/2} = \frac{1}{2}kT, \text{ where integrals 1 and 3} \\ \text{(with } n = 1) \text{ of Table 15.1 were used.}$$

$$\underline{15.38} \quad \text{(a)} \int_{-\infty}^{\infty} g(w) dw = 1 = \int_{-\infty}^{\infty} A e^{-cw^2/kT} dw = 2A(\pi^{\frac{1}{2}}/2) \times \\ (kT/c)^{\frac{1}{2}} \text{ and } A = (c/\pi kT)^{\frac{1}{2}}, \text{ where integrals 1 and 2 in} \\ \text{Table 15.1 were used. (b)} \langle \epsilon_w \rangle = \int_{-\infty}^{\infty} \epsilon_w g(w) dw = \\ A \int_{-\infty}^{\infty} cw^2 e^{-cw^2/kT} dw = 2Ac(2!\pi^{\frac{1}{2}}/2^3 1!)(kT/c)^{3/2} = \frac{1}{2}kT, \\ \text{where } A = (c/\pi kT)^{\frac{1}{2}} \text{ and integrals 1 and 3 of Table 15.1} \\ \text{were used.}$$

$$\underline{15.39} \quad \frac{1}{2}mv^2 = \frac{3}{2}kT \text{ and } v_{\text{rms}} = (3kT/m)^{\frac{1}{2}} = \\ [3(1.38 \times 10^{-16} \text{ erg/K})(298 \text{ K})/(1.0 \times 10^{-10} \text{ g})]^{\frac{1}{2}} =$$

0.035 cm/s.

15.40 $\langle v^2 \rangle = 3RT/M$ and $\langle v \rangle^2 = 8RT/\pi M$, so $\langle v^2 \rangle \neq \langle v \rangle^2$.

15.41 The possible values of s are 1, 2, 3, 4, 5, 6 and the probability of each value is $1/6$. Hence $\langle s \rangle = \sum_s s p(s) = 1(1/6) + 2(1/6) + 3(1/6) + 4(1/6) + 5(1/6) + 6(1/6) = 21/6 = 3.5$. Also, $\langle s^2 \rangle = \sum_s s^2 p(s) = 1^2(1/6) + 2^2(1/6) + 3^2(1/6) + 4^2(1/6) + 5^2(1/6) + 6^2(1/6) = 91/6 = 15.17$. $\langle s \rangle^2 = (3.5)^2 = 12.25 \neq \langle s^2 \rangle$.

15.42 (a) $\sigma_{v_x}^2 = \langle v_x^2 \rangle - \langle v_x \rangle^2 = kT/m - 0$ and $\sigma_{v_x} = (kT/m)^{1/2}$.

(b) $\langle v_x \rangle = 0$ and $\sigma = (kT/m)^{1/2}$. The distribution function (15.42) is $(2\pi)^{-1/2} \sigma^{-1} e^{-v_x^2/2\sigma^2}$ and the desired fraction is

$$(2\pi)^{-1/2} \sigma^{-1} \int_{-\sigma}^{\sigma} e^{-v_x^2/2\sigma^2} dv_x = 2(2\pi)^{-1/2} \sigma^{-1} \int_0^{\sigma} e^{-v_x^2/2\sigma^2} dv_x =$$

$2(2\pi)^{-1/2} \sigma^{-1} \int_0^1 e^{-s^2/2} \sigma ds = 2I(1) = 0.68$, where we made the substitution $s = v_x/\sigma$ and used Eq. (15.51) and the table following it.

15.43 $h(xy) = f(x) + g(y)$. We take $(\partial/\partial x)_y$ of this equation. Let $z \equiv xy$. The partial derivative of the left side is $\partial h(xy)/\partial x = (dh/dz)(\partial z/\partial x) = h'(z)y$. The partial derivative of the right side is $df(x)/dx = h'(z)y$; we have $h'(z) = y^{-1} df(x)/dx$. Similarly, taking $(\partial/\partial y)_x$ of $h(xy) = f(x) + g(y)$ gives $h'(z) = x^{-1} dg(y)/dy$. Hence $x^{-1} dg(y)/dy = y^{-1} df(x)/dx$ and $y[dg(y)/dy] = x[df(x)/dx] \equiv k$. By the argument that follows Eq. (15.33), k must be a constant.

Hence $df(x) = (k/x) dx$ and $f(x) = k \ln x + a$, where a is an integration constant.

15.44 Molecules with $v_x = b$ have the tips of their velocity vectors lying in the plane $v_x = b$. (This plane is parallel to the plane formed by the v_y and v_z axes and is a distance b from it.) The region corresponding to $b \leq v_x \leq c$ is the region between the parallel planes at $v_x = b$ and $v_x = c$.

15.45 (a) 1, since the probability density $G(v)$ satisfies $\int_0^\infty G(v) dv = 1$, Eq. (15.25). (b) A crude approximation to the area under the 300 K curve is found by taking the area of a triangle with height 2×10^{-5} s/cm (the peak of the curve) and base 10^5 cm/s (the width of the region for which $G(v)$ has a substantial value). The area of this triangle is $\frac{1}{2}(10^5 \text{ cm/s})(2 \times 10^{-5} \text{ s/cm}) = 1$.

15.46 (a) H_2 . The lighter H_2 molecules move faster, so that their average kinetic energy equals that of O_2 . (b) $\langle \epsilon_{tr} \rangle$ is the same for both. (c) $\rho = PM/RT$ is greater for O_2 because of the greater mass of the O_2 molecules. (d) From (15.67), λ decreases as the molecular diameter increases. O_2 is larger than H_2 , so $\lambda_{H_2} > \lambda_{O_2}$. (e) The H_2 molecules are moving faster and so collide more often with the wall.

15.47 Substitution of $\mu_i = \mu_i^\circ(T) + RT \ln (P_i/P^\circ)$ into $\mu_i^\alpha + M_i g z^\alpha = \mu_i^\beta + M_i g z^\beta$ gives $\mu_i^\circ(T) + RT \ln (P_i^\alpha/P^\circ) +$

$$M_i g z^\alpha = \mu_i^\circ(T) + RT \ln (P_i^\beta/P^\circ) + M_i g z^\beta \text{ or } RT \ln (P_i^\alpha/P_i^\beta) = M_i g (z^\beta - z^\alpha). \quad \ln (P_i^\beta/P_i^\alpha) = -M_i g (z^\beta - z^\alpha)/RT \text{ and } P_i^\beta = P_i^\alpha \exp [-M_i g (z^\beta - z^\alpha)/RT],$$

15.48 (a) False. See Sec. 15.5. (b) True. See Fig. 15.5.
 (c) True. (d) False. See Eq. (15.60). (e) True. (f) True.
 See Eq. (15.13). (g) False.

CHAPTER 16

16.1 (a) Equation (16.1) gives $|q| = |kA(\Delta T/\Delta x)\Delta t| = (0.80 \text{ J/K-cm-s})(24 \text{ cm}^2)(60 \text{ s})(50 \text{ K})/(200 \text{ cm}) = 288 \text{ J}.$

(b) $\Delta S_{\text{rod}} = 0$ since the rod's state is not changed. The temperature of each end of the rod differs only slightly from the temperature of the reservoir it is in contact with, so we can use $dS = dq_{\text{rev}}/T = dq/T$ for each reservoir. Therefore $\Delta S = \Delta S_{\text{hot res.}} + \Delta S_{\text{cold res.}} = (-288 \text{ J})/(325 \text{ K}) + (288 \text{ J})/(275 \text{ K}) = 0.161 \text{ J/K}.$

16.2 $\bar{C}_V = 3R/2$ for this monatomic gas, and Eq. (16.12) gives $k =$

$$\frac{5}{16} \left(\frac{3}{2} + \frac{9}{4} \right) (8.314 \text{ J/mol-K}) \left[\frac{(8.314 \text{ J/mol-K})(273 \text{ K})}{\pi(0.00400 \text{ kg/mol})} \right]^{\frac{1}{2}} \times \frac{1}{(6.02 \times 10^{23} \text{ /mol})(2.2 \times 10^{-10} \text{ m})^2}$$

$= 0.00142 \text{ J/K-cm-s. At } 100^\circ\text{C, } k = 0.166 \text{ J/K-m-s.}$

16.3 $\bar{C}_V + 9R/4 = \bar{C}_P - R + 9R/4 = \bar{C}_P + 5R/4 = (35.309 \text{ J/mol-K}) + (5/4)(8.3145 \text{ J/mol-K}) =$

$45.7 \text{ J/mol-K. Then } k = (5/16)(45.7 \text{ J/mol-K}) \times [(8.314 \text{ J/mol-K})(298 \text{ K})/\pi(0.0160 \text{ kg/mol})]^{\frac{1}{2}} \times 1/(6.02 \times 10^{23} \text{ mol}^{-1})(4.1 \times 10^{-10} \text{ m})^2 = 0.031 \text{ J/K-s-m} = 31 \times 10^{-5} \text{ J K}^{-1} \text{ s}^{-1} \text{ cm}^{-1}, \text{ where (16.12) was used.}$

16.4 $\rho = M/\bar{V} = (18.015 \text{ g/mol})/(18.1 \text{ cm}^3/\text{mol}) = 0.995$

$$\begin{aligned} \text{g/cm}^3 &= 995 \text{ kg/m}^3 \text{ and } k = 2.8(8.314 \text{ J/mol-K}) \times \\ &[17.99/(17.72)(995 \text{ kg/m}^3)(4.46 \times 10^{-10} \text{ m}^2/\text{N})]^{1/2}/ \\ &(6.022 \times 10^{23} \text{ mol}^{-1})^{1/3}(18.1 \text{ cm}^3/\text{mol})^{2/3} = \\ &6.05 \times 10^{-5} \text{ J K}^{-1} \text{ cm}^{-2} \text{ m s}^{-1} = 6.05 \text{ mJ K}^{-1} \text{ cm}^{-1} \text{ s}^{-1}. \end{aligned}$$

16.5 The maximum $\langle v_y \rangle$ for laminar flow is the value that makes $\text{Re} = 2000$, so $\langle v_y \rangle_{\text{max}} = 2000\eta/\rho d = 2000(0.0089 \text{ dyn s cm}^{-2})/(1.00 \text{ g/cm}^3)(1.00 \text{ cm}) = 18 \text{ cm/s}$.

16.6 (a) $(32/760) \text{ atm}(8.314 \times 10^7 \text{ ergs})/(82.06 \text{ cm}^3 \text{ atm}) = 4.26_6 \times 10^4 \text{ dyn/cm}^2$. Equation (16.17) gives $\eta = (\pi r^4/8V)(|\Delta P|/|\Delta y|)t = [\pi(0.100 \text{ cm})^4/8(148 \text{ cm}^3)] \times [(4.26_6 \times 10^4 \text{ dyn/cm}^2)/(24.0 \text{ cm})](120 \text{ s}) = 0.0566 \text{ dyn cm}^{-2} \text{ s} = 5.66 \text{ cP}$. (b) In time t , a volume $V = \pi r^2 \langle d \rangle$ flows through the pipe of cross-sectional area πr^2 where $\langle d \rangle$ is the average distance travelled by the fluid. We have $\langle d \rangle = \langle v_y \rangle t$ and $\langle v_y \rangle = \langle d \rangle/t = (V/\pi r^2)/t = V/\pi r^2 t = (r^2/8\eta)|\Delta P|/|\Delta y|$, where Eq. (16.17) was used. So $\langle v_y \rangle = [(0.100 \text{ cm})^2/8(0.0566 \text{ dyn cm}^{-2} \text{ s})](4.26_6 \times 10^4 \text{ dyn/cm}^2)/(24.0 \text{ cm}) = 39.3 \text{ cm/s}$. Then $\text{Re} = \rho \langle v_y \rangle d/\eta = (1.35 \text{ g/cm}^3)(39.3 \text{ cm/s})(0.200 \text{ cm})/(0.0566 \text{ dyn cm}^{-2} \text{ s}) = 187 < 2000$, so the flow is laminar.

16.7 (a) From (16.17), $(P_2 - P_1)/(y_2 - y_1) = -(8\eta/\pi r^4) \times (V/t) = -8[(0.04 \text{ dyn s cm}^{-2})/\pi(1.2_5 \text{ cm})^4](5000 \text{ cm}^3)/(60 \text{ s}) = -3.5 \text{ dyn/cm}^3 = -35 \text{ Pa/m}$. (b) $\langle v_y \rangle = V/\cancel{A}t = (5000 \text{ cm}^3)/\pi(1.2_5 \text{ cm})^2(60 \text{ s}) = 17 \text{ cm/s}$. (c) $\text{Re} =$

$\rho \langle v_y \rangle d / \eta = (1.0 \text{ g/cm}^3)(17 \text{ cm/s})(2.5 \text{ cm}) / (0.04 \text{ dyn s/cm}^2)$
 $= 1100 < 2000$, so the flow is laminar and use of Eq.

(16.17) is justified. For a flow rate of 30 L/min, $\langle v_y \rangle$ and Re are 6 times as large and $\text{Re} = 6400 > 2000$, so the aortic flow is turbulent during vigorous activity.

$$\underline{16.8} \quad P_1^2 - P_2^2 = (4.00 - 1.00) \text{ atm}^2 = (3.00 \text{ atm}^2) \times (8.314 \text{ J})^2 / (82.06 \times 10^{-6} \text{ m}^3 \text{ atm})^2 = 3.08 \times 10^{10} \text{ N}^2/\text{m}^4.$$

Equation (16.18) gives $dn/dt = \pi(0.000210 \text{ m})^4 \times (3.08 \times 10^{10} \text{ N}^2/\text{m}^4) / [16(0.0000192 \text{ N s/m}^2)(8.314 \text{ J/mol-K}) \times (273 \text{ K})(2.20 \text{ m})] = 0.000123 \text{ mol/s}$, which is 0.00392 g/s .

$$\underline{16.9} \quad \eta_{\text{C}_6\text{H}_{14}} = \eta_{\text{H}_2\text{O}} (\rho_{\text{C}_6\text{H}_{14}} t_{\text{C}_6\text{H}_{14}} / \rho_{\text{H}_2\text{O}} t_{\text{H}_2\text{O}}) = (1.002 \text{ cP}) \times (0.659 \text{ g/cm}^3)(67.3 \text{ s}) / (0.998 \text{ g/cm}^3)(136.5 \text{ s}) = 0.326 \text{ cP}.$$

16.10 (a) The pressures at the left and right ends of C exert forces $P\pi s^2$ and $-(P + dP)\pi s^2$, respectively, on C.

The viscous force on C is given by (16.13) as $\eta \frac{d}{ds} (dv_y/ds)$
 $= \eta(2\pi s dy)(dv_y/ds)$. So $-(P + dP)\pi s^2 + P\pi s^2 + \eta(2\pi s dy) \times$

$(dv_y/ds) = 0$ and $dv_y/ds = (s/2\eta)(dP/dy)$. Integration gives $v_y = (s^2/4\eta)(dP/dy) + c$, where c is a constant. Use of $v_y = 0$ at $s = r$ gives $c = -(r^2/4\eta)(dP/dy)$. Therefore

$v_y = (1/4\eta)(r^2 - s^2)(-dP/dy)$. (b) The volume of fluid in the shell that passes a given location in time dt equals the volume of a cylindrical shell with length $v_y(s) dt$ and inner and outer radii s and $s + ds$; this volume is

$$\pi(s + ds)^2 \cdot v_y(s) dt - \pi s^2 v_y(s) dt = 2\pi s v_y(s) ds dt, \text{ since}$$

$(ds)^2$ is negligible compared with ds . Integration over all shells from $s = 0$ to r gives $dV = [\int_0^r 2\pi s v_y(s) ds] dt$. Substitution of $dV = dm/\rho$ and $v_y = (1/4\eta)(r^2 - s^2)(-dP/dy)$ gives $dm/dt = (\pi\rho/2\eta)(-dP/dy) \int_0^r (r^2 s - s^3) ds = (\pi r^4 \rho/8\eta)(-dP/dy)$. Separating P and y and integrating from one end to the other, we have $-\int_{P_2}^{P_1} dP = (dm/dt)(8\eta/\pi r^4 \rho) \times \int_{y_2}^{y_1} dy$, which becomes $dm/dt = (\pi r^4 \rho/8\eta)(P_1 - P_2)/(y_2 - y_1)$. We have $dm/dt = d(\rho V)/dt = \rho dV/dt = \rho V/t$, since the flow rate is constant with time. Hence (16.17) follows. (c)

Substitution of $\rho = PM/RT$ into (16.92), separation of P and y and integration gives $(RT/M)(dm/dt)(8\eta/\pi r^4) \int_{y_1}^{y_2} dy = -\int_{P_1}^{P_2} P dP = \frac{1}{2}(P_1^2 - P_2^2)$; use of $(RT/M)(dm/dt) = RT d(m/M)/dt = RT dn/dt$ gives (16.18).

16.11 Equation (16.21) gives $v = 2(7.8 - 1.0) \text{ g cm}^{-3} \times (980.7 \text{ cm/s}^2)(0.050 \text{ cm})^2/9(0.0089 \text{ dyn s cm}^{-2}) = 420 \text{ cm/s}$. For glycerol, $v = 2(7.8 - 1.25) 10^{-3} \text{ kg (10}^{-2} \text{ m)}^{-3} \times (9.807 \text{ m/s}^2)(0.00050 \text{ m})^2/9(0.954 \text{ N s m}^{-2}) = 0.0037 \text{ m/s} = 0.37 \text{ cm/s}$.

16.12 From (16.25), $d^2 = 5(MRT)^{\frac{1}{2}}/16\pi^{\frac{1}{2}}N_A\eta = 0.1763 \times (0.04401 \text{ kg/mol})^{\frac{1}{2}}(8.314 \text{ J/mol-K})^{\frac{1}{2}}T^{\frac{1}{2}}/(6.022 \times 10^{23}/\text{mol})\eta = 1.77 \times 10^{-25} \text{ m}^2 (\text{T/K})^{\frac{1}{2}}/[\eta/(\text{kg m}^{-1} \text{ s}^{-1})] = 1.77 \times 10^{-24} \text{ m}^2 (\text{T/K})^{\frac{1}{2}}/(\eta/P)$, where P stands for poise. At 0°C , $d^2 = 1.77 \times 10^{-24} \text{ m}^2 (273)^{\frac{1}{2}}/(139 \times 10^{-6})$ and $d = 4.59 \times 10^{-10} \text{ m} = 4.59 \text{ \AA}$. At 490°C , $d = 3.85 \text{ \AA}$; at 850°C , $d = 3.69 \text{ \AA}$.

16.13 The diameters of H_2 and D_2 are the same and (16.25) shows that η is proportional to $M^{\frac{1}{2}}$. So $\eta_{D_2}/\eta_{H_2} = (M_{D_2}/M_{H_2})^{\frac{1}{2}}$ and $\eta_{D_2} = (4.03/2.02)^{\frac{1}{2}} \times (8.53 \times 10^{-5} \text{ P}) = 1.20 \times 10^{-4} \text{ P}$.

16.14 (a) $M_n = \sum_i x_i M_i = 0.5(200,000 \text{ g/mol}) + 0.5(600,000 \text{ g/mol}) = 400,000 \text{ g/mol}$. $M_w = (\sum_i x_i M_i^2) / (\sum_i x_i M_i) = [0.5(200,000 \text{ g/mol})^2 + 0.5(600,000 \text{ g/mol})^2] / (400,000 \text{ g/mol}) = 500,000 \text{ g/mol}$. (b) Let us take 600,000 g of each species. We then have 3.0 moles of the molecular-weight 200,000 species and 1.0 mole of the molecular-weight 600,000 species. Hence $M_n = \sum_i x_i M_i = 0.75(200,000 \text{ g/mol}) + 0.25(600,000 \text{ g/mol}) = 300,000 \text{ g/mol}$. $M_w = [0.75(200,000 \text{ g/mol})^2 + 0.25(600,000 \text{ g/mol})^2] / (300,000 \text{ g/mol}) = 400,000 \text{ g/mol}$.

16.15 We plot $(\eta_r - 1)/\rho_B$ vs. ρ_B . The points fit a straight line well, and extrapolation to $\rho_B = 0$ gives $[\eta] = \lim_{\rho_B \rightarrow 0} (\eta_r - 1)/\rho_B = 0.147 \text{ dm}^3/\text{g} = 147 \text{ cm}^3/\text{g}$. Then $147 \text{ cm}^3/\text{g} = (0.034 \text{ cm}^3/\text{g})(M_B/M^\circ)^{0.65}$ and $M_B = 390000 \text{ g/mol}$. $M_{r,B} = 390000$.

16.16 (a) $(\Delta x)_{\text{rms}} = (2Dt)^{\frac{1}{2}}$, so $t = (\Delta x)_{\text{rms}}^2 / 2D = (1 \text{ cm}^2) / 2(10^{-21} \text{ cm}^2/\text{s}) = 5 \times 10^{20} \text{ s} = 2 \times 10^{13} \text{ yr}$. (b) $t = (1 \text{ cm}^2) / 2(10^{-30} \text{ cm}^2/\text{s}) = 5 \times 10^{29} \text{ s} = 2 \times 10^{22} \text{ yr}$.

16.17 (a) $(\Delta x)_{\text{rms}} = (2Dt)^{\frac{1}{2}} = [2(0.52 \times 10^{-5} \text{ cm}^2/\text{s})(60 \text{ s})]^{\frac{1}{2}} = 0.025 \text{ cm}$. (b) $t = 3600 \text{ s}$ and $(\Delta x)_{\text{rms}} = 0.19 \text{ cm}$.

(c) $t = 86400 \text{ s}$ and $(\Delta x)_{\text{rms}} = 0.95 \text{ cm}$.

16.18 Let the origin be at the $t = 0$ location of the particle and let the particle be at point (x, y, z) at time t . Then $\langle r^2 \rangle = \langle x^2 + y^2 + z^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle$. By symmetry, $\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle$, so $\langle r^2 \rangle = 3\langle x^2 \rangle = 3(2Dt) = 6Dt$ and $r_{\text{rms}} = \langle r^2 \rangle^{\frac{1}{2}} = (6Dt)^{\frac{1}{2}}$.

16.19 From Eq. (16.35), $k = 3x_{\text{rms}}^2 \pi \eta r / tT$. For $t = 30 \text{ s}$, $k = 3(7.1 \times 10^{-4} \text{ cm})^2 \pi (0.011 \text{ dyn-s/cm}^2)(2.1 \times 10^{-5} \text{ cm}) / (30 \text{ s})(290 \text{ K}) = 1.26 \times 10^{-16} \text{ erg/K}$. Then $N_A = R/k = (8.314 \times 10^7 \text{ ergs/mol-K}) / (1.26 \times 10^{-16} \text{ erg/K}) = 6.6 \times 10^{23} / \text{mol}$. For $t = 60 \text{ s}$, we get $k = 1.41 \times 10^{-16} \text{ erg/K}$ and $N_A = 5.9 \times 10^{23} \text{ mol}^{-1}$. For 90 s , $k = 1.07 \times 10^{-16} \text{ erg/K}$ and $N_A = 7.8 \times 10^{23} \text{ mol}^{-1}$.

16.20 $\langle \Delta x \rangle = (1/12)(-5.3 + 3.4 - 1.9 - 0.4 + 0.5 + 3.1 - 0.2 - 3.5 + 1.4 + 0.3 - 1.0 + 2.6) \mu\text{m} = -0.08 \mu\text{m}$.
 $\langle (\Delta x)^2 \rangle = (1/12)[(-5.3)^2 + (3.4)^2 + \dots] \mu\text{m}^2 = 6.28 \mu\text{m}^2$.
 $(\Delta x)_{\text{rms}} = 2.5 \mu\text{m}$.

16.21 (a) Equation (16.39) and $N/V = PN_A/RT$ give $D_{jj} = (3/8\pi^{\frac{1}{2}})[(8.314 \times 10^7 \text{ ergs/mol-K})(273 \text{ K})/(32.0 \text{ g/mol})]^{\frac{1}{2}} \times (3.6 \times 10^{-8} \text{ cm})^{-2}(82.06 \text{ cm}^3\text{-atm/mol-K})(273 \text{ K}) / (1.00 \text{ atm})(6.02 \times 10^{23} \text{ mol}^{-1}) = 0.16 \text{ cm}^2/\text{s}$. (b) Since D_{jj} is proportional to $1/P$, we have $D_{jj} = 0.016 \text{ cm}^2/\text{s}$.

16.22 Equation (16.40) and $(N_j + N_k)/V = (P_j + P_k)N_A/RT = PN_A/RT$ give $D_{jk} =$

$$\frac{3}{8\pi^{\frac{1}{2}}} \left[\frac{(8.314 \times 10^7 \text{ ergs/mol-K})(273 \text{ K})}{2 \text{ (g/mol)}} \left(\frac{1}{2.0} + \frac{1}{32.0} \right) \right]^{\frac{1}{2}} \\ \times \frac{(82.06 \text{ cm}^3\text{-atm/mol-K})(273 \text{ K})}{(3.15 \times 10^{-8} \text{ cm})^2 (1 \text{ atm})(6.02 \times 10^{23}/\text{mol})} \\ D_{jk} = 0.62 \text{ cm}^2/\text{s}$$

$$\frac{16.23}{D_{jj}} \approx [(6.02 \times 10^{23}/\text{mol})/(18.1 \text{ cm}^3/\text{mol})]^{1/3} \times \\ (1.38 \times 10^{-16} \text{ ergs/K})(298 \text{ K})/2\pi(0.00890 \text{ dyn-s/cm}^2) \\ = 2.4 \times 10^{-5} \text{ cm}^2/\text{s}.$$

16.24 The N_2 and H_2O molecules are not greatly different in size, so Eq. (16.43) is appropriate. We have $D_{1B}^\infty \approx$
 $(1.38 \times 10^{-16} \text{ erg/K})(298 \text{ K})/$
 $4\pi(0.0089 \text{ dyn-s/cm}^2)(1.85 \times 10^{-8} \text{ cm}) = 2.0 \times 10^{-5} \text{ cm}^2/\text{s}.$

16.25 (a) Equations (16.25) and (16.39) give $6\eta/5\rho =$
 $(6\pi/32)\langle v \rangle \lambda = (3\pi/16)\langle v \rangle \lambda = D_{jj}.$ (b) $D_{jj} = 6\eta RT/5PM =$
 $6(0.000297 \text{ dyn-s/cm}^2)(82.06 \text{ cm}^3\text{-atm/mol-K})(273.1 \text{ K})/$
 $5(1.00 \text{ atm})(20.18 \text{ g/mol}) = 0.40 \text{ cm}^2/\text{s}.$

16.26 Since a hemoglobin molecule is much larger than a water molecule, we use Eq. (16.42). We have $\bar{V}/N_A = 4\pi r_1^3/3$
and $r_1 = (3\bar{V}/4N_A\pi)^{1/3} =$
 $[3(48000 \text{ cm}^3/\text{mol})/4(6.02 \times 10^{23}/\text{mol})\pi]^{1/3} = 2.67 \times 10^{-7}$
 $\text{cm}.$ Then $D_{1B}^\infty \approx (1.38 \times 10^{-16} \text{ erg/K})(298 \text{ K})/$
 $6\pi(0.0089 \text{ dyn-s/cm}^2)(2.67 \times 10^{-7} \text{ cm}) = 9.2 \times 10^{-7} \text{ cm}^2/\text{s}.$

16.27 (a) Let $z = x^2$. Then $d(x^2)/dt = dz/dt =$
 $(dz/dx)(dx/dt) = 2x(dx/dt).$ Also, $d^2(x^2)/dt^2 =$

$(d/dt)[d(x^2)/dt] = (d/dt)[2x(dx/dt)] = 2(dx/dt)^2 + 2x(d^2x/dt^2)$. Substitution of these two equations into the equation in the problem transforms it to Eq. (16.33).

(b) Averaging, we get $0 - \frac{1}{2}f\langle d(x^2)/dt \rangle = \frac{1}{2}m\langle d^2(x^2)/dt^2 \rangle - \langle m(dx/dt)^2 \rangle$. We have $\epsilon_x = \frac{1}{2}mv_x^2 = \frac{1}{2}m(dx/dt)^2$, so $2\langle \epsilon_x \rangle = \langle m(dx/dt)^2 \rangle$. Also, $\epsilon = \epsilon_x + \epsilon_y + \epsilon_z$ and $\langle \epsilon \rangle = \langle \epsilon_x \rangle + \langle \epsilon_y \rangle + \langle \epsilon_z \rangle$. By symmetry, $\langle \epsilon_x \rangle = \langle \epsilon_y \rangle = \langle \epsilon_z \rangle$; thus $\langle \epsilon_x \rangle = \langle \epsilon \rangle / 3 = (3/2)kT/3 = \frac{1}{2}kT$. So $\langle m(dx/dt)^2 \rangle = 2\langle \epsilon_x \rangle = kT$.

(c) Substitution of $\langle m(dx/dt)^2 \rangle = kT$ into twice the first equation in part (b) gives $-f\langle d(x^2)/dt \rangle = m\langle d^2(x^2)/dt^2 \rangle - 2kT$. Let $s = d\langle x^2 \rangle / dt$. Since the derivative of a sum is the sum of the derivatives, we have $s = \langle d(x^2)/dt \rangle$ and $ds/dt = \langle d^2(x^2)/dt^2 \rangle$. Thus $-fs = m ds/dt - 2kT$ and $m ds/dt + fs = 2kT$. (d) $ds/dt = (2kT - fs)/m$ and $m(2kT - fs)^{-1} ds = dt$. Integration gives $-(m/f) \ln(2kT - fs) = t + c$ and $2kT - fs = e^{-ft/m} e^{-fc/m}$. From part (e), $e^{-ft/m} \approx 0$, so $s \equiv d\langle x^2 \rangle / dt = 2kT/f$. Integration gives $\langle x^2 \rangle = 2kTt/f + b$. The integration constant b is 0 if we take $x = 0$ at $t = 0$ for each particle. Hence, $\langle x^2 \rangle = (2kT/f)t$.

(e) $m = (3 \text{ g/cm}^3)[4\pi(10^{-5} \text{ cm})^3/3] = 10^{-14} \text{ g}$ and $f = 6\pi\eta r = 6\pi(0.01 \text{ dyn-s/cm}^2)(10^{-5} \text{ cm}) = 2 \times 10^{-6} \text{ dyn-s/cm}$. Then $e^{-ft/m} = \exp [-(2 \times 10^{-6} \text{ dyn-s/cm})(1 \text{ s})/(10^{-14} \text{ g})] = e^{-200000000} = 10^{-900000000}$.

16.28 (a) Substitution of dn_A and dn_B from (16.30) into $0 = dV = \bar{V}_A dn_A + \bar{V}_B dn_B$ gives $0 = \bar{V}_A[-\cancel{A}D_{AB}(dc_A/dx) dt]$

+ $\bar{V}_B [-D_{BA} (dc_B/dx) dt]$ and $D_{AB} \bar{V}_A (dc_A/dx) + D_{BA} \bar{V}_B (dc_B/dx) = 0$. (b) Division of (9.16) by V gives $1 = c_A \bar{V}_A + c_B \bar{V}_B$. Since there is no volume change on mixing, \bar{V}_A and \bar{V}_B are independent of the concentrations and hence are independent of the x coordinate. Differentiation of the last equation with respect to x gives $0 = \bar{V}_A (dc_A/dx) + \bar{V}_B (dc_B/dx)$. Substitution of $\bar{V}_A (dc_A/dx) = -\bar{V}_B (dc_B/dx)$ into the result of (a) gives $D_{AB} = D_{BA}$.

16.29 The number of moles of the diffusing species that lie between L and M equals $c_L V_L = c_L A(\Delta x)_{rms}$, where V_L is the volume between L and M. The number of moles moving left to right through plane M in time t is therefore $\frac{1}{2} c_L A(\Delta x)_{rms}$. Similarly, $\frac{1}{2} c_R A(\Delta x)_{rms}$ moles move right to left through M in time t . The net rate of flow of the diffusing species through M is thus $dn/dt = \Delta n/\Delta t = \frac{1}{2} (c_L - c_R) A(\Delta x)_{rms} / t$. Since dc/dx is constant, the average concentration c_L equals the concentration midway between planes L and M. Likewise, the average concentration c_R between M and R equals the concentration midway between M and R. The distance from the plane midway between L and M to the plane midway between M and R is $\frac{1}{2}(\Delta x)_{rms} + \frac{1}{2}(\Delta x)_{rms} = (\Delta x)_{rms}$; so the concentration gradient is $dc/dx = \Delta c/\Delta x = (c_R - c_L)/(\Delta x)_{rms}$. Substitution into (16.30) gives $\frac{1}{2} (c_L - c_R) A(\Delta x)_{rms} / t = -D A (c_R - c_L)/(\Delta x)_{rms}$ and $(\Delta x)_{rms} = (2Dt)^{\frac{1}{2}}$.

$$\text{16.30 } M_1 = RTs^\infty / D_{1B}^\infty (1 - \rho \bar{V}_1) =$$

$$\frac{(8.314 \times 10^7 \text{ erg/mol-K})(293.1 \text{ K})(4.47 \times 10^{-13} \text{ s})}{(6.9 \times 10^{-7} \text{ cm}^2/\text{s})[1 - (0.998 \text{ g/cm}^3)(0.749 \text{ cm}^3/\text{g})]}$$

$$= 63000 \text{ g/mol}$$

16.31 $I = dQ/dt = Q/t$ since I is constant. $Q = It = (1.0 \text{ A})(1.0 \text{ s}) = 1.0 \text{ C}$. The number of electrons is $(1.0 \text{ C})(6.02 \times 10^{23} \text{ electrons})/(96485 \text{ C}) = 6.2 \times 10^{18}$.

16.32 $R = \rho l/A = (1.67 \times 10^{-6} \Omega \text{ cm})(250 \text{ cm})/(0.040 \text{ cm}^2) = 0.0104 \Omega$.

16.33 $|\Delta\phi| = IR$ and $I = |\Delta\phi|/R = (25 \text{ V})/(100 \Omega) = 0.25 \text{ A}$.

16.34 $E = j/\kappa = I/A\kappa = (0.10 \text{ A})/(10 \text{ cm}^2)(0.010 \Omega^{-1} \text{ cm}^{-1}) = 1.0 \text{ V/cm}$.

16.35 $Q = It = (2.00 \text{ A})(30.0 \times 60 \text{ s}) = 3600 \text{ C}$.

$(3600 \text{ C}) \frac{1 \text{ mole } e^-}{96485 \text{ C}} \frac{1 \text{ mole Cu}}{2 \text{ moles } e^-} \frac{63.55 \text{ g Cu}}{1 \text{ mole Cu}} = 1.19 \text{ g of Cu}$

16.36 (a) $K_{\text{cell}} = \kappa R = [(0.012856/1.000495) \Omega^{-1} \text{ cm}^{-1}] \times$

$(411.82 \Omega) = 5.2917 \text{ cm}^{-1}$. (b) $\kappa_{\text{H}_2\text{O}} = K_{\text{cell}}/R =$

$(5.2917 \text{ cm}^{-1})/(368000 \Omega) = 0.00001438 \Omega^{-1} \text{ cm}^{-1}$. $\kappa =$

$K_{\text{cell}}/R = (5.2917 \text{ cm}^{-1})/(10875 \Omega) = 0.00048659 \Omega^{-1} \text{ cm}^{-1} =$

$\kappa_{\text{H}_2\text{O}} + \kappa_{\text{MX}_2}$ and $\kappa_{\text{MX}_2} = (0.00048659 - 0.00001438) \Omega^{-1} \text{ cm}^{-1}$

$= 0.00047221 \Omega^{-1} \text{ cm}^{-1}$. (c) $\Lambda_m = \kappa/c =$

$(0.00047221 \Omega^{-1} \text{ cm}^{-1})/(10^{-6} \text{ mol/cm}^3) = 472.21 \text{ cm}^2/\Omega\text{-mol}$.

(d) $\Lambda_{\text{eq}} = \Lambda_m/\nu_+ z_+ = \Lambda_m/2 = 236.10 \Omega^{-1} \text{ cm}^2 \text{ equiv}^{-1}$.

16.37 (a) $\Lambda_m = \kappa/c = (1.242 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1})/$

$[(5.000 \times 10^{-3} \text{ mol})/(1000 \text{ cm}^3)] = 248.4 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

(b) $\Lambda_{\text{eq}} = \Lambda_m/\nu_+ z_+ = \Lambda_m/1(2) = 124.2 \Omega^{-1} \text{ cm}^2 \text{ equiv}^{-1}$.

16.38 Equation (16.67) gives $u(\text{Na}^+) =$

$$(10.00 \text{ cm})(0.002313/\Omega\text{-cm})(0.1115 \text{ cm}^2)/(0.00160 \text{ A})(3453 \text{ s}) \\ = 4.668 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}. \text{ Equation (16.72) gives } t(\text{Na}^+) \\ = 1(96485 \text{ C/mol})[(0.02000 \text{ mol})/(1000 \text{ cm}^3)] \times \\ (0.0004668 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})/(0.002313 \Omega^{-1} \text{ cm}^{-1}) = 0.3894.$$

16.39 (a) Substitution of Eq. (16.67) (which applies to any ion) into (16.72) gives $t_B = |z_B| \mathcal{F} c_B (xK\mathcal{A}/It)/K = |z_B| \mathcal{F} c_B x\mathcal{A}/Q$, where $Q = It$. (b) As in Fig. 16.15, the method gives the transport number of the cation. The equation in (a) with $x\mathcal{A} = V$ gives $t(\text{Gd}^{3+}) = 3(96485 \text{ C/mol}) \times [(0.03327 \text{ mol})/(1000 \text{ cm}^3)](1.111 \text{ cm}^3)/(0.005594 \text{ A})(4406 \text{ s}) = 0.434$. Then $t(\text{Cl}^-) = 1 - 0.434 = 0.566$.

16.40 The coulometer reaction is $\text{Ag}^+ + e^- = \text{Ag}$. The 0.16024 g of Ag is 0.0014855 moles of Ag, so $Q = (0.0014855 \text{ mol})(96485 \text{ C/mol}) = 143.33 \text{ C}$. Let $n = 0.0014855 \text{ mol}$. Then n moles of Cl^- enter the cathode compartment due to the reduction reaction $\text{AgCl} + e^- = \text{Ag} + \text{Cl}^-$. The total number of moles of charge on the ions that cross the plane between the middle and cathode compartments is n ; this charge is composed of t_-n moles of Cl^- leaving and t_+n moles of K^+ entering the cathode compartment. The net change in number of moles of Cl^- in the cathode compartment is thus $n - t_-n = (1 - t_-)n = t_+n$, which is also the change in number of moles of K^+ in this compartment. The final composition of the cathode compartment is $(0.0019404)(120.99 \text{ g}) = 0.23477 \text{ g}$ of KCl and

$120.99 \text{ g} - 0.235 \text{ g} = 120.755 \text{ g}$ of H_2O . The initial composition of this compartment is 120.755 g of water plus x grams of KCl , where $x/(120.755 + x) = 0.0014941$. We get $x = 0.18069$. The change in KCl mass in the cathode compartment is 0.05408 g , which is 0.0007254 moles. Thus, $t_+ n = t_+ (0.0014855 \text{ mol}) = 0.0007254 \text{ mol}$ and $t_+ = 0.4883$. Then $t_- = 1 - t_+ = 0.5117$.

16.41 (a) Using Eq. (16.84), we have $\Lambda_m^\infty(\text{LiNO}_3) = \lambda_m^\infty(\text{Li}^+) + \lambda_m^\infty(\text{NO}_3^-)$ and the following three equations:
 (1) $\Lambda_m^\infty(\text{LiCl}) = \lambda_m^\infty(\text{Li}^+) + \lambda_m^\infty(\text{Cl}^-)$; (2) $\Lambda_m^\infty(\text{KNO}_3) = \lambda_m^\infty(\text{K}^+) + \lambda_m^\infty(\text{NO}_3^-)$; (3) $\Lambda_m^\infty(\text{KCl}) = \lambda_m^\infty(\text{K}^+) + \lambda_m^\infty(\text{Cl}^-)$. We take (1) + (2) - (3) to get $\Lambda_m^\infty(\text{LiNO}_3) = \Lambda_m^\infty(\text{LiCl}) + \Lambda_m^\infty(\text{KNO}_3) - \Lambda_m^\infty(\text{KCl}) = (90.9 + 114.5 - 105.0) \text{ cm}^2/\Omega\text{-mol} = 100.4 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.
(b) (4) $\Lambda_m^\infty(\text{HCl}) = \lambda_m^\infty(\text{H}^+) + \lambda_m^\infty(\text{Cl}^-)$; (5) $\Lambda_m^\infty(\text{NaCl}) = \lambda_m^\infty(\text{Na}^+) + \lambda_m^\infty(\text{Cl}^-)$; (6) $\Lambda_m^\infty(\text{NaC}_2\text{H}_3\text{O}_2) = \lambda_m^\infty(\text{Na}^+) + \lambda_m^\infty(\text{C}_2\text{H}_3\text{O}_2^-)$. Taking (4) + (6) - (5), we get $\lambda_m^\infty(\text{H}^+) + \lambda_m^\infty(\text{C}_2\text{H}_3\text{O}_2^-) = \Lambda_m^\infty(\text{HCl}) + \Lambda_m^\infty(\text{NaC}_2\text{H}_3\text{O}_2) - \Lambda_m^\infty(\text{NaCl}) = (426 + 91 - 126) \text{ cm}^2/\Omega\text{-mol} = 391 \text{ cm}^2/\Omega\text{-mol}$.

16.42 From (16.85) for NaCl , $t_+^\infty = 0.463 =$

(1) $\lambda_{m,+}^\infty / (96.9 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1})$ and $\lambda_m^\infty(\text{Na}^+) = 44.9 \text{ cm}^2/\Omega\text{-mol}$. Then $\lambda_m^\infty(\text{Cl}^-) = (96.9 - 44.9) \text{ cm}^2/\Omega\text{-mol} = 52.0 \text{ cm}^2/\Omega\text{-mol}$. We now use (16.84) for the other electrolytes. For NaNO_3 , $106.4 \text{ cm}^2/\Omega\text{-mol} = 44.9 \text{ cm}^2/\Omega\text{-mol} + \lambda_m^\infty(\text{NO}_3^-)$ and $\lambda_m^\infty(\text{NO}_3^-) = 61.5 \text{ cm}^2/\Omega\text{-mol}$. For LiNO_3 , $100.2 \text{ cm}^2/\Omega\text{-mol} = \lambda_m^\infty(\text{Li}^+) + 61.5 \text{ cm}^2/\Omega\text{-mol}$ and $\lambda_m^\infty(\text{Li}^+) = 38.7 \text{ cm}^2/\Omega\text{-mol}$. For

NaCNS, $107.0 \text{ cm}^2/\Omega\text{-mol} = 44.9 \text{ cm}^2/\Omega\text{-mol} + \lambda_m^\infty(\text{CNS})$ and $\lambda_m^\infty(\text{CNS}) = 62.1 \text{ cm}^2/\Omega\text{-mol}$. For HCl, $192 \text{ cm}^2/\Omega\text{-mol} = \lambda_m^\infty(\text{H}^+) + 52.0 \text{ cm}^2/\Omega\text{-mol}$ and $\lambda_m^\infty(\text{H}^+) = 140 \text{ cm}^2/\Omega\text{-mol}$. For $\text{Ca}(\text{CNS})_2$, $244 \text{ cm}^2/\Omega\text{-mol} = \lambda_m^\infty(\text{Ca}^{2+}) + 2(62.1) \text{ cm}^2/\Omega\text{-mol}$ and $\lambda_m^\infty(\text{Ca}^{2+}) = 120 \text{ cm}^2/\Omega\text{-mol}$.

16.43 (a) $u_B^\infty = \lambda_{m,B}^\infty / |z_B| \mathcal{F} = (67.4 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}) / 1(96485 \text{ C/mol}) = 6.99 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. (b) $v_B^\infty = u_B^\infty E = (6.99 \times 10^{-4} \text{ cm}^2/\text{V-s})(24 \text{ V/cm}) = 0.017 \text{ cm/s}$. (c) $r_B \approx |z_B| e / 6\pi\eta u_B^\infty = 1(1.6022 \times 10^{-19} \text{ C}) / 6\pi(0.008904 \times 10^{-1} \text{ N s m}^{-2})[6.99 \times 10^{-4} (10^{-2} \text{ m})^2/\text{V-s}] = 1.37 \times 10^{-10} \text{ m} = 1.37 \text{ \AA}$.

16.44 We use $\Lambda_m^\infty = \nu_+ \lambda_{m,+}^\infty + \nu_- \lambda_{m,-}^\infty$. (a) $\Lambda_m^\infty = (73.6 + 71.4) \text{ cm}^2/\Omega\text{-mol} = 145.0 \text{ cm}^2/\Omega\text{-mol}$. (b) $\Lambda_m^\infty = [2(73.6) + 160] \text{ cm}^2/\Omega\text{-mol} = 307 \text{ cm}^2/\Omega\text{-mol}$. (c) $\Lambda_m^\infty = (106.1 + 160) \text{ cm}^2/\Omega\text{-mol} = 266 \text{ cm}^2/\Omega\text{-mol}$. (d) $\Lambda_m^\infty = [118.9 + 2(198)] \text{ cm}^2/\Omega\text{-mol} = 515 \text{ cm}^2/\Omega\text{-mol}$.

16.45 From (16.85), $t^\infty(\text{Mg}^{2+}) = 1(106.1) / [1(106.1) + 2(71.4)] = 0.426$ and $t^\infty(\text{NO}_3^-) = 1 - 0.426 = 0.574$.

16.46 From (16.85), $t_+^\infty = \nu_+ \lambda_{m,+}^\infty / \Lambda_m^\infty = 2\lambda_{m,+}^\infty / (259.6 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}) = 0.386$ and $\lambda_m^\infty(\text{Na}^+) = 50.1 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. From (16.84), $\Lambda_m^\infty = 259.6 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} = 2(50.1 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}) + \lambda_m^\infty(\text{SO}_4^{2-})$ and $\lambda_m^\infty(\text{SO}_4^{2-}) = 159.4 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

16.47 We assume the electrodes are inert, so only Ag^+

and NO_3^- carry the current in the solution. $t_- \approx t_-^\infty = v_{-m,-}^\infty / (v_{+m,+}^\infty + v_{-m,-}^\infty) = 71.4 / (61.9 + 71.4) = 0.536$. If 10^{-3} mol of Ag^+ is deposited according to $\text{Ag}^+ + e^- \rightarrow \text{Ag}$, then 10^{-3} Faradays of charge must have flowed through the circuit. The nitrate ions carry a fraction t_- of the current in the solution, so the nitrate ions carried $t_-(10^{-3}$ Faradays) of charge through the solution. Hence $10^{-3}t_-$ moles of NO_3^- crossed a plane in the solution, and this is $(1.00 \times 10^{-3})(0.536)$ mol = 0.536 mmol.

16.48 Because of its higher charge, Mg^{2+} is hydrated to a much greater extent than Na^+ and so its radius is much greater than that of Na^+ . Therefore u in (16.70) has similar values for these two ions.

16.49 (a) $\lambda_m^\infty(\text{Cl}^-)$, $u^\infty(\text{Cl}^-)$; (b) no (interionic forces differ in the two solutions).

16.50 κ .

16.51 (a) Use of (16.70) in (16.80) gives $\lambda_{m,B}^\infty = |z_B| \mathcal{F} u_B^\infty \approx |z_B|^2 e \mathcal{F} / 6\pi\eta r_B$. So $\ln \lambda_m^\infty \approx \ln (z_B^2 e \mathcal{F} / 6\pi\eta r_B) - \ln \eta$ and $d \ln \lambda_m^\infty / dT \approx -(1/\eta) d\eta/dT$. (b) $d\eta/dT \approx \Delta\eta/\Delta T = (0.8705 - 0.9111) \text{ cP} / (2 \text{ K}) = -0.0203 \text{ cP/K}$ and $(1/\eta)(d\eta/dT) = (1/0.8904 \text{ cP})(-0.0203 \text{ cP/K}) = -0.023 \text{ K}^{-1}$, so $d \ln \lambda_m^\infty / dT \approx 0.023 \text{ K}^{-1}$. (c) Integration gives $\ln (\lambda_{m,2}^\infty / \lambda_{m,1}^\infty) \approx (0.023 \text{ K}^{-1})(T_2 - T_1)$ and $\lambda_{m,2}^\infty = \lambda_{m,1}^\infty \exp[(0.023 \text{ K}^{-1})(T_2 - T_1)] = (71.4 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})e^{0.23} = 89.9 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

16.52 (a) $\Lambda_m^\infty = (73.5 + 71.4) \text{ cm}^2/\Omega\text{-mol} = 144.9 \text{ cm}^2/\Omega\text{-mol}.$

From (16.87), $\Lambda_m = 144.9 \text{ cm}^2/\Omega\text{-mol}$

$- [60.6 + 0.230(144.9)](\text{cm}^2/\Omega\text{-mol})(0.00200)^{\frac{1}{2}} = 140.7$

$\text{cm}^2/\Omega\text{-mol}. \quad \kappa = \Lambda_m c = (140.7 \text{ cm}^2/\Omega\text{-mol}) \times$

$(0.00200 \text{ mol})/(1000 \text{ cm}^3) = 0.000281 \Omega^{-1} \text{ cm}^{-1}. \quad (\underline{b})$ Ne-

glecting the conductivity of the water, we have $R = \rho \ell / \mathcal{A}$

$= \ell / \kappa \mathcal{A} = (10.0 \text{ cm}) / (0.000281 \Omega^{-1} \text{ cm}^{-1})(1.00 \text{ cm}^2) =$

$35,500 \Omega.$

16.53 $K_c = [H^+][OH^-]$, since $\gamma_{\pm} = 1$ at the extremely low

I_m value in this solution. Equation (16.90) with $c_+ = 0$ in

the denominator gives the initial estimate $c_+ \approx$

$(5.47 \times 10^{-8} \Omega^{-1} \text{ cm}^{-1}) / [(350 + 198) \text{ cm}^2/\Omega\text{-mol}] = 9.98 \times$

$10^{-11} \text{ mol/cm}^3 = 9.98 \times 10^{-8} \text{ mol/dm}^3.$ We have $S =$

$60.6 \text{ cm}^2/\Omega\text{-mol} + 0.230(548 \text{ cm}^2/\Omega\text{-mol}) = 186.6 \text{ cm}^2/\Omega\text{-mol}.$

Using the initial estimate of c_+ in the denominator of Eq.

(16.90), we have $c_+ \approx (5.47 \times 10^{-8} \Omega^{-1} \text{ cm}^{-1}) /$

$[548 \text{ cm}^2/\Omega\text{-mol} - (186.6 \text{ cm}^2/\Omega\text{-mol})(9.98 \times 10^{-8})^{\frac{1}{2}}] =$

$9.98 \times 10^{-11} \text{ mol/cm}^3 = 9.98 \times 10^{-8} \text{ mol/dm}^3,$ as before.

Hence, $K_c = (9.98 \times 10^{-8} \text{ mol/dm}^3)^2 = 9.97 \times 10^{-15} \text{ mol}^2/\text{dm}^6.$

16.54 (a) Since $z_+ = |z_-|$, Eq. (16.90) applies. We have

$\lambda_{m,+}^\infty + \lambda_{m,-}^\infty = (118.9 + 160) \text{ cm}^2/\Omega\text{-mol} = 279 \text{ cm}^2/\Omega\text{-mol}$ and

$S = 8[a + b(\lambda_{m,+}^\infty + \lambda_{m,-}^\infty)] = 998 \text{ cm}^2/\Omega\text{-mol}.$ Therefore

$$c_+ = \frac{2.21 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}}{279 \text{ cm}^2/\Omega\text{-mol} - (998 \text{ cm}^2/\Omega\text{-mol})[c_+/(10^{-3} \text{ mol/cm}^3)]^{\frac{1}{2}}}$$

With $c_+ = 0$ in the denominator, we get the initial estimate $c_+ \approx 7.92 \times 10^{-6} \text{ mol/cm}^3$. With $c_+ = 7.92 \times 10^{-6} \text{ mol/cm}^3$, we get the improved estimate $c_+ \approx 1.16 \times 10^{-5} \text{ mol/cm}^3$.

Further repetitions yield the successive estimates $1.29 \times 10^{-5} \text{ mol/cm}^3$, $1.33 \times 10^{-5} \text{ mol/cm}^3$, $1.35 \times 10^{-5} \text{ mol/cm}^3$, and $1.35_5 \times 10^{-5} \text{ mol/cm}^3$. Hence $c_+ = 1.35 \times 10^{-2} \text{ mol/dm}^3$. The solution is dilute, so we can take the molality as 0.0135 mol/kg . The Davies equation with $I_m = 0.0540$

mol/kg then gives $\log \gamma_{\pm} = -0.352$ and $\gamma_{\pm} = 0.445$. We can neglect the difference between molality-scale and concentration-scale activity coefficients in this dilute solution, so the concentration-scale K_{sp} is $K_{sp} =$

$$(0.445)^2 (0.0135 \text{ mol/dm}^3)^2 = 3.6 \times 10^{-5} \text{ mol}^2/\text{dm}^6. \quad (\text{b}) \text{ No.}$$

$K_{sp} = \gamma_{\pm}^2 [\text{Ca}^{2+}][\text{SO}_4^{2-}]$. We found the ionic concentrations and γ_{\pm} . The existence of the additional equilibrium $\text{Ca}^{2+} + \text{SO}_4^{2-} = \text{CaSO}_4(\text{aq})$ does not invalidate our work.

16.55 We have $\lambda_{m,+}^{\infty} + \lambda_{m,-}^{\infty} = (350 + 40.8) \text{ cm}^2/\Omega\text{-mol} = 391 \text{ cm}^2/\Omega\text{-mol}$ and $S = [60.6 + 0.230(391)] \text{ cm}^2/\Omega\text{-mol} = 150.5 \text{ cm}^2/\Omega\text{-mol}$. Therefore

$$c_+ = \frac{4.95 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1}}{391 \text{ cm}^2/\Omega\text{-mol} - (150\frac{1}{2} \text{ cm}^2/\Omega\text{-mol})[c_+/(10^{-3} \text{ mol/cm}^3)]^{\frac{1}{2}}}$$

With $c_+ = 0$ in the denominator, we get the initial estimate $c_+ \approx 1.27 \times 10^{-7} \text{ mol/cm}^3$. Recalculation with this c_+ value in the denominator gives $c_+ = 1.27 \times 10^{-7} \text{ mol/cm}^3 = 1.27 \times 10^{-4} \text{ mol/dm}^3$, which is the H_3O^+ concentration. For

this dilute solution, we can take the ionic molalities as 1.27×10^{-4} mol/kg. The Davies equation then gives $\gamma_{\pm} = 0.987$. Neglecting the slight difference between concentration-scale and molality-scale γ 's, we have $K_c = (0.987)^2 (0.000127 \text{ mol/dm}^3)^2 / [(0.001028 - 0.000127) \text{ mol/dm}^3] = 1.74 \times 10^{-5} \text{ mol/dm}^3$.

16.56 We have $\lambda_{m,+}^{\infty} + \lambda_{m,-}^{\infty} = (106 + 160) \text{ cm}^2/\Omega\text{-mol} = 266 \text{ cm}^2/\Omega\text{-mol}$ and $S = 8[60.6 + 0.23(266)] \text{ cm}^2/\Omega\text{-mol} = 974 \text{ cm}^2/\Omega\text{-mol}$. Then

$$c_+ = \frac{6.156 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1}}{266 \text{ cm}^2/\Omega\text{-mol} - (974 \text{ cm}^2/\Omega\text{-mol})[c_+/(10^{-3} \text{ mol/cm}^3)]^{\frac{1}{2}}}$$

With $c_+ = 0$ in the denominator, we get the initial estimate $c_+ \approx 2.31 \times 10^{-7} \text{ mol/cm}^3$. With this value of c_+ , we get the improved estimate $c_+ \approx 2.45 \times 10^{-7} \text{ mol/cm}^3$. Another repetition yields the final result $c_+ = 2.45_5 \times 10^{-7} \text{ mol/cm}^3 = 2.46 \times 10^{-4} \text{ mol/dm}^3$. For this dilute solution, we can take the ion molalities as $2.46 \times 10^{-4} \text{ mol/kg}$, so $I_m = 9.8 \times 10^{-4} \text{ mol/kg}$. The Davies equation gives $\log \gamma_{\pm} = -0.061$ and $\gamma_{\pm} = 0.87$. We can assume the molality-scale and concentration-scale activity coefficients to be equal in this dilute solution. We have $[\text{Mg}^{2+}] = [\text{SO}_4^{2-}] = 2.46 \times 10^{-4} \text{ mol/dm}^3$ and $[\text{MgSO}_4(\text{aq})] = 2.50 \times 10^{-4} \text{ mol/dm}^3 - 2.45_5 \times 10^{-4} \text{ mol/dm}^3 = 4.5 \times 10^{-6} \text{ mol/dm}^3$. Hence, $K_c = (4.5 \times 10^{-6} \text{ mol/dm}^3) / (0.87)^2 (2.46 \times 10^{-4} \text{ mol/dm}^3)^2 = 100 \text{ dm}^3/\text{mol}$.

16.57 Omitting the S term and using Eq. (16.59), we have for (16.90): $c_+ = K/(\lambda_{m,+}^\infty + \lambda_{m,-}^\infty) = \Lambda_m c/(\lambda_{m,+}^\infty + \lambda_{m,-}^\infty)$. Then $\alpha = c_+/c = \Lambda_m/(\lambda_{m,+}^\infty + \lambda_{m,-}^\infty)$.

16.58 The Onsager equation predicts a $c^{\frac{1}{2}}$ dependence of Λ_m in dilute solutions, so we plot Λ_m vs. $c^{\frac{1}{2}}$. The points give a rather good straight-line fit; the intercept at $c = 0$ is $\Lambda_m^\infty = 270.3 \text{ cm}^2/\Omega\text{-mol}$.

16.59 $RT/\mathcal{F} = (8.314 \text{ J/mol-K})(298.1 \text{ K})/(96485 \text{ C/mol}) = 0.02569 \text{ V} \equiv b$. (a) $\mathcal{E}_J/b =$

$$\frac{350(1)(0.01 - 0.10) + 76.3(-1)(0.01 - 0.10)}{350(0.01 - 0.10) + 76.3(0.01 - 0.10)}$$

$$\times \ln \frac{350(0.10) + 76.3(0.10)}{350(0.01) + 76.3(0.01)} = 1.478 \quad \text{and} \quad \mathcal{E}_J = 0.038 \text{ V}$$

(b) This interchanges the solutions in (a), so $\mathcal{E}_J =$

$\phi_{\text{soln,R}} - \phi_{\text{soln,L}} = -0.038 \text{ V}$. (c) $\mathcal{E}_J/b =$

$$\frac{350(0 - 0.1) - 78.4(0 - 0.1) + 73.5(0.2 - 0) - 76.3(0.2 - 0)}{350(0 - 0.1) + 78.4(0 - 0.1) + 73.5(0.2 - 0) + 76.3(0.2 - 0)}$$

$$\times \ln \frac{350(0.1) + 78.4(0.1)}{73.5(0.2) + 76.3(0.2)} = 0.770 \quad \text{and} \quad \mathcal{E}_J = 0.020 \text{ V}$$

(d) Replacing all the 0.2's in (c) by 4, we get $\mathcal{E}_J =$

0.004₇ V. [Note the greatly reduced \mathcal{E}_J compared to (c).]

16.60 From (16.32), $(\Delta x)_{\text{rms}} = (2Dt)^{1/2}$. Substitution of the Stokes-Einstein equation (16.42) for D gives $(\Delta x)_{\text{rms}} \approx (kTt/3\pi\eta_{\text{H}_2\text{O}}r_{\text{Mg}^{2+}})^{1/2}$. Use of (16.70) for $r_{\text{Mg}^{2+}}$ gives

$(\Delta x)_{\text{rms}} \approx (2kT u_{\text{Mg}^{2+}}^{\infty} / z_{\text{Mg}^{2+}} |e|)^{1/2}$. In 1 s, $(\Delta x)_{\text{rms}} \approx$
 $[2(1.38 \times 10^{-23} \text{ J/K})(298 \text{ K})(55 \times 10^{-9} \text{ m}^2/\text{V-s})(1 \text{ s}) /$
 $2(1.60 \times 10^{-19} \text{ C})]^{1/2} = 3.8 \times 10^{-5} \text{ m} = 380000 \text{ \AA} = 0.0038$
 cm , where u^{∞} was taken from p. 496 of the text. In 10 s,
 $(\Delta x)_{\text{rms}} \approx (10/1)^{1/2} (38 \text{ \mu m}) = 120 \text{ \mu m}$.

16.61 (a) Increases; (b) increases; (c) increases;
 (d) increases; (e) increases; (f) increases.

CHAPTER 17

17.1 (a) $n_A/V = P_A/RT =$

$$(0.10 \text{ atm})/(82.06 \text{ cm}^3\text{-atm/mole-K})(298 \text{ K}) = 4.09 \times 10^{-6} \text{ mole/cm}^3 = 4.09 \times 10^{-3} \text{ mole/dm}^3. \quad r = k[N_2O_5] =$$

$$(1.73 \times 10^{-5} \text{ s}^{-1})(4.09 \times 10^{-3} \text{ mole/dm}^3) = 7.1 \times 10^{-8} \text{ mole/dm}^3\text{-s}. \quad J = rV = (7.1 \times 10^{-8} \text{ mole/dm}^3\text{-s})(12.0 \text{ dm}^3) =$$

$$8.5 \times 10^{-7} \text{ mole/s}. \quad (\text{b}) \quad r = [1/(-2)] d[N_2O_5]/dt = 7.1 \times 10^{-8} \text{ mole/dm}^3\text{-s} \text{ and } d[N_2O_5]/dt = -1.4 \times 10^{-7} \text{ mole/dm}^3\text{-s}.$$

$$(\text{c}) \quad (1.4 \times 10^{-7} \text{ mole/dm}^3\text{-s})(6.02 \times 10^{23}/\text{mole})(1 \text{ s})(12 \text{ dm}^3) = 1.0 \times 10^{18}. \quad (\text{d}) \quad N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2. \text{ Here, } J = -dn_{N_2O_5}/dt \text{ as compared to } J = -\frac{1}{2}dn_{N_2O_5}/dt \text{ for } 2N_2O_5 \rightarrow 4NO_2 + O_2. \text{ So } J = 2(8.5 \times 10^{-7} \text{ mole/s}) = 17 \times 10^{-7} \text{ mole/s}. \quad r = J/V = 14 \times 10^{-8} \text{ mole/dm}^3\text{-s}. \quad r = k[N_2O_5] \text{ and } k = r/[N_2O_5]; \text{ since } r \text{ is doubled, so is } k, \text{ and } k = 3.46 \times 10^{-5} \text{ s}^{-1}.$$

17.2 (a) $P_A V = n_A RT$ and $P_A = [A]RT$. The equation

$$-(1/a)dP_A/dt = k_P P_A^n \text{ becomes } -(RT/a)d[A]/dt = k_P [A]^n (RT)^n$$

$$\text{and } r = -(1/a)d[A]/dt = (RT)^{n-1} k_P [A]^n. \text{ Comparison with}$$

$$r = k[A]^n \text{ gives } k_P = k(RT)^{1-n}. \quad (\text{b}) \text{ Yes. } (\text{c}) \text{ } k \text{ has units}$$

$$(\text{dm}^3/\text{mole})^{n-1} \text{ s}^{-1} = \text{dm}^3 \text{ mole}^{-1} \text{ s}^{-1}, \text{ so } n = 2 \text{ and } k_P =$$

$$k(RT)^{-1} = (2.00 \times 10^{-4} \text{ dm}^3/\text{mole-s})/$$

$$(0.08206 \text{ dm}^3\text{-atm/mole-K})(400 \text{ K}) = 6.09 \times 10^{-6} \text{ atm}^{-1} \text{ s}^{-1}.$$

17.3 $r_1 = k_1[A]$ and $r_2 = k_2[B]$. Since $[B]$ might be much greater than $[A]$, it is possible for r_2 to exceed r_1 even though k_1 exceeds k_2 .

17.4 (a) Since the first step produces one C molecule while the second step consumes two C's, the first step must occur twice for each occurrence of the second step. The second step produces one F and the third step consumes one F, so the second and third steps have the same stoichiometric number. The stoichiometric numbers are thus 2 for the first step, 1 for the second step, and 1 for the third step. Adding twice the first step to the second and third steps, we get $2A + 2B + 2C + F + B \rightarrow 2C + 2D + F + 2A + G$ and the overall reaction is $3B \rightarrow 2D + G$. (b) Species A is consumed in the first step, regenerated in the last step, and does not appear in the overall reaction; hence A is a catalyst. B is a reactant. C and F are reaction intermediates. D and G are products.

17.5 From Eq. (17.5), the units of k are $(\text{dm}^3/\text{mol})^{n-1} \text{s}^{-1}$. Comparison with the value of k shows that $n - 1 = 1$, $n = 2$.

17.6 (a) $[A]/[A]_0 = e^{-k_A t}$, so $0.65 = e^{-k_A (325 \text{ s})}$ and $\ln 0.65 = -k_A (325 \text{ s})$. We get $k_A = 0.0013_3 \text{ s}^{-1}$. From Eq. (17.11), $k = k_A/a = k_A/2 = 0.00066 \text{ s}^{-1}$. (b) $t = -(1/k_A) \times \ln ([A]/[A]_0) = -[1/(0.0013_3 \text{ s}^{-1})] \ln (0.30 \text{ or } 0.10) = 905 \text{ s or } 1731 \text{ s}$.

17.7 (a) $k_A t_{1/2} = 0.693$. From (17.11), $k_A = ak = 2(1.73 \times 10^{-5} \text{ s}^{-1}) = 3.46 \times 10^{-5} \text{ s}^{-1}$. So $t_{1/2} = 0.693/k_A = 0.693/(3.46 \times 10^{-5} \text{ s}^{-1}) = 2.00 \times 10^4 \text{ s}$. (b) $[A] = [A]_0 e^{-k_A t} = (0.010 \text{ mole/dm}^3) e^{-(3.46 \times 10^{-5} \text{ s}^{-1})(24 \times 3600 \text{ s})}$

$$= 5.0 \times 10^{-4} \text{ mole/dm}^3.$$

$$\underline{17.8} \quad d[A]/dt = -k_A[A]^3, \quad \int_1^2 [A]^{-3} d[A] = -\int_1^2 k_A dt,$$

$$-\frac{1}{2}[A]^{-2} \Big|_1^2 = -k_A(t_2 - t_1), \quad 1/[A]_2^2 - 1/[A]_1^2 = 2k_A(t_2 - t_1)$$

or $1/[A]^2 - 1/[A]_0^2 = 2k_A t$, where we took $t_1 = 0$ and $t_2 = t$.

17.9 (a) Eqs. (17.22) and (17.19) with $A = \text{NO}_2$, $B = \text{F}_2$, $a = 2$, and $b = 1$ apply. $[A]_0 = (2.00 \text{ mol})/(400 \text{ dm}^3) = 0.00500 \text{ mol/dm}^3$ and $[B]_0 = 0.00750 \text{ mol/dm}^3$.

$$(a[B]_0 - b[A]_0)kt = [2(0.00750) - 0.00500](\text{mol/dm}^3) \times (38 \text{ dm}^3/\text{mol-s})(10.0 \text{ s}) = 3.80. \text{ Using } [B]/[B]_0 = 1 - ba^{-1}[A]_0/[B]_0 + ba^{-1}[A]/[B]_0, \text{ we have for Eq. (17.22):}$$

$$3.80 = \ln \{ (0.667 + [66.7 \text{ dm}^3/\text{mol}][A]) / (200 \text{ dm}^3/\text{mol})[A] \}$$

and $e^{3.80} = 0.00333/(\text{dm}^3/\text{mol})[A] + 0.333$. We find $[A] = 7.5 \times 10^{-5} \text{ mol/dm}^3 = [\text{NO}_2]$. Then $n_A = (400 \text{ dm}^3) \times$

$$(7.5 \times 10^{-5} \text{ mol/dm}^3) = 0.0300 \text{ mol NO}_2. \text{ Let } 2z \text{ moles of NO}_2 \text{ react in } 10 \text{ s. Then } 2 - 2z = 0.0300 \text{ and } z = 0.985. \text{ Then } n_{\text{F}_2} = 3 - z = 2.015 \text{ moles and } n_{\text{NO}_2\text{F}} = 2z = 1.97 \text{ mol.}$$

(b) $r = k[\text{NO}_2][\text{F}_2] = (38 \text{ dm}^3/\text{mol-s})(0.00500 \text{ mol/dm}^3) \times (0.00750 \text{ mol/dm}^3) = 0.00142 \text{ mol/dm}^3\text{-s}$ initially. After 10 s, part (a) gives $[\text{NO}_2] = 7.5 \times 10^{-5} \text{ mol/dm}^3$ and $[\text{F}_2] = 2.015 \text{ mol}/(400 \text{ dm}^3) = 5.04 \times 10^{-3} \text{ mol/dm}^3$. So $r = (38 \text{ dm}^3/\text{mol-s})(7.5 \times 10^{-5} \text{ mol/dm}^3)(5.04 \times 10^{-3} \text{ mol/dm}^3) = 1.44 \times 10^{-5} \text{ mol/dm}^3\text{-s}.$

17.10 (a) As noted in Section 1.8, $(d/dx) \int f(x) dx =$

$f(x)$. Using this identity, we have $dy/dx = e^{w(x)}(dw/dx)(\int e^{-w(x)} f(x) dx + c) + e^{w(x)}[e^{-w(x)} f(x)]$.

Since $w(x) = \int g(x) dx$, we have $dw/dx = g(x)$ and $dy/dx = e^w g(\int e^{-w} f dx + c) + f$. The right side of the differential equation is $f + gy = f + ge^w(\int e^{-w} f dx + c)$, which is the same as dy/dx . Hence, y is the correct solution. (b) In

(17.39), we take $y = [B]$, $x = t$, $f(x) = k_1[A]_0 e^{-k_1 t}$, $g(x) = -k_2$. Then $w = -\int k_2 dt = -k_2 t$ and $y = [B] = e^{-k_2 t}(\int e^{k_2 t} k_1[A]_0 e^{-k_1 t} dt + c) = e^{-k_2 t}\{k_1[A]_0 e^{(k_2 - k_1)t} / (k_2 - k_1) + c\} = k_1[A]_0 e^{-k_1 t} / (k_2 - k_1) + c e^{-k_2 t}$. To evaluate c , we use the fact that $[B] = 0$ at $t = 0$; so $0 = k_1[A]_0 / (k_2 - k_1) + c$ and $c = -k_1[A]_0 / (k_2 - k_1)$. Hence $[B] = \{k_1[A]_0 / (k_2 - k_1)\}(e^{-k_1 t} - e^{-k_2 t})$.

17.11 No. A kinetically reversible reaction is one where a significant amount of back reaction occurs. A thermodynamically reversible process must go through equilibrium states only, so a kinetically reversible reaction is a thermodynamically irreversible process.

17.12 From the equation following (17.16), $r = k[A]^2$ integrates to $[A] = [A]_0 / (1 + akt[A]_0)$, and $r = k[A]^2$ becomes $r = k[A]_0^2 / (1 + akt[A]_0)^2$.

17.13 $r = k[A]^0 = k =$

$-d[A]/dt$, which integrates to $[A] = -kt + c$. At $t = 0$, $[A]_0 = 0 + c$. So $[A] = [A]_0 - kt$. The graph is linear.



17.14 For $n = 1$, the integrated rate law is (17.30), for which $[A]$ reaches 0 only at $t = \infty$. For $n \neq 1$, the integrated rate law is (17.28). Setting $[A] = 0$ in (17.28), we see there are two cases to consider. If $n < 1$, then the left side of (17.28) is zero when $[A] = 0$, and the time $t^\#$ required for $[A]$ to reach 0 satisfies $0 = 1 + [A]_0^{n-1}(n-1)k_A t^\#$ and $t^\# = 1/[A]_0^{n-1}(1-n)$, which is positive, since $n < 1$. Hence $[A]$ reaches 0 in a finite time when $n < 1$. For $n > 1$, the left side of (17.28) becomes infinite when $[A]$ equals 0 and an infinite amount of time is required for $[A]$ to reach 0.

17.15 $a^{-1} d[A]/dt = -k[A]^2[B]$. Use of (17.19) gives $\int_1^2 [A]^{-2}([B]_0 - ba^{-1}[A]_0 + ba^{-1}[A])^{-1} d[A] = -\int_1^2 ak dt$. A table of integrals gives $\int [1/x^2(p + sx)] dx = -1/px + (s/p^2) \ln [(p + sx)/x]$. We have $x = [A]$, $p = [B]_0 - ba^{-1}[A]_0$, and $s = ba^{-1}$, so

$$\frac{ba^{-1}}{([B]_0 - ba^{-1}[A]_0)^2} \ln \frac{[B]_0 - ba^{-1}[A]_0 + ba^{-1}[A]}{[A]} \Big|_1^2 - \frac{1}{([B]_0 - ba^{-1}[A]_0)[A]} \Big|_1^2 = -ak(t_2 - t_1)$$

$$\frac{1}{a[B]_0 - b[A]_0} \left(\frac{1}{[A]_0} - \frac{1}{[A]} + \frac{b}{a[B]_0 - b[A]_0} \ln \frac{[B]/[B]_0}{[A]/[A]_0} \right) = -kt$$

where we used (17.19) and took $t_1 = 0$ and $t_2 = t$.

17.16 For $t_1 = 0.5$ s and $t_2 = 1.0$ s, we have $[A]_1 \approx [A]_0 - k_A[A]_0 t_1 = [1 - (0.15 \text{ s}^{-1})(0.5 \text{ s})] \text{ mol/dm}^3 = 0.925 \text{ mol/dm}^3$ and $[A]_2 \approx [A]_1 - k_A[A]_1(t_2 - t_1) = 0.925 \text{ mol/dm}^3 - (0.15 \text{ s}^{-1})(0.925 \text{ mol/dm}^3)(0.5 \text{ s}) = 0.856 \text{ mol/dm}^3$. For $\Delta t = 0.2$ s, we get 0.97, 0.9409, 0.9127, 0.8853, 0.8587 mol/dm^3 for $[A]_1, \dots, [A]_5$, respectively. The values 0.856 and 0.8587 mol/dm^3 may be compared with the exact value $[A]_0 e^{-k_A t} = (1 \text{ mol/dm}^3)e^{-(0.15 \text{ s}^{-1})(1 \text{ s})} = 0.8607 \text{ mol/dm}^3$. (For $\Delta t = 0.1$ s, the estimate found is 0.8597 mol/dm^3 .) A BASIC program is

```

10 K = 0.15
20 A = 1
30 INPUT "DELTA T="; DT
40 INPUT "TFINAL="; TF
50 N = TF/DT
60 FOR I = 1 TO N
70 A = A - K*A*DT
80 NEXT I
90 PRINT "AFINAL="; A
95 GOTO 30
99 END

```

17.17 In equation (17.28), let $[A]/[A]_0 = \alpha$. Then $\alpha^{1-n} = 1 + [A]_0^{n-1}(n-1)k_A t_\alpha$ and $t_\alpha = (\alpha^{1-n} - 1)/[A]_0^{n-1}(n-1)k_A$. Taking the log of each side, we get the desired result for $n \neq 1$. For $n = 1$, we set $[A]/[A]_0 = \alpha$ in (17.30) to get $\alpha = e^{-k_A t_\alpha}$ and $\ln \alpha = -k_A t_\alpha$.

17.18 For $n \neq 1$, the equation following (17.50) gives $\log \phi = \log [(\alpha^{1-n} - 1)/(n-1)]$. For $\alpha = 0.05$ and $n = 0$,

$\log \phi = \log [(0.05 - 1)/(-1)] = -0.0223$; for $n = 1/2$, $3/2$, 2 , and 3 , one finds $\log \phi = 0.1911$, 0.8416 , 1.2788 , and 2.2999 , respectively. For $n = 1$, we have $\log \phi = \log (-\ln \alpha) = \log (-\ln 0.05) = 0.4765$.

17.19 (a) We use the fractional-life method, plotting $\log t_\alpha$ vs. $\log [A]_0$. The data are

$\log t_\alpha$	2.771	2.823	2.954	3.057
$\log [A]_0$	-2.090	-2.191	-2.509	-2.726

The slope of the straight line through these points is $-0.44 = 1 - n$, so $n = 1.44 \approx 1.5$. The order is $3/2$.

(b) Putting $[A]/[A]_0 = \alpha = 0.69$ and $n = 1.5$ in Eq. (17.28), we get $k_A = 0.408/t_\alpha [A]_0^{1/2}$. Substitution of the four pairs of t_α and $[A]_0$ values gives $10^3 k_A / (\text{dm}^{3/2}/\text{mol}^{1/2}\text{-s})$ as 7.67 , 7.64 , 8.14 , and 8.25 . Averaging, we get $k_A = 7.9 \times 10^{-3} \text{ dm}^{3/2}/\text{mol}^{1/2}\text{-s}$.

17.20 (a) Both plots give pretty good fits to a straight line. The $\log [A]$ vs. t plot (corresponding to $n = 1$) gives a somewhat better fit, but considering the inaccuracy of kinetics data, one could not absolutely rule out $n = 2$ from the plot. (b) A good fit is obtained for $n = 1$ and for $n = 3/2$; the fit for $n = 2$ is not good. To decide between $n = 1$ and $n = 3/2$, one would need data at later times.

17.21 Equation (17.22) with $a = 1$ and $b = 1$ applies. Let

$B = S_2O_3^{2-}$ and $A = C_3H_7Br$. Then $a[B]_0 - b[A]_0 = 57.1 \text{ mmol/dm}^3$. We use $[A] - [A]_0 = [B] - [B]_0$ to calculate the $[A]$ concentrations. A plot of $\ln \{([B]/[B]_0)/[A]/[A]_0\} \equiv \ln z$ vs. t is linear with slope $(a[B]_0 - b[A]_0)k$. The data are

$\ln z$	0	0.104	0.189	0.474	1.035
t/s	0	1110	2010	5052	11232

The slope is $9.2_0 \times 10^{-5} \text{ s}^{-1}$, so $k = (9.2_0 \times 10^{-5} \text{ s}^{-1}) / (0.0571 \text{ mole/dm}^3) = 1.61 \times 10^{-3} \text{ dm}^3 \text{ mole}^{-1} \text{ s}^{-1}$.

17.22 The reaction has the form $2A \rightarrow B$. We have $P = P_A + P_B = (c_A + c_B)RT$. Let $2z \text{ mol/dm}^3$ of A react to form $z \text{ mol/dm}^3$ of B . Then $c_A = c_{A,0} - 2z$ and $c_B = z = \frac{1}{2}(c_{A,0} - c_A)$. Hence $P = (c_A + \frac{1}{2}c_{A,0} - \frac{1}{2}c_A)RT = \frac{1}{2}(c_A + c_{A,0})RT$. Also, $P_0 = c_{A,0}RT$, so $c_A = (2P - P_0)/RT$ and $\alpha = c_A/c_{A,0} = 2P/P_0 - 1$, where $P_0 = 632 \text{ torr}$. We calculate the α values and plot α vs. $\log t$; comparison with the Powell-plot master curves shows the order is 2. Alternatively, we can use the fractional-life method: The calculated values of $100c_A/(\text{mol/dm}^3)$ are 1.692, 1.556, 1.436, 1.345, 1.174, 1.035, 0.8929, 0.7349, 0.6252, and 0.4780. We plot c_A vs. t and take $\alpha = 0.75$. From the graph, we find the times needed for $100c_A/(\text{mol/dm}^3)$ to undergo the following changes: 1.6 to 1.2, 1.4 to 1.05, 1.2 to 0.90, 1.0 to 0.75, 0.8 to 0.6. Values of $\log t_{0.75}$ are

$\log t_{0.75}$	3.138	3.204	3.297	3.375	3.467
$\log [100c_A/(\text{mol/dm}^3)]$	0.204	0.146	0.079	0	-0.097

where c_A is the initial A concentration. The plot has slope $-1.1 = 1 - n$, so $n = 2$. (b) Equation (17.16) applies. We plot $1/c_A = 1/[A]$ vs. t . The data are

$(\text{mol/dm}^3)/c_A$	59.11	64.29	69.66	74.34	85.15	etc.
t/s	0	367	731	1038	1751	

The slope is $0.0141_5 \text{ dm}^3 \text{ mole}^{-1} \text{ s}^{-1} = k_A = ak = 2k$, and $k = 0.0071 \text{ dm}^3 \text{ mole}^{-1} \text{ s}^{-1}$.

17.23 (a) The first two columns of data show that tripling $[A]_0$ at constant $[B]_0$ and $[C]_0$ triples r_0 , so $\alpha = 1$. The first and third columns show that tripling $[B]_0$ at constant $[A]_0$ and $[C]_0$ multiplies the rate by 9, so $\beta = 2$. The second and fourth columns show that $\gamma = 0$. (b)

$r_0 = k[A]_0[B]_0^2$, and use of the first column of data gives $k = (0.0060 \text{ c}^\circ \text{ s}^{-1}) / (0.20 \text{ c}^\circ)(0.30 \text{ c}^\circ)^2 = 0.33 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$. (c) For the rate law (1) in Eq. (17.6), $[\text{HBr}]$ is

initially zero and initial-rate data would yield the erroneous result $r = k[\text{H}_2][\text{Br}_2]^{1/2}$.

17.24 In the first run, we have $[A]_0 \gg [B]_0$, so $[A]_0$ is essentially constant. The B concentrations are 0.400, 0.200, 0.100, and 0.050 mmole/dm³ at 0, 120, 240, and 360 sec. The half-life is thus constant at 120 s; hence the order with respect to B is 1. In the second run $[B]_0$ is constant and the A concentrations are 0.400, 0.200, 0.100, and 0.050 mmole/dm³ at 0, 69, 208, and 485 ksec. The

half-lives are 69, 139, and 277 ksec. The half-life is doubled when the A concentration is cut in half, so $t_{1/2}$ is proportional to $1/[A]$ and [see Eq. (17.29)] the order with respect to A is 2. Hence $r = k[A]^2[B]$. On the first run, $r = -d[B]/dt = k[A]_0^2[B] \equiv k_B[B]$. The reaction is pseudo first order and Eq. (17.14) gives $[B] = [B]_0 e^{-k_B t}$; we have $k_B = -t^{-1} \ln ([B]/[B]_0) = -(120 \text{ s})^{-1} \ln \frac{1}{2} = 0.00578 \text{ s}^{-1} = k(0.400 \text{ mole/dm}^3)^2$ and $k = 0.036 \text{ dm}^6/\text{mole}^2\text{-s}$.

17.25 (a) We plot $\alpha = [A]/[A]_0$ vs. $\log t$; comparison with the Powell-plot master curves shows the order is $3/2$. (Alternatively, the fractional-life method can be used.)

(b) From (17.28) with $n = 1.5$, a plot of $([A]_0/[A])^{1/2}$ vs. t is linear with slope $\frac{1}{2}[A]_0^{1/2}k_A$. The data are

$([A]_0/[A])^{1/2}$	1	1.098	1.206	1.294	1.399	1.612	2.01
t/sec	0	100	200	300	400	600	1000

The slope is $0.00100 \text{ s}^{-1} = 0.5(0.600 \text{ mole/dm}^3)^{1/2}k_A$ and $k_A = 0.00258 \text{ s}^{-1} \text{ dm}^{3/2} \text{ mole}^{-1/2} = ak = k$.

17.26 For the first run, $[A]_0 \gg [B]_0$, so $[A]$ is essentially constant. A Powell plot of $\alpha = [B]/[B]_0$ vs. $\log t$ shows the order with respect to B is 2. (Alternatively, the fractional-life method can be used.) For the second run, $[A]$ is also essentially constant. For runs 1 and 2, we have $r_1 = -d[B]/dt = k[A]_{0,1}^\alpha [B]^2 \equiv j_1 [B]^2$ and $r_2 = k[A]_{0,2}^\alpha [B]^2 \equiv j_2 [B]^2$. Hence $j_1/j_2 = k[A]_{0,1}^\alpha / k[A]_{0,2}^\alpha = ([A]_{0,1}/[A]_{0,2})^\alpha$. The pseudo order is 2; a plot of $1/[B]$

vs. t is linear with slope j . For run 1, such a plot has slope $0.0120 \text{ dm}^3 \text{ mole}^{-1} \text{ s}^{-1}$; for run 2, the slope is $0.0068_1 \text{ dm}^3 \text{ mole}^{-1} \text{ s}^{-1}$. Then $(0.800/0.600)^\alpha = 0.0120/0.0068_1 = 1.76_2$ and $\alpha = (\log 1.76_2)/(\log 1.333) = 1.97 \approx 2$. Also, $j_1 = k[A]_{0,1}^2$ and $k = (0.0120 \text{ dm}^3 \text{ mole}^{-1} \text{ s}^{-1})/(0.800 \text{ mole/dm}^3)^2 = 0.0188 \text{ dm}^9 \text{ mole}^{-3} \text{ s}^{-1}$. (Data from the second run give $0.0189 \text{ dm}^9 \text{ mole}^{-3} \text{ s}^{-1}$.)

17.27 For an elementary reaction, $k_f/k_b = K_c$. We have $-RT \ln K_p^\circ = \Delta G^\circ = [2(51.31) - 97.89] \text{ kJ/mol} = 4730 \text{ J/mol}$. Then $\ln K_p^\circ = -1.908$ and $K_p^\circ = 0.148$. From Eq. (6.25), $K_p^\circ = K_c^\circ RT/(\text{bar-dm}^3/\text{mol})$ and $K_c^\circ = 0.148(\text{bar-dm}^3/\text{mol})/(0.08314 \text{ dm}^3\text{-bar/mol-K})(298.1 \text{ K}) = 0.00597$; so $K_c = 0.00597 \text{ mol/dm}^3$. Then $k_b = k_f/K_c = (4.8 \times 10^4 \text{ s}^{-1})/(0.00597 \text{ mol/dm}^3) = 8.0 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

17.28 From (17.4), $r = -d[A]/dt = \frac{1}{2}d[C]/dt$, so $d[A]/dt = -r$ and $d[C]/dt = 2r$. From (17.5) for this elementary reaction, $r = k[A][B]$. Hence $d[A]/dt = -k[A][B]$ and $d[C]/dt = 2k[A][B]$.

17.29 (a) For runs 1 and 3, the ClO^- initial concentration is cut in half while the other initial concentrations are kept constant; since the rate is cut in half, we conclude that the order with respect to ClO^- is 1. Similarly, runs 2 and 3 tell us that the order with respect to I^- is 1. For runs 3 and 4, the OH^- initial concentration is multiplied by $\frac{1}{4}$ and the rate is quadrupled; so the order with

respect to OH^- is -1. Thus $r = k[\text{I}^-][\text{ClO}^-]/[\text{OH}^-]$. For run 1: $0.00048 \text{ c}^\circ/\text{s} = k(0.00200 \text{ c}^\circ)(0.00400 \text{ c}^\circ)/(1.000 \text{ c}^\circ)$ and $k = 60 \text{ s}^{-1}$. (b) We assume a mechanism with a rate-determining step (rds). From rules 1b and 2 in Sec. 17.6, the total composition of the rds reactants is

$\text{I}^- + \text{ClO}^- - \text{OH}^- + x\text{H}_2\text{O} = \text{ClIO}_x\text{H}_{2x-1}^-$ and the species OH^- is a product in an equilibrium step that precedes the rds and OH^- does not appear in the rds. To keep $2x - 1$ nonnegative, x must be 1 or greater. The simplest assumption is $x = 1$. This gives the rds composition as ClIOH^- . A plausible mechanism that meets the preceding two requirements and that gives the proper stoichiometry is $\text{OCl}^- + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{HOCl}$ (rapid equilb.), $\text{HOCl} + \text{I}^- \rightarrow \text{HOI} + \text{Cl}^-$ (rds), $\text{HOI} + \text{OH}^- \rightarrow \text{OI}^- + \text{H}_2\text{O}$ (rapid).

17.30 The rate-determining-step reactants composition is NO_2Cl . One plausible mechanism is $\text{NO}_2\text{Cl} \rightarrow \text{NO}_2 + \text{Cl}$ (slow), $\text{Cl} + \text{NO}_2\text{Cl} \rightarrow \text{NO}_2 + \text{Cl}_2$ (rapid). Another possibility is $\text{NO}_2\text{Cl} \rightarrow \text{NO}_2 + \text{Cl}$ (slow), $\text{Cl} + \text{Cl} \rightarrow \text{Cl}_2$ (rapid), with stoichiometric numbers 2 and 1, respectively, for steps 1 and 2.

17.31 The rate-determining-step reactants' composition is NO_2F_2 . A plausible mechanism is $\text{NO}_2 + \text{F}_2 \rightarrow \text{NO}_2\text{F} + \text{F}$ (slow), $\text{F} + \text{NO}_2 \rightarrow \text{NO}_2\text{F}$ (rapid).

17.32 $\text{XeF}_4 + \text{NO} \rightarrow \text{XeF}_3 + \text{NOF}$.

17.33 The rate-determining-step reactants have composition N_2O_5 . A likely mechanism is the slow step $N_2O_5 \rightarrow NO_2 + NO_3$ followed by a series of rapid steps that yield the correct stoichiometry. One of the many possibilities for this series of rapid steps is $NO_2 + Cl_2O \rightarrow NO_2Cl + OCl$, $OCl + NO_3 \rightarrow NO_3Cl + O$, $O + O \rightarrow O_2$. (The stoichiometric number of all steps but the last is 2.)

17.34 The rate-determining-step reactants have overall composition $HgTl^{3+}$, and Hg^{2+} is a product in an equilibrium that precedes the rate-determining step. Two other mechanisms besides (17.64) are: $Hg_2^{2+} + Tl^{3+} \rightleftharpoons HgTl^{3+} + Hg^{2+}$ (rapid equilib.), $HgTl^{3+} \rightarrow Hg^{2+} + Tl^+$ (slow); and $Hg_2^{2+} + Tl^{3+} \rightleftharpoons Hg^+ + Tl^{2+} + Hg^{2+}$ (rapid equilib.), $Hg^+ + Tl^{2+} \rightarrow Hg^{2+} + Tl^+$ (slow).

17.35 The reverse reaction would then proceed by the one-step mechanism $N_2 + 3H_2 \rightarrow 2NH_3$. But a tetramolecular elementary step is far too unlikely to occur.

17.36 (a) $d[O_2]/dt = 2k_2[O][O_3] + k_1[O_3][M] - k_{-1}[O_2][O][M]$. $d[O_3]/dt = -k_1[O_3][M] + k_{-1}[O_2][O][M] - k_2[O][O_3]$. (b) $d[O]/dt = 0 = k_1[O_3][M] - k_{-1}[O_2][O][M] - k_2[O][O_3]$, so $k_1[O_3][M] - k_{-1}[O_2][O][M] = k_2[O][O_3]$. Substitution into the expressions for $d[O_2]/dt$ and $d[O_3]/dt$ in (a) gives $d[O_2]/dt = 3k_2[O][O_3]$ and $d[O_3]/dt = -2k_2[O][O_3]$. (c) From (b) we get $[O] = k_1[O_3][M]/(k_{-1}[O_2][M] + k_2[O_3])$. We have $r = -\frac{1}{2}d[O_3]/dt = k_2[O][O_3]$

$= k_1 k_2 [O_3]^2 [M] / (k_{-1} [O_2] [M] + k_2 [O_3]) = k_1 k_2 [O_3]^2 / (k_{-1} [O_2] + k_2 [O_3] / [M])$. Also, $r = (1/3) d[O_2] / dt = k_2 [O] [O_3] = \text{etc.}$ (d) If step 1 is in equilibrium, then $k_1 / k_{-1} = [O_2] [O] [M] / [O_3] [M]$ and $[O] = k_1 [O_3] / k_{-1} [O_2]$.

As noted in the problem statement, $r =$

$\frac{1}{3} d[O_2] / dt = k_2 [O] [O_3] = k_1 k_2 [O_3]^2 / k_{-1} [O_2]$. (e) If $k_2 [O_3] / [M] \ll k_{-1} [O_2]$ (i.e., if $k_{-1} [O_2] [M] \gg k_2 [O_3]$), the second term in the denominator of the steady-state expression can be neglected, thereby giving the rate-determining-step expression.

17.37 (a) $d[NO] / dt = 0 = k_b [NO_2] [NO_3] - k_c [NO] [NO_3]$ and

$k_c [NO] [NO_3] = k_b [NO_2] [NO_3]$. $d[NO_3] / dt = 0 =$

$k_a [N_2 O_5] - k_{-a} [NO_2] [NO_3] - k_b [NO_2] [NO_3] - k_c [NO] [NO_3] =$

$k_a [N_2 O_5] - k_{-a} [NO_2] [NO_3] - k_b [NO_2] [NO_3] - k_b [NO_2] [NO_3]$

and $[NO_3] = k_a [N_2 O_5] / (k_{-a} + 2k_b) [NO_2]$. Then $r =$

$-\frac{1}{2} d[N_2 O_5] / dt = -\frac{1}{2} (-k_a [N_2 O_5] + k_{-a} [NO_2] [NO_3]) =$

$\frac{1}{2} k_a [N_2 O_5] - \frac{1}{2} k_{-a} k_a [N_2 O_5] / (k_{-a} + 2k_b) =$

$[k_a k_b / (k_{-a} + 2k_b)] [N_2 O_5] = k [N_2 O_5]$ and $k = k_a k_b / (k_{-a} + 2k_b)$.

(b) If step b is the rate-determining step and step a is

in equilibrium, then $k_a / k_{-a} = [NO_2] [NO_3] / [N_2 O_5]$. The rate

of the reaction equals the rate of the rate-determining

step b, so $r = k_b [NO_2] [NO_3] = (k_b k_a / k_{-a}) [N_2 O_5]$. (c) If

$k_{-a} \gg 2k_b$, then the steady-state rate law of part (a) reduces

to the rate-determining-step rate law of (b). (Of

course, this is a necessary condition for the validity of

the rate-determining-step approximation.) (d) From this

problem, we see that k of the N_2O_5 decomposition is a function of k_a , k_{-a} , and k_b . Hence, it is clear that the mechanism of the reaction in Prob. 17.33 starts off with steps a and b of the mechanism in Eq. (17.8). After step b, we need steps that give the correct stoichiometry. A possible mechanism is $\text{N}_2\text{O}_5 \rightleftharpoons \text{NO}_2 + \text{NO}_3$ (rapid equilib.), $\text{NO}_2 + \text{NO}_3 \rightarrow \text{NO} + \text{O}_2 + \text{NO}_2$ (slow, rate determining), $\text{NO}_2 + \text{Cl}_2\text{O} \rightarrow \text{NO}_2\text{Cl} + \text{OCl}$, $\text{OCl} + \text{NO} \rightarrow \text{NO}_2\text{Cl}$, $\text{NO}_2\text{Cl} + \text{O}_2 \rightarrow \text{NO}_3\text{Cl} + \text{O}$, $\text{O} + \text{O} \rightarrow \text{O}_2$. (The stoichiometric number of all steps but the last is 2.)

17.38 For (17.60), $r = \frac{1}{2}d[\text{NO}_2]/dt = k_2[\text{N}_2\text{O}_2][\text{O}_2]$; the initial equilibrium gives $[\text{N}_2\text{O}_2]/[\text{NO}]^2 = K_{c,1} = k_1/k_{-1}$ and $[\text{N}_2\text{O}_2] = (k_1/k_{-1})[\text{NO}]^2$, so $r = (k_2k_1/k_{-1})[\text{NO}]^2[\text{O}_2]$. For (17.61), $r = \frac{1}{2}d[\text{NO}_2]/dt = k_2[\text{NO}_3][\text{NO}]$ and $k_1/k_{-1} = [\text{NO}_3]/[\text{NO}][\text{O}_2]$, so $r = (k_2k_1/k_{-1})[\text{NO}]^2[\text{O}_2]$. For (17.62), $r = k[\text{NO}]^2[\text{O}_2]$.

17.39 $k = Ae^{-E_a/RT}$, $k(T_2)/k(T_1) = \exp [(E_a/R)(T_1^{-1} - T_2^{-1})]$

$$k_{720} = (0.0012 \text{ dm}^3/\text{mol-s}) \exp \left[\frac{177000 \text{ J/mol}}{8.314 \text{ J/mol-K}} \left(\frac{1}{660 \text{ K}} - \frac{1}{720 \text{ K}} \right) \right]$$

$$= 0.018 \text{ dm}^3 \text{ mole}^{-1} \text{ s}^{-1}$$

17.40 $k = Ae^{-E_a/RT}$ and $\ln k = \ln A - E_a/RT$. We plot $\ln k$ vs. $1/T$. The data are

$\ln (k \text{ c}^\circ \text{ s})$	-7.52	-5.99	-4.27	-3.69	-2.75
$10^3/T$	1.669	1.590	1.502	1.464	1.429
					K^{-1}

The slope is $-19500 \text{ K}^{-1} = -E_a/(8.314 \text{ J/mol-K})$ and $E_a = 162 \text{ kJ/mol}$. The intercept at $1/T = 0$ is $25.0 = \ln(A \text{ c}^\circ \text{ s})$; $A = 7 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. (The intercept is calculated from the slope and one point on the graph.)

17.41 $k = Ae^{-E_a/RT}$, $k_{T_2}/k_{T_1} = \exp [(E_a/R)(1/T_1 - 1/T_2)]$,
 $\ln (k_{T_2}/k_{T_1}) = (E_a/R)(1/T_1 - 1/T_2) = \ln (0.000030/0.0012)$
 $= [E_a/(1.987 \text{ cal/mol-K})][1/(700 \text{ K}) - 1/(629 \text{ K})]$ and $E_a \approx 45.5 \text{ kcal/molé}$. $A = ke^{E_a/RT} = (0.0012 \text{ dm}^3 \text{ mole}^{-1} \text{ s}^{-1}) \times$
 $\exp [(45,500 \text{ cal/mole})/(1.987 \text{ cal/mole-K})(700 \text{ K})]$ and
 $A \approx 1.9 \times 10^{11} \text{ dm}^3 \text{ mole}^{-1} \text{ s}^{-1}$.

17.42 $k = Ae^{-E_a/RT}$. As $T \rightarrow \infty$, E_a/RT goes to 0 and k goes to A . As $T \rightarrow \infty$, the collision rate goes to infinity and the fraction of collisions having at least the activation energy goes to 1, so the collision-theory picture leads one to expect the rate to increase without limit as $T \rightarrow \infty$, rather than approaching an upper limit as predicted by the Arrhenius equation.

17.43 (a) $\ln k = \ln A - E_a/RT$. A plot of $\ln N$ vs. $1/T$ (where N is the chirping rate) has slope $-E_a/R$. We have

$\ln N$	5.18 ₂	4.83 ₆	4.60 ₅
$10^3/T$	3.354	3.408	3.443
			K^{-1}

The plot is linear with slope $-6.5_0 \times 10^3 \text{ K}^{-1} =$

$-E_a/(1.987 \text{ cal/mole-K})$ and $E_a = 12.9 \text{ kcal/mole}$. (b) At 14.0°C , $10^3/T = 3.482_5 \text{ K}^{-1}$ and we read the value $\ln N = 4.346$ from the graph. Thus $N = 77$ per minute. The rule gives the Fahrenheit temperature as $40 + \frac{1}{2}(77) = 59^\circ\text{F}$. Actually, 14.0°C is 57°F , so the crickets are in error by 2°F .

17.44 (a) $A = 2.05 \times 10^{13} \text{ s}^{-1}$ and $E_a = 24.65 \text{ kcal/mole}$.

(b) $k(0^\circ\text{C}) = (2.05 \times 10^{13} \text{ s}^{-1}) \times$

$\exp [(-24,650 \text{ cal/mole})/(1.987 \text{ cal/mole-K})(273.15 \text{ K})]$

$= 3.87 \times 10^{-7} \text{ s}^{-1}$. (c) The units of k and the rate law in

Eq. (17.6) show that the order is 1. Equations (17.15) and

(17.11) give $k_A t_{\frac{1}{2}} = 0.693 = k t_{\frac{1}{2}} = 2k t_{\frac{1}{2}}$ and $t_{\frac{1}{2}} = 0.693/2k$.

From the given $k(T)$ expression, we find $k(-50^\circ\text{C}) =$

$1.47 \times 10^{-11} \text{ s}^{-1}$ and $k(50^\circ\text{C}) = 4.36 \times 10^{-4} \text{ s}^{-1}$. We find

$t_{\frac{1}{2}}(-50^\circ\text{C}) = 2.36 \times 10^{10} \text{ s}$; $t_{\frac{1}{2}}(0^\circ\text{C}) = 8.95 \times 10^5 \text{ s}$; and

$t_{\frac{1}{2}}(50^\circ\text{C}) = 795 \text{ s}$.

17.45 From (17.43), the observed rate constant is $k =$

$k_1 + k_2 = A_1 e^{-E_{a,1}/RT} + A_2 e^{-E_{a,2}/RT}$. From Eq. (17.68),

$E_a = RT^2 d \ln k/dT = RT^2(d/dT) \ln (k_1 + k_2) =$

$RT^2[1/(k_1 + k_2)](dk_1/dT + dk_2/dT) = [RT^2/(k_1 + k_2)] \times$

$[(E_{a,1}/RT^2)A_1 e^{-E_{a,1}/RT} + (E_{a,2}/RT^2)A_2 e^{-E_{a,2}/RT}]$

$= (E_{a,1}k_1 + E_{a,2}k_2)/(k_1 + k_2)$.

17.46 $\Delta H_{298}^\circ = (-393.509 + 90.25 + 110.525 - 33.18) \text{ kJ/mol}$

$= -225.91 \text{ kJ/mol}$. Since $\Delta n_g = 0$, we have $\Delta H^\circ = \Delta U^\circ$,

and use of $E_{a,f} - E_{a,b} = \Delta U^\circ$ gives $116 \text{ kJ/mol} - E_{a,b} = -226 \text{ kJ/mol}$. So $E_{a,b} = 342 \text{ kJ/mol}$.

17.47 The equilibrium condition for step 1 gives $k_1/k_{-1} = [\dot{C}][D]/[A][B]$. We have $r = d[G]/dt = k_2[C]^2 = k_2(k_1[A][B]/k_{-1}[D])^2 = (k_1^2 k_2/k_{-1}^2)[A]^2[B]^2/[D]^2$, so $k = k_1^2 k_2/k_{-1}^2$ and $Ae^{-E_a/RT} = A_1^2 e^{-2E_{a,1}/RT} A_2 e^{-E_{a,2}/RT} / A_{-1}^2 e^{-2E_{a,-1}/RT}$. Then $E_a = 2E_{a,1} + E_{a,2} - 2E_{a,-1} = (60 + 49 - 48) \text{ kcal/mol} = 61 \text{ kcal/mol}$.

17.48 (a) $k_2/k_1 = Ae^{-E_a/RT_2}/Ae^{-E_a/RT_1} = e^{(E_a/R)(1/T_1 - 1/T_2)}$. $\ln(k_2/k_1) = (E_a/R)(1/T_1 - 1/T_2)$ and $\ln 6.50 = [E_a/(8.314 \text{ J/mol-K})] \times [(300.0 \text{ K})^{-1} - (310.0 \text{ K})^{-1}]$ and $E_a = 145 \text{ kJ/mol} = 34.6 \text{ kcal/mol}$.

(b) $k_2/k_1 = \exp [(19000 \text{ J})/(8.314 \text{ J/mol-K})][(300 \text{ K})^{-1} - (310 \text{ K})^{-1}] = 1.28$.

17.49 (a) For $H_2 + I_2 \rightarrow 2HI$, $\Delta G_{700}^\circ = -23.6 \text{ kJ/mol} = -RT \ln K_P$ and $K_P = 57.7 = K_c$, since $\Delta n = 0$. Then $K_c^{1/s} = k_f/k_b = 0.064/0.0012 = 53 = (58)^{1/s}$, so $s = 1$.
(b) $K_c^{1/s} = K_c = k_f/k_b = 0.0025/0.000030 = 83$.

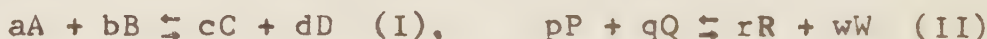
17.50 $k_f/k_b = K_c^{1/s}$. (a) $k_f/k_b = K_c$. Let $r = k_b Z$ be the rate law of the reverse reaction. At equilibrium, the forward and reverse rates are equal, so $k_b Z_{eq} = k_f [BrO_3^-]_{eq} [SO_3^{2-}]_{eq} [H^+]_{eq}$ and $Z_{eq}/[BrO_3^-]_{eq} [SO_3^{2-}]_{eq} [H^+]_{eq} = k_f/k_b = K_c = [Br^-]_{eq} [SO_4^{2-}]_{eq}^3 / [BrO_3^-]_{eq} [SO_3^{2-}]_{eq}^3$. Therefore $k_b Z = k_b [Br^-][SO_4^{2-}]^3 [H^+] / [SO_3^{2-}]^2$. (b) $k_f/k_b = K_c^{1/2}$. From part (a), $k_f/k_b = Z_{eq}/[BrO_3^-]_{eq} [SO_3^{2-}]_{eq} [H^+]_{eq} = K_c^{1/2} =$

$$[\text{Br}^-]_{\text{eq}}^{\frac{1}{2}} [\text{SO}_4^{2-}]_{\text{eq}}^{3/2} / [\text{BrO}_3^-]_{\text{eq}}^{\frac{1}{2}} [\text{SO}_3^{2-}]_{\text{eq}}^{3/2} \text{ and } k_b Z = k_b [\text{Br}^-]^{\frac{1}{2}} [\text{SO}_4^{2-}]^{3/2} [\text{H}^+] [\text{BrO}_3^-]^{\frac{1}{2}} / [\text{SO}_3^{2-}]^{\frac{1}{2}}.$$

17.51 $k_f/k_b = K_c^{1/s}$ and $\ln k_f - \ln k_b = (1/s) \ln K_c$. Differentiation of this equation with respect to T and use of Eq. (17.68) and the result of Prob. 6.13 gives $E_{a,f}/RT^2 - E_{a,b}/RT^2 = (1/s)\Delta U^\circ/RT^2$ and $E_{a,f} - E_{a,b} = \Delta U^\circ/s$.

17.52 We reverse the designations of forward and back reactions and use primes to denote the newly designated constants; i.e., $k'_f = k_b$ and $k'_b = k_f$; also, $K'_c = 1/K_c$. Since the mechanism of the reverse reaction consists of the reverse of the mechanism of the forward reaction and [as noted after Eq. (17.58)] the reverse-reaction's rate-determining step is the reverse of that for the forward reaction, we have $s' = s$. Substitution into $k_f/k_b = K_c^{1/s}$ gives $k'_b/k'_f = (1/K'_c)^{1/s'}$ and $k'_f/k'_b = (K'_c)^{1/s'}$. Q.E.D.

17.53 Consider two chemical reactions



Let us form a third reaction that is the sum of m times the first reaction and n times the second reaction:



The concentration-scale equilibrium constants of these reactions are

$$K_I = [C]^c [D]^d / [A]^a [B]^b, \quad K_{II} = [R]^r [W]^w / [P]^p [Q]^q$$

$$K_{III} = [C]^{cm} [D]^{dm} [R]^{rn} [W]^{wn} / [A]^{am} [B]^{bm} [P]^{pn} [Q]^{qn}$$

(where all concentrations are equilibrium concentrations)

and we see that $K_{III} = K_I^m K_{II}^n$. A similar result holds for a reaction formed by multiplying more than two reactions by integers and adding them. Since the elementary reactions of a mechanism multiplied by their stoichiometric numbers and then added yield the overall reaction, we have $K_c = K_1^{s_1} K_2^{s_2} \dots K_m^{s_m} = \prod_i (K_i)^{s_i}$, where K_c is the equilibrium constant of the overall reaction and K_1, K_2, \dots, K_m are the equilibrium constants of the elementary reactions.

But we know that for an elementary reaction, $K_i = k_i/k_{-i}$ [Eq. (17.53)], so $K_c = \prod_i (k_i/k_{-i})^{s_i}$.

17.54 Step (b) has stoichiometric number $s = 1$, so $k_f/k_b = K_c^{1/s} = K_c$. Let $r_b = k_b Z$ be the rate law of the reverse reaction. We know that the forward reaction has rate law $r_f = k_f [N_2O_5]$. At equilibrium, $k_f [N_2O_5]_{eq} = k_b Z_{eq}$ and $Z_{eq}/[N_2O_5]_{eq} = k_f/k_b = K_c = [NO_2]_{eq}^4 [O_2]_{eq} / [N_2O_5]_{eq}^2$, so $r_b = k_b Z = k_b [NO_2]^4 [O_2] / [N_2O_5]$.

17.55 $1/k_{uni} = k_{-1}/k_1 k_2 + 1/[M]k_1$. Since $P_0 V = n_{tot} RT$, we have $[M] = P_0/RT$ and $1/k_{uni} = k_{-1}/k_1 k_2 + RT/P_0 k_1$. A plot of $1/k_{uni}$ vs. $1/P_0$ is linear with slope RT/k_1 and intercept $k_{-1}/k_1 k_2$. The data are

$1/k_{uni}$	10440	9620	9260	9010	s
$10^3/P_0$	9.09	4.74	2.58	1.316	torr ⁻¹

The slope is $1.81 \times 10^5 \text{ s torr} = 238 \text{ s atm} = (0.08206 \text{ dm}^3\text{-atm/mole-K})(743.1 \text{ K})/k_1$ and $k_1 = 0.256 \text{ dm}^3 \text{ mole}^{-1} \text{ s}^{-1}$. The intercept is $8780 \text{ s} = k_{-1}/k_1 k_2 =$

$1/k_{\text{uni}, P=\infty}$. So $k_{\text{uni}, P=\infty} = 11.3_9 \times 10^{-5} \text{ s}^{-1}$ and $k_{-1}/k_2 = (8780 \text{ s})(0.256 \text{ dm}^3 \text{ mole}^{-1} \text{ s}^{-1}) = 2250 \text{ dm}^3/\text{mole}$.

17.56 The B and C molecules are smaller than the A molecules and so undergo collisions with A less often than A molecules do.

17.57 (a) Step (1) is the initiation step, (2) and (3) are the propagation steps, and (4) is the termination step.

(b) The chain-propagating steps (2) and (3) occur many times for each occurrence of step (1) or step (4). The overall reaction is therefore the sum of steps (2) and (3),

namely, $\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}$. (c) We use the steady-state approximation for the intermediates CH_3 and CH_3CO :

$$d[\text{CH}_3]/dt = 0 = k_1[\text{CH}_3\text{CO}] - k_2[\text{CH}_3][\text{CH}_3\text{CHO}] + k_3[\text{CH}_3\text{CO}] - 2k_4[\text{CH}_3]^2. \quad d[\text{CH}_3\text{CO}]/dt = 0 = k_2[\text{CH}_3][\text{CH}_3\text{CHO}] - k_3[\text{CH}_3\text{CO}].$$

Addition of these two equations gives $0 = k_1[\text{CH}_3\text{CHO}] - 2k_4[\text{CH}_3]^2$ and $[\text{CH}_3] = (k_1/2k_4)^{1/2}[\text{CH}_3\text{CHO}]^{1/2}$. Then $r =$

$$d[\text{CH}_4]/dt = k_2[\text{CH}_3][\text{CH}_3\text{CHO}] = k_2(k_1/2k_4)^{1/2}[\text{CH}_3\text{CHO}]^{3/2}.$$

(Alternatively, we can find $[\text{CH}_3\text{CO}]$ and use $r = d[\text{CO}]/dt$.)

17.58 The reverse of step I has a near-zero E_a , so E_a of step I equals ΔU_I° . From the Appendix, $\Delta H_I^\circ = 104 \text{ kcal/mole}$ and $\Delta U_I^\circ = 103\frac{1}{2} \text{ kcal/mole}$ at 300 K. This $103\frac{1}{2} \text{ kcal/mole}$ E_a is far higher than the 45 kcal/mole E_a of $\text{Br}_2 + \text{M} \rightarrow 2\text{Br} + \text{M}$ [see the discussion after Eq. (17.95)], so the dissociation of H_2 by M can be neglected. Step II is the reverse of step 3 in (17.88). Appendix data give $\Delta H_3^\circ = \Delta U_3^\circ = -41\frac{1}{2}$

$\text{kcal/mole} = E_{a,3} - E_{a,-3}$ and $E_{a,-3} = E_{a,II} = 42\frac{1}{2} \text{ kcal/mole}$
 (since $E_{a,3} = 1 \text{ kcal/mole}$). $E_{a,II}$ is far higher than the
 $18 \text{ kcal/mole } E_a$ of $\text{Br} + \text{H}_2 \rightarrow \text{HBr} + \text{H}$, so Br reacts pref-
 erentially with H_2 rather than with HBr, and reaction II
 can be neglected. The atom combination reaction $\text{H} + \text{Br} +$
 $\text{M} \rightarrow \text{HBr} + \text{M}$ has $E_{a,III} \approx 0$. Reaction 3 in (17.88), namely,
 $\text{H} + \text{Br}_2 \rightarrow \text{HBr} + \text{Br}$, has $E_{a,3} \approx 1 \text{ kcal/mole}$, not much diff-
 erent from $E_{a,III}$; thus the rate constants k_3 and k_{III} are
 of the same order of magnitude. We have $r_3 = k_3[\text{H}][\text{Br}_2]$
 and $r_{III} = k_{III}[\text{H}][\text{Br}][\text{M}]$. The concentration of the re-
 actant Br_2 is high and is of the same order of magnitude
 as the M concentration. The very low concentration of the
 reactive intermediate Br makes $r_{III} \ll r_3$, so we can
 neglect reaction III.

17.59 (a) Initiation is step 1; propagation is steps 2 and
 3; termination is step -1. (b) $[\text{Cl}]^2/[\text{Cl}_2] = k_1/k_{-1}$ and
 $[\text{COCl}]/[\text{Cl}][\text{CO}] = k_2/k_{-2}$. So $[\text{Cl}] = (k_1/k_{-1})^{\frac{1}{2}}[\text{Cl}_2]^{\frac{1}{2}}$ and
 $[\text{COCl}] = (k_2/k_{-2})(k_1/k_{-1})^{\frac{1}{2}}[\text{CO}][\text{Cl}_2]^{\frac{1}{2}}$. For the forward re-
 action, $r_f = d[\text{COCl}_2]/dt = k_3[\text{COCl}][\text{Cl}_2]$. (Since we want
 the rate law for the forward reaction, we assume negligi-
 ble amount of product has formed and we do not consider
 the reverse of step 3.) Substitution for $[\text{COCl}]$ from (b)
 gives $r_f = (k_3 k_2 k_1^{\frac{1}{2}}/k_{-2} k_{-1}^{\frac{1}{2}})[\text{Cl}_2]^{3/2}[\text{CO}]$. (c) $r_b =$
 $-d[\text{COCl}_2]/dt = k_{-3}[\text{COCl}_2][\text{Cl}] = (k_{-3} k_1^{\frac{1}{2}}/k_{-1}^{\frac{1}{2}})[\text{Cl}_2]^{\frac{1}{2}}[\text{COCl}_2]$.
 [As a check, putting $r_f = r_b$, we get

$[\text{COCl}_2]_{\text{eq}}/[\text{CO}]_{\text{eq}}[\text{Cl}_2]_{\text{eq}} = (k_2/k_{-2})(k_3/k_{-3}) = K_c$, where the result of Prob. 17.53 was used.]

17.60 (a) $k = k_2(k_1/k_{-1})^{\frac{1}{2}}$ and $Ae^{-E_a/RT} = A_2A_1^{\frac{1}{2}}A_{-1}^{-\frac{1}{2}} \times e^{-(E_{a,2} + \frac{1}{2}E_{a,1} - \frac{1}{2}E_{a,-1})/RT}$, so $E_a = E_{a,2} + \frac{1}{2}E_{a,1} - \frac{1}{2}E_{a,-1}$.

(b) As noted after Eq. (17.95), $E_{a,-1} \approx 0$ and $E_{a,1} \approx \Delta U_1^\circ$. Data in the Appendix give $\Delta H_1^\circ = 46.1 \text{ kcal/mole}$; then $\Delta U_1^\circ = \Delta H_1^\circ - RT = 45.5 \text{ kcal/mole}$ at 298 K. So $E_{a,2} = E_a - \frac{1}{2}E_{a,1} = (40.6 - 22.7) \text{ kcal/mole} = 18 \text{ kcal/mole}$. The ratio k_1/k_{-1} is K_c for the reaction $\text{Br}_2(\text{g}) \rightleftharpoons 2\text{Br}(\text{g})$; data in the Appendix give $\Delta G_{298}^\circ = 38.64 \text{ kcal/mole}$; (6.14) and (6.25) give

$K_{P,298}^\circ = 4.7 \times 10^{-29}$ and $K_{c,298}^\circ = 1.9 \times 10^{-30}$. So $k_1/k_{-1} = 1.9 \times 10^{-30} \text{ mole/dm}^3$ at 298 K. Substitution in $Ae^{-E_a/RT} = A_2e^{-E_{a,2}/RT}(k_1/k_{-1})^{\frac{1}{2}}$ at 298 K gives $A_2 = (1.6 \times 10^{11} \text{ dm}^{3/2}/\text{mole}^{\frac{1}{2}}\text{-s})(1.9 \times 10^{-30} \text{ mole/dm}^3)^{-\frac{1}{2}} \times \exp \{[(18000 - 40600) \text{ cal/mol}]/(1.987 \text{ cal/mol-K})(298 \text{ K})\} = 3 \times 10^9 \text{ dm}^3 \text{ mole}^{-1} \text{ s}^{-1}$. Then $k_2 = A_2e^{-E_{a,2}/RT} = (3 \times 10^9 \text{ dm}^3/\text{mole-s})e^{-(18000 \text{ cal/mole})/RT}$.

17.61 (a) $[R_{\text{tot}}^\bullet] = (fk_1/k_t)^{\frac{1}{2}}[I]^{\frac{1}{2}} = (0.008 \text{ mol/dm}^3)^{\frac{1}{2}} \times (0.5 \times 5 \times 10^{-5} \text{ s}^{-1}/(2 \times 10^7 \text{ dm}^3/\text{mol-s}))^{\frac{1}{2}} = 1.0 \times 10^{-7} \text{ mol/dm}^3$. $\langle \text{DP} \rangle = k_p[M]/(fk_1k_t)^{\frac{1}{2}}[I]^{\frac{1}{2}} = (3 \times 10^3 \text{ dm}^3/\text{mol-s}) \times (2 \text{ mol/dm}^3)/(0.5 \times 1000 \text{ dm}^3/\text{mol-s}^2)^{\frac{1}{2}}(0.008 \text{ mol/dm}^3)^{\frac{1}{2}} = 3000$. $-d[M]/dt = k_p(fk_1/k_t)^{\frac{1}{2}}[M][I]^{\frac{1}{2}} = k_p[M][R_{\text{tot}}^\bullet] = (3000 \text{ dm}^3/\text{mol-s})(2 \text{ mol/dm}^3)(1.0 \times 10^{-7} \text{ mol/dm}^3) = 0.0006 \text{ mol/dm}^3\text{-s}$. $d[P_{\text{tot}}]/dt = k_t[R_{\text{tot}}^\bullet]^2 = (2 \times 10^7 \text{ dm}^3/\text{mol-s}) \times (1.0 \times 10^{-7} \text{ mol/dm}^3)^2 = 2 \times 10^{-7} \text{ mol/dm}^3\text{-s}$. (b) When term-

ination is by disproportionation, two polymer molecules (instead of one) are formed whenever two radicals combine. This doubles $d[P_{\text{tot}}]/dt$ and hence cuts $\langle DP \rangle$ in half. Thus $d[P_{\text{tot}}]/dt = 4 \times 10^{-7} \text{ mol/dm}^3\text{-s}$ and $\langle DP \rangle = 1500$. The other quantities are unchanged.

17.62 The initiation reaction $2M \rightarrow 2R\cdot$ contributes a term $2k_i[M]^2$ to $-d[M]/dt$ and (17.97) is modified to $-d[M]/dt = 2k_i[M]^2 + k_p[M][R_{\text{tot}}\cdot]$. To apply the steady-state condition $d[R_{\text{tot}}\cdot]/dt = 0$, we note that the initiation step has $(d[R_{\text{tot}}\cdot]/dt)_i = 2fk_i[M]^2$. So $0 = (d[R_{\text{tot}}\cdot]/dt)_i + (d[R_{\text{tot}}\cdot]/dt)_t = 2fk_i[M]^2 - 2k_t[R_{\text{tot}}\cdot]^2$ and $[R_{\text{tot}}\cdot] = (fk_i/k_t)^{1/2}[M]$. Substitution in the above $-d[M]/dt$ equation gives $-d[M]/dt = [2k_i + k_p(fk_i/k_t)^{1/2}][M]^2$. Use of the above $[R_{\text{tot}}\cdot]$ expression in (17.105) gives $d[P_{\text{tot}}]/dt = k_t[R_{\text{tot}}\cdot]^2 = fk_i[M]^2$. Equation (17.104) becomes $\langle DP \rangle = -(d[M]/dt)/d[P_{\text{tot}}]/dt = [2k_i + k_p(fk_i/k_t)^{1/2}]/fk_i$.

17.63 $d[A]/dt = -k_f[A] + k_b[C]^2$. Let $[A]_{\text{eq}}$ and $[C]_{\text{eq}}$ be the equilibrium concentrations under the new conditions, and let $x \equiv [A]_{\text{eq}} - [A]$. Then $dx/dt = -d[A]/dt$. Since 2 moles of C are formed when 1 mole of A reacts, we have $[C]_{\text{eq}} - [C] = -2x$. Then $-dx/dt = -k_f([A]_{\text{eq}} - x) + k_b([C]_{\text{eq}}^2 + 4x[C]_{\text{eq}} + 4x^2) = -k_f[A]_{\text{eq}} + k_b[C]_{\text{eq}}^2 + xk_b(k_f/k_b + 4[C]_{\text{eq}} + 4x)$. At equilibrium, $d[A]/dt = 0$ and the first equation in this paragraph gives $-k_f[A]_{\text{eq}} +$

$k_b[C]_{eq}^2 = 0$. Since the perturbation is small, $[C]$ is close to $[C]_{eq}$ and we can neglect $4x$ in comparison with $4[C]_{eq}$. We then have $dx/dt = -xk_b(k_f/k_b + 4[C]_{eq}) = -\tau^{-1}x$, where $\tau = (k_f + 4k_b[C]_{eq})^{-1}$. Integration gives $x = x_0 e^{-t/\tau}$ or $[A] - [A]_{eq} = ([A]_0 - [A]_{eq})e^{-t/\tau}$.

17.64 (a) $CH_3CH_2CH_3$, CH_3CH_3 , $CH_3CH_2CH_2CH_3$, and N_2 .

(b) $CH_3CH_2CH_3$ and N_2 (cage effect).

17.65 Equation (17.112) gives $k_D = 2\pi(6.02 \times 10^{23}/\text{mol}) \times (4 \times 10^{-8} \text{ cm})(8.4 \times 10^{-5} \text{ cm}^2/\text{s}) = 1.3 \times 10^{13} \text{ cm}^3/\text{mole-s} = 1.3 \times 10^{10} \text{ dm}^3 \text{ mole}^{-1} \text{ s}^{-1}$.

17.66 (a) From Eqs. (17.114) and (17.115), $\ln k_D = \ln T - \ln \eta + \ln(\text{const.})$. Then Eq. (17.68) gives $E_a = RT^2 d \ln k_D/dT = RT^2[1/T - (1/\eta)d\eta/dT] = RT - (RT^2/\eta)d\eta/dT$. (b) $E_a = (1.987 \text{ cal/mol-K})(298 \text{ K}) - (1.987 \text{ cal/mol-K})(298 \text{ K})^2(-0.023 \text{ K}^{-1}) = 4.7 \text{ kcal/mole} = 19 \text{ kJ/mol}$.

17.67 The data give

$1/r_0$	35.7	20.8	12.5	6.45	$\text{dm}^3\text{-s/mmole}$
$1/[S]_0$	0.800	0.400	0.200	0.050	dm^3/mmole

The slope is $39 \text{ s} = K_M/k_2[E]_0$ and the intercept is

$4.7 \text{ dm}^3\text{-s/mmole} = 1/k_2[E]_0$. So $k_2 =$

$$(2.8 \times 10^{-9} \text{ mole/dm}^3)^{-1}(4700 \text{ dm}^3\text{-s/mole})^{-1} = 7.6 \times 10^4 \text{ s}^{-1}$$

$$\text{and } K_M = (39 \text{ s})/(4.7 \text{ dm}^3\text{-s/mmole}) = 8.3 \times 10^{-3} \text{ mole/dm}^3.$$

17.68 Since $[P] \approx 0$ and since $[ES]$ is assumed small, it follows that $[S] \approx [S]_0$. From (17.122) with $[S] \approx [S]_0 = K_M = (k_{-1} + k_2)/k_1$ and $[P] = 0$, we have $[ES]/[E]_0 = (k_{-1} + k_2)/(k_{-1} + k_2 + k_{-1} + k_2) = \frac{1}{2}$. From (17.125), $r_0 = k_2[E]_0 K_M / 2K_M = k_2[E]_0 / 2 = r_{0,\max} / 2$, since $r_{0,\max} = k_2[E]_0$.

17.69 We plot $\log t_{\frac{1}{2}}$ vs. $\log P_0$. The data are

$\log t_{\frac{1}{2}}$ 0.88₁ 0.56₈ 0.23₀

$\log P_0$ 2.42₃ 2.11₄ 1.76₃

The slope is $0.98 = 1 - n$ and $n = 0$.

17.70 The overall reaction is $N_2 + 3H_2 \rightarrow 2NH_3$. To produce this overall reaction from the steps listed, we must multiply steps a, b, c, d, e, and f by 1, 3, 2, 2, 2, and 2, respectively, and then add them. These are the stoichiometric numbers of steps a to f. The fact that the rate-determining step probably has stoichiometric number $s = 1$ indicates that the rate-determining step is probably step (a), $N_2 + 2* \rightarrow 2N*$.

17.71 The rate of the bimolecular desorption reaction $2A(\text{ads}) \rightarrow A_2(\text{g})$ is proportional to $(n_A/\cancel{A})(n_A/\cancel{A})$ and so is proportional to θ_A^2 ; $r_{\text{des}} = k_d \theta_A^2$. The rate r_{ads} of the adsorption reaction $A_2(\text{g}) \rightarrow 2A(\text{ads})$ is proportional to the A_2 —surface collision rate, which is proportional to P . Since two adjacent vacant sites are required for A_2 to be adsorbed dissociatively, the adsorption rate is

also proportional to $(1 - \theta_A)(1 - \theta_A)$, the square of the fraction of vacant sites. Hence, $r_{\text{ads}} = k_a(1 - \theta_A)^2 P$. So $r_{\text{ads}} = r_{\text{des}}$ and $k_a(1 - \theta_A)^2 P = k_d \theta_A^2$ or $k_a^{1/2}(1 - \theta_A)P^{1/2}/k_d^{1/2} = \theta_A$. Solving for θ_A , we get $\theta_A = (k_a/k_d)^{1/2} P^{1/2} / [1 + (k_a/k_d)^{1/2} P^{1/2}]$, which is (13.38) with $b = k_a/k_d$.

17.72 (a) We assume that each CO molecule occupies one adsorption site. (This isn't always true.) The number of sites per cm^2 is $(2.3 \times 10^{-9} \text{ mol})(6.02 \times 10^{23}/\text{mol}) = 1.38 \times 10^{15}$. (b) The total number of sites is $(1.38 \times 10^{15}/\text{cm}^2) \times (5.00 \text{ cm}^2) = 6.9 \times 10^{15}$. The number of occupied sites is $(9.2 \times 10^{-10} \text{ mol})(6.02 \times 10^{23}/\text{mol}) = 5.5 \times 10^{14}$. So $\theta = (5.5 \times 10^{14})/(6.9 \times 10^{15}) = 0.080$. The adsorption rate per unit area is $r_s = (5.5 \times 10^{14})/t(5.00 \text{ cm}^2) = (1.1 \times 10^{14} \text{ cm}^{-2})t^{-1}$ and the equation in Sec. 17.17 that defines s becomes $s = (1.1 \times 10^{14}/\text{cm}^2)(2\pi \text{MRT})^{1/2}/tP N_A$. We have $tP = (0.43 \times 10^{-6} \text{ torr} \cdot \text{s})(1 \text{ atm}/760 \text{ torr}) \times (101325 \text{ Pa}/1 \text{ atm}) = 5.7 \times 10^{-5} \text{ Pa} \cdot \text{s}$ and $s = (1.1 \times 10^{14} \text{ m}^{-2})[2\pi(0.028 \text{ kg/mol})(8.314 \text{ J/mol-K})(300 \text{ K})]^{1/2}/(5.7 \times 10^{-5} \text{ s N/m}^2)(6.02 \times 10^{23}) = 0.67$. Since θ is close to 0, this is approximately s_0 .

17.73 (a) $t_{1/2} = 0.693/k_{\text{des}} = 0.693e^{E_{a,\text{des}}/RT}/A_{\text{des}} = 0.693e^{(151000 \text{ J/mol})/(8.314 \text{ J/mol-K})(300 \text{ K})}/(2.4 \times 10^{14}/\text{s}) = 5.6 \times 10^{11} \text{ s}$; (b) $5.3 \times 10^{-4} \text{ s}$.

17.74 (In the first printing of the text, this problem is defective, since T is not specified.) For $T = 300 \text{ K}$,

we have $d = (2Dt)^{\frac{1}{2}} = (2D_0 e^{-E_{a,mig}/RT_t})^{\frac{1}{2}} =$
 $[2(0.014 \text{ cm}^2/\text{s})e^{-(88000 \text{ J/mol})/(8.314 \text{ J/mol-K})(300 \text{ K})(1 \text{ s})}]^{\frac{1}{2}} =$
 $3.7 \times 10^{-9} \text{ cm}$. At 100 s, d is $100^{\frac{1}{2}} = 10$ times d at 1 s,
 which is $3.7 \times 10^{-8} \text{ cm}$.

17.75 (a) With $E_{a,ads} \approx 0$, Eq. (17.71) gives $E_{a,des} \approx$
 $-\Delta U_{ads}^\circ \approx -\Delta H_{ads}^\circ$. $t_{\frac{1}{2}} = 0.693/k_{des} = 0.693e^{E_{a,des}/RT}/A_{des}$
 $\approx 0.693e^{|\Delta H_{ads}|/RT}/A_{des} = 0.693 \times$
 $e^{(50000 \text{ J/mol})/(8.314 \text{ J/mol-K})(300 \text{ K})}/(10^{15} \text{ s}^{-1}) = 3.5 \times$
 10^{-7} s . (b) 180 s. (c) $4.6 \times 10^{19} \text{ s}$.

17.76 Let the half-reaction be $M^z + ne^- = M^{z'}$ or its re-
 verse (where z and z' are the charges on the species M).
 Let B in Eq. (17.128) be the species e^- . Then $|v_B| = n$
 and $r_s = A^{-1}|v_B|^{-1}|dn_B/dt| = (1/A n)|dn_{e^-}/dt|$, where n_{e^-}
 (not to be confused with n , the number of electrons in
 the half-reaction) is the number of moles of electrons.
 Since the Faraday constant is the absolute value of the
 charge per mole of electrons, we have $|Q| = \mathcal{F}n_{e^-}$, so
 $|dn_{e^-}/dt| = \mathcal{F}^{-1}|dQ/dt| = I/\mathcal{F}$ and $r_s = (1/A n \mathcal{F})I = j/n\mathcal{F}$.

17.77 $N = (0.000420 \text{ g})(1 \text{ mole}/347 \text{ g})(6.022 \times 10^{23}/\text{mole})$
 $= 7.29 \times 10^{17}$ atoms of ^{233}U . Then $\lambda = A/N =$
 $(9.88 \times 10^4 \text{ s}^{-1})/(7.29 \times 10^{17}) = 1.35_5 \times 10^{-13} \text{ s}^{-1}$. $t_{\frac{1}{2}} =$
 $0.693/\lambda = 0.693/(1.35_5 \times 10^{-13} \text{ s}^{-1}) = 5.11 \times 10^{12} \text{ s} =$
 $1.62 \times 10^5 \text{ yr}$.

17.78 (a) $(20.0 \text{ g})(1 \text{ mol}/63.0 \text{ g})0.00200(6.022 \times 10^{23}/\text{mol}) =$
 3.82×10^{20} atoms of ^3H . Then $A = \lambda N = 0.693N/t_{\frac{1}{2}} =$

$$0.693(3.82 \times 10^{20}) / (12.4 \times 365.25 \times 24 \times 60 \times 60 \text{ s}) = 6.77 \times 10^{11} \text{ s}^{-1}. \quad (\underline{b}) \quad A = A_0 e^{-\lambda t} = A_0 e^{-0.693t/t_{1/2}} = (6.77 \times 10^{11} / \text{s}) e^{-0.693(6.20/12.4)} = 4.79 \times 10^{11} \text{ s}^{-1}.$$

17.79 (a) $(1.00 \text{ g})(1 \text{ mole}/12.01 \text{ g})(6.022 \times 10^{23} / \text{mole}) = 5.01 \times 10^{22}$ atoms in one gram of carbon. Then $N = A/\lambda = At_{1/2}/0.693 = (12.5 \text{ min}^{-1})(5730 \times 365 \times 24 \times 60 \text{ min})/0.693 =$

$$5.43 \times 10^{10} \text{ atoms of } ^{14}\text{C}. \text{ So, } \% ^{14}\text{C} = 100(5.43 \times 10^{10}) / (5.01 \times 10^{22}) = 1.08 \times 10^{-10} \%. \quad (\underline{b}) \quad A = A_0 e^{-\lambda t} = A_0 e^{-0.693t/t_{1/2}} = [12.5 \text{ min}^{-1} (\text{g C})^{-1}] e^{-0.693(50000/5730)} = 0.0296 \text{ min}^{-1} (\text{g C})^{-1}. \quad (\underline{c}) \quad 7.0 = 12.5 e^{-0.693t/(5730 \text{ yr})}, \ln(7.0/12.5) = -0.693t/(5730 \text{ yr}) \text{ and } t = 4800 \text{ yr}.$$

17.80 Let $A = ^{238}\text{U}$ and $B = ^{235}\text{U}$. We have $N_A = N_{A,0} e^{-\lambda_A t}$ and $N_B = N_{B,0} e^{-\lambda_B t}$. We want $N_{A,0} = N_{B,0}$ at $t = 0$. So $N_A/N_B = \exp [(\lambda_B - \lambda_A)t] = \exp [0.693t(1/t_{1/2,B} - 1/t_{1/2,A})]$.

So $\ln(99.28/0.72) = 0.693t[1/(7.0 \times 10^8 \text{ yr}) - 1/(4.51 \times 10^9 \text{ yr})]$ and $t = 5.9 \times 10^9 \text{ yr}$.

17.81 $A = A_0 e^{-\lambda t}$ and $\lambda = 0.693/t_{1/2} = (\ln 2)/t_{1/2}$, so $A = A_0 e^{(\ln 2)(-1)t/t_{1/2}} = A_0 2^{(-1)t/t_{1/2}} = A_0 (\frac{1}{2})^{t/t_{1/2}}$.

17.82 (a) Let the steps be called I, II, III, IV. Step III requires two ^3He nuclei, but only one ^3He is produced in step II. Hence the stoichiometric number of step II is 2; this requires that the stoichiometric number of step I be 2. The stoichiometric number of step IV is also 2, so as to get rid of the two positrons formed when step I is

multiplied by 2. Multiplication of steps I, II, III, and IV by 2, 2, 1, and 2 gives as the overall reaction

$$4\text{}^1_1\text{H} + 2\text{}^0_{-1}\text{e} \rightarrow \text{}^4_2\text{He} + 2\nu + 6\gamma.$$
 (b) The $\Delta\bar{U}$ is -2.6×10^{12} J/mole. There are $(3.9 \times 10^{26} \text{ J}) / (2.6 \times 10^{12} \text{ J/mole}) = 1.5 \times 10^{14}$ moles of $\text{}^4\text{He}$ produced each second. (c) The number of neutrinos produced each second is

$2(1.5 \times 10^{14} \text{ moles})(6.02 \times 10^{23} / \text{mole}) = 1.8 \times 10^{38}$. The area of a sphere of radius 1.5×10^8 km is
 $4\pi(1.5 \times 10^{11} \text{ m})^2 = 2.8 \times 10^{23} \text{ m}^2$. One $\text{cm}^2 = 10^{-4} \text{ m}^2$ and the number of neutrinos hitting a square centimeter of the earth in 1 sec is $(1.8 \times 10^{38})[(10^{-4} \text{ m}^2) / (2.8 \times 10^{23} \text{ m}^2)] = 6 \times 10^{10}$ (which is a lot of neutrinos).

17.83 For this elementary reaction, $r = k_{\max} [B][C] = -d[B]/dt = -(d/dt)(n_B/V) = -(d/dt)(N_B/N_A V) = -(1/V)(dN_B/dt)/N_A = Z_{BC}/N_A$ and $k_{\max} = Z_{BC}/N_A [B][C]$. At each collision, one B molecule disappears, and Z_{BC} is the collision rate per unit volume, so $Z_{BC} = -(1/V)(dN_B/dt)$.

(b) We have $[B] = N_B/VN_A$ and $[C] = N_C/VN_A$, so (15.62) gives $k_{\max} = Z_{BC}/N_A [B][C] = N_A (r_B + r_C)^2 (8RT\pi)^{\frac{1}{2}} (M_B^{-1} + M_C^{-1})^{\frac{1}{2}} = (6.02 \times 10^{23} / \text{mol})(4 \times 10^{-10} \text{ m})^2 [8(8.314 \text{ J/mol-K})(300 \text{ K})\pi]^{\frac{1}{2}} \times [(0.030 \text{ kg/mol})^{-1} + (0.050 \text{ kg/mol})^{-1}]^{\frac{1}{2}} = 1.8 \times 10^8 \text{ m}^3 \text{ s}^{-1} \text{ mol}^{-1} = 1.8 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

17.84 (a) T. (b) T. (c) T. (d) T. (e) T. From (17.2) and (4.97), $J = (1/v_1) dn_1/dt = d\xi/dt$. (f) F. See Eq. (17.77). (g) T. (h) F; e.g., see (17.60). (i) T. (j) T. (k) F.

18.1 (a) $dR/d\nu = 0 =$

$$\frac{2\pi h}{c^2} \left[\frac{3\nu^2}{e^{h\nu/kT} - 1} - \frac{\nu^3(h/kT)e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} \right]$$

So $3 = (h\nu_{\max}/kT)e^{h\nu_{\max}/kT} / (e^{h\nu_{\max}/kT} - 1) = xe^x / (e^x - 1)$,

where $x = h\nu_{\max}/kT$. Then $3e^x - 3 = xe^x$ and multiplication by e^{-x} gives $x + 3e^{-x} = 3$. (b) For $x = 0, 1, 2, 3$, the function $x + 3e^{-x}$ equals 3, 2.104, 2.406, and 3.149. So the nonzero root lies between 2 and 3. We have

$(3 - 2.406)/(3.149 - 2.406) = 0.80$, so interpolation gives $x \approx 2.80$. For $x = 2.80, 2.81, 2.82, 2.83$, we find $x + 3e^{-x} = 2.98243, 2.99061, 2.99882, 3.00704$. The root lies between 2.82 and 2.83, and interpolation gives $x = 2.821_4$.

(c) At 300 K, $\nu_{\max} = kTx/h =$

$(1.3807 \times 10^{-16} \text{ erg/K})(300 \text{ K})(2.821)/(6.626 \times 10^{-27} \text{ erg}\cdot\text{s})$
 $= 1.76 \times 10^{13} \text{ s}^{-1}$. At 3000 K, ν_{\max} is 10 times as large, namely, $1.76 \times 10^{14} \text{ s}^{-1}$. From Fig. 21.2, these frequencies

lie in the infrared. (d) $T = h\nu_{\max}/xk =$

$(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(3.5 \times 10^{14} \text{ s}^{-1})/2.821(1.38 \times 10^{-23} \text{ J/K})$
 $= 6000 \text{ K}$. (e) $\nu_{\max} = kTx/h = (1.38 \times 10^{-23} \text{ J/K})(306 \text{ K}) \times$
 $2.821/(6.626 \times 10^{-34} \text{ J}\cdot\text{s}) = 1.80 \times 10^{13} \text{ s}^{-1}$. Infrared.

18.2 (a) The total emission per unit time and per unit

area is $\int_0^\infty R(\nu) d\nu = (2\pi h/c^2) \int_0^\infty [\nu^3/(e^{h\nu/kT} - 1)] d\nu$. Let $z = h\nu/kT$; then $dz = (h/kT) d\nu$. We have $\int_0^\infty R(\nu) d\nu =$

$$(2\pi\hbar/c^2)(kT/h)^4 \int_0^\infty [z^3/(e^z - 1)] dz = (2\pi\hbar/c^2)(kT/h)^4 \pi^4/15 \\ = 2\pi^5 k^4 T^4 / 15 c^2 h^3. \quad (\underline{b}) \text{ The emission rate is } \\ (2\pi^5 k^4 T^4 / 15 c^2 h^3)(4\pi r^2) =$$

$$\frac{8\pi^6 (1.381 \times 10^{-23} \text{ J/K})^4 (5800 \text{ K})^4 (0.7 \times 10^9 \text{ m})^2}{15(2.998 \times 10^8 \text{ m/s})^2 (6.626 \times 10^{-34} \text{ J s})^3} =$$

$$3.9_6 \times 10^{26} \text{ J/s (similar to the value given in Prob.}$$

$$17.82). \quad (\underline{c}) \text{ In 1 year, } \Delta E = (3.9_6 \times 10^{26} \text{ J/s}) \times \\ (365 \times 24 \times 60 \times 60 \text{ s}) = 1.2_5 \times 10^{34} \text{ J. So } \Delta m = \Delta E/c^2 = \\ (1.2_5 \times 10^{34} \text{ J}) / (2.998 \times 10^8 \text{ m/s})^2 = 1.4 \times 10^{17} \text{ kg.}$$

18.3 (a) $h\nu = W + \frac{1}{2}mv^2$ and $h\nu_{\text{thr}} = W$. For K we have $\nu_{\text{thr}} = W/h = (2.2 \text{ eV})(1.60 \times 10^{-19} \text{ J/eV}) / (6.626 \times 10^{-34} \text{ J s}) = 5.3 \times 10^{14} \text{ s}^{-1}$ and $\lambda_{\text{thr}} = c/\nu_{\text{thr}} = (3.0 \times 10^{10} \text{ cm/s}) / (5.3 \times 10^{14} \text{ s}^{-1}) = 5.7 \times 10^{-5} \text{ cm}$. For Ni we find $\nu_{\text{thr}} = 1.2 \times 10^{15} \text{ s}^{-1}$ and $\lambda_{\text{thr}} = 2.5 \times 10^{-5} \text{ cm}$. (b) K-yes; Ni-no. (c) $\frac{1}{2}mv^2 = h\nu - W = (6.63 \times 10^{-34} \text{ J s})(3.00 \times 10^8 \text{ m/s}) / (4.00 \times 10^{-7} \text{ m}) - (2.2 \text{ eV})(1.60 \times 10^{-19} \text{ J/eV}) = 1.4 \times 10^{-19} \text{ J} = 0.9 \text{ eV}$.

18.4 $E = h\nu = hc/\lambda = (6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^8 \text{ m/s}) / (700 \times 10^{-9} \text{ m}) = 2.8 \times 10^{-19} \text{ J}$.

18.5 $E_{\text{photon}} = h\nu = hc/\lambda = (6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m/s}) / (590 \times 10^{-9} \text{ m}) = 3.37 \times 10^{-19} \text{ J}$. Then $100 \text{ J/s} = N(3.37 \times 10^{-19} \text{ J})$ and $N = 2.97 \times 10^{20} \text{ photons/second}$.

$$\underline{18.6} \quad h\nu = W + \frac{1}{2}mv^2 = W + K_{\max} \text{ and } K_{\max} = h\nu - W.$$

$10^{12} K_{\max} / \text{ergs}$	3.41	2.56	1.95	0.75
$10^{-14} \nu / \text{s}^{-1}$	9.593	8.213	7.408	5.490

where we used $\nu = c/\lambda$. The slope is $6.5_3 \times 10^{-27} \text{ erg} \cdot \text{s} = h$. W can be found from the graph as the value of $h\nu$ at $K_{\max} = 0$ or as the negative of the intercept at $\nu = 0$. We find $W = 2.8_5 \times 10^{-12} \text{ erg} = 1.8 \text{ eV}$.

$$\underline{18.7} \text{ (a) } \lambda = h/mv = (6.626 \times 10^{-27} \text{ erg} \cdot \text{s}) / (1.67 \times 10^{-24} \text{ g})(6.0 \times 10^6 \text{ cm/s}) = 6.6 \times 10^{-10} \text{ cm. (b) } \lambda = (6.626 \times 10^{-34} \text{ J s}) / (0.050 \text{ kg})(1.20 \text{ m/s}) = 1.1 \times 10^{-32} \text{ m} = 1.1 \times 10^{-30} \text{ cm.}$$

$$\underline{18.8} \quad E = mc^2 = h\nu, \text{ so } m = h\nu/c^2 = h/\lambda c. \text{ (a) } m = (6.626 \times 10^{-34} \text{ J s}) / (10^3 \times 10^{-9} \text{ m})(3.00 \times 10^8 \text{ m/s}) = 2.2 \times 10^{-36} \text{ kg. (b) } m = (6.626 \times 10^{-34} \text{ J s}) / (10^2 \times 10^{-9} \text{ m})(3.00 \times 10^8 \text{ m/s}) = 2.2 \times 10^{-35} \text{ kg.}$$

$$\underline{18.9} \text{ (a) } \sin \theta = \lambda/w \text{ and } \lambda = h/mv, \text{ so } \sin \theta = h/mvw = \frac{6.626 \times 10^{-27} \text{ erg} \cdot \text{s}}$$

$$(9.11 \times 10^{-28} \text{ g})(6.0 \times 10^8 \text{ cm/s})(2400 \times 10^{-8} \text{ cm}) = 5.05 \times 10^{-4} \text{ and } \theta = 0.0289^\circ = 5.05 \times 10^{-4} \text{ rad. (b) Let } z \text{ be the width of the central maximum. Figure 18.4 gives } \tan \theta = \overline{PE}/\overline{DE} = \frac{1}{2}z/(40 \text{ cm}) \text{ and } z = 2(40 \text{ cm}) \tan 0.0289^\circ = 0.040 \text{ cm. (c) } \Delta p_x = 2h/w = 2(6.63 \times 10^{-27} \text{ erg s}) / (2400 \times 10^{-8} \text{ cm}) = 5.5 \times 10^{-22} \text{ g cm/s.}$$

$$\underline{18.10} \quad \Delta x \Delta p_x \gtrsim h \text{ and } \Delta p_x \gtrsim h/\Delta x = (6.6 \times 10^{-34} \text{ J s}) /$$

$(1 \times 10^{-10} \text{ m}) = 6.6 \times 10^{-24} \text{ kg m s}^{-1}$. We have $\Delta p_x = \Delta(mv_x) = m \Delta v_x$ and $\Delta v_x = \Delta p_x / m \gtrsim (6.6 \times 10^{-24} \text{ kg m s}^{-1}) / (9.1 \times 10^{-31} \text{ kg}) = 7 \times 10^6 \text{ m/s}$, which is very large.

18.11 $|z|^2 = zz^*$ and $|z| = (zz^*)^{\frac{1}{2}}$. (a) $|-2| = 2$; (b) $|3 - 2i| = [(3 - 2i)(3 + 2i)]^{\frac{1}{2}} = (9 + 4)^{\frac{1}{2}} = 13^{\frac{1}{2}}$; (c) $|\cos \theta + i \sin \theta| = [(\cos \theta + i \sin \theta)(\cos \theta - i \sin \theta)]^{\frac{1}{2}} = (\cos^2 \theta + \sin^2 \theta)^{\frac{1}{2}} = 1^{\frac{1}{2}} = 1$; (d) $|ye^{iax}| = (ye^{iax} y^* e^{-ia^* x^*})^{\frac{1}{2}} = (yy^*)^{\frac{1}{2}} [e^{i(ax - a^* x^*)}]^{\frac{1}{2}}$ and if x and a are real numbers, $|ye^{iax}| = |y|$.

18.12 Let $ls_{18.9}$ and $rs_{18.9}$ denote the left side and right side of (18.9), respectively. We have $ls_{18.9} = rs_{18.9}$. To see if $c\Psi$ is a solution of (18.9), we replace Ψ in (18.9) by $c\Psi$ and see if (18.9) is satisfied. With $c\Psi$ as the proposed solution, the left side of (18.9) becomes $(-\hbar/i)(\partial/\partial t)(c\Psi) = c(-\hbar/i)(\partial\Psi/\partial t) = c ls_{18.9}$. The right side becomes $-(\hbar^2/2m_1)[\partial^2(c\Psi)/\partial x_1^2 + \dots] - \dots - (\hbar^2/2m_n)[\partial^2(c\Psi)/\partial x_n^2 + \dots] + Vc\Psi = c rs_{18.9}$. Since Ψ is a solution of (18.9), we have $ls_{18.9} = rs_{18.9}$. Then $c ls_{18.9} = c rs_{18.9}$ and so $c\Psi$ satisfies (18.9).

18.13 $\int_a^b \int_c^d [\int_s^t f(r)g(\theta)h(\phi) dr] d\theta d\phi = \int_a^b \int_c^d g(\theta)h(\phi) [\int_s^t f(r) dr] d\theta d\phi = \int_s^t f(r) dr \times \int_a^b [\int_c^d g(\theta)h(\phi) d\theta] d\phi = \int_s^t f(r) dr \int_c^d g(\theta) d\theta \int_a^b h(\phi) d\phi$

18.14 The time-dependent Schrödinger equation is more general, since the time-independent equation applies only

to stationary states.

18.15 Let $f = f_1 + if_2$ and $g = g_1 + ig_2$, where f_1 is the real part of f , and f_2 is the coefficient of the imaginary part of f . Then $(fg)^* = [(f_1 + if_2)(g_1 + ig_2)]^* = [f_1g_1 - f_2g_2 + i(f_2g_1 + f_1g_2)]^* = f_1g_1 - f_2g_2 - i(f_2g_1 + f_1g_2)$. Also, $f^*g^* = (f_1 + if_2)^*(g_1 + ig_2)^* = (f_1 - if_2)(g_1 - ig_2) = f_1g_1 - f_2g_2 - i(f_2g_1 + f_1g_2) = (fg)^*$.

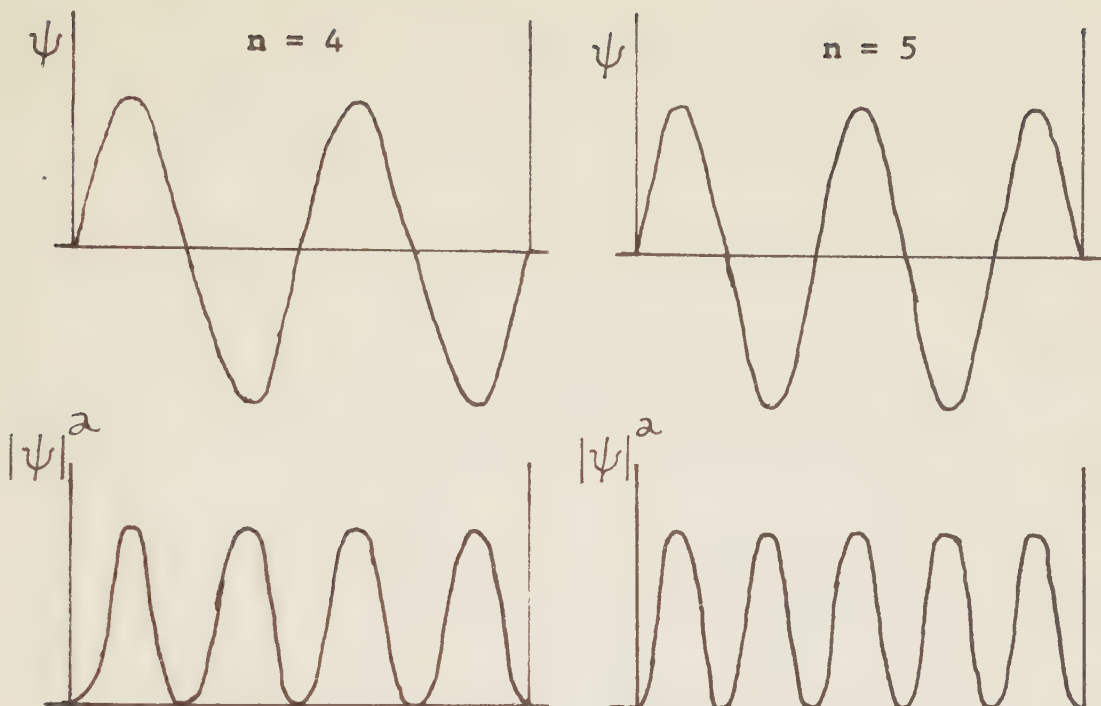
18.16 $E = n^2h^2/8ma^2$, $\Delta E = h\nu = hc/\lambda$, $\lambda = hc/\Delta E = hc[8ma^2/h^2(n_2^2 - n_1^2)] = 8ma^2c/h(n_2^2 - n_1^2) =$

$$\frac{8(1.0 \times 10^{-27} \text{ g})(6.0 \times 10^{-8} \text{ cm})^2(3.0 \times 10^{10} \text{ cm/s})}{(6.63 \times 10^{-27} \text{ erg} \cdot \text{s})(25 - 16)} =$$

$$1.45 \times 10^{-5} \text{ cm.}$$

18.17 (a) $\int_0^{\frac{1}{2}a} |\psi|^2 dx = (2/a) \int_0^{\frac{1}{2}a} \sin^2 (n\pi x/a) dx = (2/a)[\frac{1}{2}x - \frac{1}{4}(a/n\pi) \sin (2n\pi x/a)] \Big|_0^{\frac{1}{2}a} = \frac{1}{4} - (1/2n\pi) \sin \frac{1}{2}n\pi$ where we used $\int \sin^2 cx dx = \frac{1}{2}x - \frac{1}{4c} \sin 2cx$ (p. 599 in the text). (b) For $n = 1, 2, 3$, we get 0.091, 0.250, and 0.303, respectively.

18.18 The interval 0.0001 \AA is much, much smaller than the box length, so we can consider this to be an "infinitesimal" interval. The probability is then $|\psi|^2 dx = (2/a) \sin^2 (n\pi x/a) dx$. (a) For $n = 1$, we get $(2/2 \text{ \AA}) \sin^2 [\pi(1.6 \text{ \AA})/(2.0 \text{ \AA})](0.0001 \text{ \AA}) = 3.45 \times 10^{-5}$. (b) For $n = 2$, we get 9.05×10^{-5} .

18.19

Note that ψ^2 has zero slope at the nodes.

18.20 $d^2\psi/dx^2 = 0$. Integration with respect to x gives $d\psi/dx = c$ and a second integration gives $\psi = cx + d$, where c and d are integration constants. The continuity condition at $x = 0$ requires that $\psi = 0$ at $x = 0$, so $0 = c(0) + d$ and $d = 0$. Then $\psi = cx$. The continuity condition at $x = a$ requires that $\psi = 0$ at $x = a$, and $0 = ca$, so $c = 0$. Then $\psi = 0$.

18.21 The lowest frequency transition corresponds to $n = 1 \rightarrow 2$. Use of $\Delta E = h\nu$ gives $2^2 h^2 / 8ma^2 - 1^2 h^2 / 8ma^2 = h\nu$ and $a = (3h/8m\nu)^{1/2} = [3(6.63 \times 10^{-34} \text{ J s})]^{1/2} / [8(9.11 \times 10^{-31} \text{ kg})(2.0 \times 10^{14} \text{ s}^{-1})]^{1/2} = 1.2 \times 10^{-9} \text{ m}$.

18.22 $\int_0^a \psi_i^* \psi_j dx = 2a^{-1} \int_0^a \sin(n_i \pi x/a) \sin(n_j \pi x/a) dx$,
 $n_i \neq n_j$. A table of integrals gives $\int \sin cx \sin bx dx =$
 $[1/2(c - b)] \sin [(c - b)x] - [1/2(c + b)] \sin [(c + b)x]$,
provided $c^2 \neq b^2$. So $\int_0^a \psi_i^* \psi_j dx =$

$$\frac{2}{a} \left[\frac{\sin [(n_i - n_j)\pi x/a]}{2(n_i - n_j)\pi/a} - \frac{\sin [(n_i + n_j)\pi x/a]}{2(n_i + n_j)\pi/a} \right] \Big|_0^a = 0$$

since $\sin[(n_i - n_j)\pi] = 0$, $\sin[(n_i + n_j)\pi] = 0$, and $\sin 0 = 0$.
(The sum and difference of two integers is an integer.)

18.23 The left side of (18.22) becomes $d^2\psi/dx^2 =$
 $(2/a)^{1/2}(-1)(n^2\pi^2/a^2) \sin(n\pi x/a)$. With use of (18.27), the
right side of (18.22) becomes $-(2m/\hbar^2)(n^2h^2/8ma^2)(2/a)^{1/2} x$
 $\sin(n\pi x/a) = -(n^2\pi^2/a^2)(2/a)^{1/2} \sin(n\pi x/a)$, which equals
the left side.

18.24 (a) $E = (h^2/8ma^2)(n_x^2 + n_y^2 + n_z^2)$. There are 17 states
with $n_x^2 + n_y^2 + n_z^2 \leq 16$, namely: $n_x n_y n_z = 111, 211,$
 $121, 112, 122, 212, 221, 311, 131, 113, 222,$
 $123, 132, 213, 231, 312, 321$. (b) These states
give a total of 6 different values for $n_x^2 + n_y^2 + n_z^2$,
namely, $n_x^2 + n_y^2 + n_z^2 = 3, 6, 9, 11, 12, 14$, so there are
6 energy levels in the given range.

18.25 $\hat{A}\hat{B}f(x) - \hat{B}\hat{A}f(x) = (d^2/dx^2)[xf(x)] - x[(d^2/dx^2)f(x)]$
 $= (d/dx)[xf'(x) + f(x)] - xf''(x) = xf''(x) + f'(x) +$
 $f'(x) - xf''(x) = 2f'(x)$.

18.26 (a) When \hat{B} operates on $g(x)$, it turns g into another function, which we shall call $f(x)$. When \hat{A} operates on $f(x)$, we get another function, so $\hat{A}\hat{B}g(x)$ is a function.
 (b) Operator. (c) Function. (d) Operator. (e) Function.

18.27 (a) $\hat{p}_x^3 = [(\hbar/i)(\partial/\partial x)]^3 = -(\hbar^3/i)(\partial^3/\partial x^3)$.

(b) $\hat{p}_z^4 = [(\hbar/i)(\partial/\partial z)]^4 = \hbar^4(\partial^4/\partial z^4)$.

18.28 $(d^2/dx^2)(\sin 3x) = (d/dx)(3 \cos 3x) = -9(\sin 3x)$, so $\sin 3x$ is an eigenfunction of d^2/dx^2 with eigenvalue -9 .
 $(d^2/dx^2)(6 \cos 4x) = -96 \cos 4x = -16(6 \cos 4x)$, so $6 \cos 4x$ is an eigenfunction of d^2/dx^2 with eigenvalue -16 .
 $(d^2/dx^2)(5x^3) = 30x$, which does not equal a constant times $5x^3$; so $5x^3$ is not an eigenfunction of d^2/dx^2 .
 $(d^2/dx^2)x^{-1} = 2x^{-3} \neq (\text{const.})x^{-1}$. $(d^2/dx^2)(3e^{-5x}) = 75e^{-5x} = 25(3e^{-5x})$, and the eigenvalue is 25 .
 $(d^2/dx^2) \ln 2x = -1/x^2 \neq (\text{const.}) \ln 2x$.

18.29 (a) $\langle p_x \rangle = \int_{-\infty}^{\infty} \psi^* \hat{p}_x \psi \, dx = \int_{-\infty}^{\infty} \psi^* (\hbar/i)(\partial/\partial x) \psi \, dx = (\hbar/i) \int_{-\infty}^0 \psi^* (\partial \psi / \partial x) \, dx + (\hbar/i) \int_0^a \psi^* (\partial \psi / \partial x) \, dx + (\hbar/i) \int_a^{\infty} \psi^* (\partial \psi / \partial x) \, dx = (\hbar/i) \int_0^a \psi^* (\partial \psi / \partial x) \, dx = (\hbar/i)(2/a)(n\pi/a) \int_0^a \sin(n\pi x/a) \cos(n\pi x/a) \, dx = (2n\pi\hbar/ia^2)(a/n\pi) \frac{1}{2} \sin^2(n\pi x/a) \Big|_0^a = 0$, since $\sin n\pi = 0$ for $n = 1, 2, 3, \dots$. (We used the fact that $\psi^* = 0$ outside the box.) (b) $\langle x \rangle = \int_0^a \psi^* x \psi \, dx = \int_0^a (2/a)^{1/2} \sin(n\pi x/a) x (2/a)^{1/2} \sin(n\pi x/a) \, dx = (2/a) \int_0^a x \sin^2(n\pi x/a) \, dx$. A table of integrals gives

$$\int x \sin^2 cx \, dx = \frac{1}{4}x^2 - (x/4c) \sin 2cx - (1/8c^2) \cos 2cx,$$

so $\langle x \rangle = (2/a) \left[\frac{1}{4}x^2 - (ax/4n\pi) \sin (2n\pi x/a) - (a^2/8n^2\pi^2) \cos (2n\pi x/a) \right] \Big|_0^a = (2/a) \left(\frac{1}{4}a^2 - a^2/8n^2\pi^2 + a^2/8n^2\pi^2 \right) = a/2$, since $\sin 2n\pi = 0$ and $\cos 2n\pi = 1$ for $n = 1, 2, \dots$.

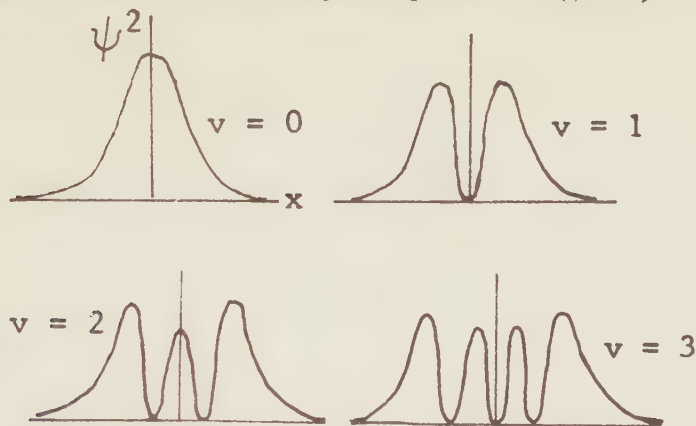
(c) $\langle x^2 \rangle = \int_0^a \psi^* x^2 \psi \, dx = (2/a) \int_0^a x^2 \sin^2 (n\pi x/a) \, dx$. A table of integrals gives $\int x^2 \sin^2 cx \, dx = x^3/6 - (x^2/4c - 1/8c^3) \sin 2cx - (x/4c^2) \cos 2cx$, so $\langle x^2 \rangle = (2/a) \left[x^3/6 - (ax^2/4n\pi - a^3/8n^3\pi^3) \sin (2n\pi x/a) - (a^2x/4n^2\pi^2) \cos (2n\pi x/a) \right] \Big|_0^a = (2/a) (a^3/6 - a^3/4n^2\pi^2) = a^2/3 - a^2/2n^2\pi^2$.

18.30 The time-independent Schrödinger equation $\hat{H}\psi = E\psi$ for (18.54) is $(\hat{H}_1 + \hat{H}_2 + \dots + \hat{H}_r)\psi = E\psi$ and $\hat{H}_1\psi + \hat{H}_2\psi + \dots + \hat{H}_r\psi = E\psi$ (1). Taking $\psi = f_1(q_1)f_2(q_2)\dots f_r(q_r)$, we have $\hat{H}_1\psi = \hat{H}_1[f_1(q_1)f_2(q_2)\dots f_r(q_r)] = f_2 \dots f_r \hat{H}_1 f_1$, since \hat{H}_1 involves only q_1 . Equation (1) becomes $f_2 \dots f_r \hat{H}_1 f_1 + f_1 f_3 \dots f_r \hat{H}_2 f_2 + \dots + f_1 \dots f_{r-1} \hat{H}_r f_r = E f_1 f_2 \dots f_r$. Division by $f_1 f_2 \dots f_r$ gives $(1/f_1) \hat{H}_1 f_1 + (1/f_2) \hat{H}_2 f_2 + \dots + (1/f_r) \hat{H}_r f_r = E$ (2). By the same kind of argument used after Eq. (18.32), each term on the left side of equation (2) must be a constant. Calling these constants E_1, E_2, \dots, E_r , we have $(1/f_1) \hat{H}_1 f_1 = E_1$ or $\hat{H}_1 f_1 = E_1 f_1$, etc., and equation (2) gives $E_1 + E_2 + \dots + E_r = E$.

18.31 $v_{\text{light}} = \Delta E/h = [(v_1 + \frac{1}{2})h\nu_{\text{osc}} - (v_2 + \frac{1}{2})h\nu_{\text{osc}}]/h =$

$$(v_1 - v_2)v_{\text{osc}} = (8 - 7)v_{\text{osc}} = v_{\text{osc}} = 6.0 \times 10^{13} \text{ s}^{-1}.$$

18.32 Squaring the curves in Fig. 18.12, we get the following curves (note the unequal peak heights):



18.33 (a) From Fig. 18.12, ψ_0 is a maximum at $x = 0$; likewise, ψ_0^2 is a maximum at $x = 0$ and this is the most probable value of x . (b) $d\psi_1^2/dx = 0 = (4\alpha^3/\pi)^{1/2}(2xe^{-\alpha x^2} - 2\alpha x^3 e^{-\alpha x^2})$, so $x = \pm 1/\alpha^{1/2} = \pm(\hbar/2\pi v m)^{1/2}$. ($x = 0$ is a minimum.)

$$\begin{aligned} \underline{18.34} \quad d^2\psi_0/dx^2 &= (\alpha/\pi)^{1/2}(d^2/dx^2)e^{-\alpha x^2/2} = \\ &(\alpha/\pi)^{1/2}(d/dx)(-\alpha x e^{-\alpha x^2/2}) = (\alpha/\pi)^{1/2}(-\alpha e^{-\alpha x^2/2} + \alpha^2 x^2 e^{-\alpha x^2/2}) \\ &= (\alpha^2 x^2 - \alpha)\psi_0 = (16\pi^4 v^2 m^2 x^2/h^2 - 4\pi^2 v m/h)\psi_0. \text{ Equation} \\ (18.63) \text{ gives } k &= 4\pi^2 v^2 m, \text{ so } \frac{1}{2}kx^2\psi_0 = 2\pi^2 v^2 m x^2\psi_0. \text{ Then} \\ -(\hbar^2/2m)(d^2\psi_0/dx^2) + \frac{1}{2}kx^2\psi_0 &= (-2\pi^2 v^2 m x^2 + \frac{1}{2}\hbar v)\psi_0 + \\ 2\pi^2 v^2 m x^2\psi_0 &= \frac{1}{2}\hbar v\psi_0 = E_0\psi_0. \end{aligned}$$

$$\begin{aligned} \underline{18.35} \quad \int_{-\infty}^{\infty} \psi_1^* \psi_1 dx &= (4\alpha^3/\pi)^{1/2} \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = \\ 2(4\alpha^3/\pi)^{1/2} \int_0^{\infty} x^2 e^{-\alpha x^2} dx &= 2(4\alpha^3/\pi)^{1/2} (2\pi^{1/2}/2^3 \alpha^{3/2}) = 1, \text{ where} \\ \text{we used integrals 1 and 3 (with } n &= 1) \text{ in Table 15.1.} \end{aligned}$$

$$\underline{18.36} \quad (\underline{a}) \quad \langle x \rangle = \int_{-\infty}^{\infty} \psi^* x \psi dx = (\alpha/\pi)^{1/2} \int_{-\infty}^{\infty} x e^{-\alpha x^2} dx = 0,$$

where integral 4 (with $n = 0$) in Table 15.1 was used. This result is obvious from Fig. 18.12. (b) $\langle x^2 \rangle = \int_{-\infty}^{\infty} \psi^* x^2 \psi dx = (\alpha/\pi)^{\frac{1}{2}} \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = 2(\alpha/\pi)^{\frac{1}{2}} \int_0^{\infty} x^2 e^{-\alpha x^2} dx = 2(\alpha/\pi)^{\frac{1}{2}} (2\pi^{\frac{1}{2}}/2^{\frac{3}{2}} \alpha^{3/2}) = 1/2\alpha = h/8\pi^2 m$, where we used integrals 1 and 3 in Table 15.1. (c) $\langle p_x \rangle = \int_{-\infty}^{\infty} \psi^* \hat{p}_x \psi dx = (\alpha/\pi)^{\frac{1}{2}} \int_{-\infty}^{\infty} e^{-\alpha x^2/2} (\hbar/i) (\partial/\partial x) e^{-\alpha x^2/2} dx = (\alpha/\pi)^{\frac{1}{2}} (\hbar/i) (-\alpha) \int_{-\infty}^{\infty} x e^{-\alpha x^2} dx = 0$ (from integral 4).

$$\begin{aligned} 18.37 \quad E = K + V &= \frac{1}{2}m(dx/dt)^2 + \frac{1}{2}kx^2 = \\ \frac{1}{2}m[(k/m)^{\frac{1}{2}}A \cos [(k/m)^{\frac{1}{2}}t + b]]^2 + \frac{1}{2}kA^2 \sin^2 [(k/m)^{\frac{1}{2}}t + b] &= \\ \frac{1}{2}kA^2 [\cos^2 [(k/m)^{\frac{1}{2}}t + b] + \sin^2 [(k/m)^{\frac{1}{2}}t + b]] &= \frac{1}{2}kA^2. \end{aligned}$$

$$\begin{aligned} (b) \quad m d^2x/dt^2 &= m(d^2/dt^2)[A \sin [(k/m)^{\frac{1}{2}}t + b]] = \\ -mA(k/m) \sin [(k/m)^{\frac{1}{2}}t + b] &= -k[A \sin [(k/m)^{\frac{1}{2}}t + b]] = -kx \end{aligned}$$

$$\begin{aligned} 18.38 \quad (a) \quad v &= (1/2\pi)(k/m)^{\frac{1}{2}} \text{ and } k = 4\pi^2 v^2 m = \\ 4\pi^2 (2.4 \text{ s}^{-1})^2 (45 \text{ g}) &= 1.02 \times 10^4 \text{ dyn/cm. } (b) \quad E = \frac{1}{2}kA^2 = \\ 0.5(1.02 \times 10^4 \text{ dyn/cm})(4.0 \text{ cm})^2 &= 8.2 \times 10^4 \text{ ergs} = \\ (v + \frac{1}{2})h\nu, \text{ so } v + \frac{1}{2} &= (8.2 \times 10^4 \text{ ergs})/ \\ (6.626 \times 10^{-27} \text{ erg} \cdot \text{s})(2.4 \text{ s}^{-1}) &= 5.1 \times 10^{30} = v. \end{aligned}$$

18.39 (a) The Hamiltonian is the sum of three one-dimensional harmonic-oscillator Hamiltonians, one for each coordinate; the separation-of-variables theorem [Eqs. (18.55) and (18.56)] gives the energy as the sum of three one-dimensional-harmonic-oscillator energies: $E = E_x + E_y + E_z = (v_x + \frac{1}{2})h\nu_x + (v_y + \frac{1}{2})h\nu_y + (v_z + \frac{1}{2})h\nu_z$, where $v_x = 0, 1, 2, \dots$, $v_y = 0, 1, 2, \dots$, $v_z = 0, 1, 2, \dots$,

and $v_x = (1/2\pi)(k_x/m)^{1/2}$, $v_y = (1/2\pi)(k_y/m)^{1/2}$, $v_z = (1/2\pi)(k_z/m)^{1/2}$, where m is the particle's mass. (b) The lowest level has $v_x = v_y = v_z = 0$ and $E = \frac{1}{2}h(v_x + v_y + v_z)$.

18.40 $H = (1/2\mu)(\mu^2 v_x^2 + \mu^2 v_y^2 + \mu^2 v_z^2) + V + (1/2M)(M^2 v_X^2 + M^2 v_Y^2 + M^2 v_Z^2) = V + \frac{1}{2}\mu(v_x^2 + v_y^2 + v_z^2) + \frac{1}{2}M(v_X^2 + v_Y^2 + v_Z^2)$. Using Eq. (18.67), we have $v_x = dx/dt = dx_2/dt - dx_1/dt = v_{x,2} - v_{x,1}$. Similarly, $v_y = v_{y,2} - v_{y,1}$ and $v_z = v_{z,2} - v_{z,1}$. Since $X = (m_1 x_1 + m_2 x_2)/M$, we have $v_X = dX/dt = [m_1(dx_1/dt) + m_2(dx_2/dt)]/M = (m_1 v_{x,1} + m_2 v_{x,2})/(m_1 + m_2)$; similar equations hold for v_Y and v_Z . So $H = V + \frac{1}{2}[m_1 m_2/(m_1 + m_2)](v_{x,1}^2 - 2v_{x,1}v_{x,2} + v_{x,2}^2 + \dots) + \frac{1}{2}(m_1 + m_2)(m_1 + m_2)^{-2}(m_1^2 v_{x,1}^2 + 2m_1 m_2 v_{x,1}v_{x,2} + m_2^2 v_{x,2}^2 + \dots) = V + \frac{1}{2}(m_1 + m_2)^{-1}[(m_1 + m_2)m_1 v_{x,1}^2 + (m_1 + m_2)m_2 v_{x,2}^2 + \dots] = V + \frac{1}{2}(m_1 v_{x,1}^2 + m_2 v_{x,2}^2 + m_1 v_{y,1}^2 + m_2 v_{y,2}^2 + m_1 v_{z,1}^2 + m_2 v_{z,2}^2) = V + \frac{1}{2}m_1 v_1^2 + \frac{1}{2}m_2 v_2^2 = V + m_1^2 v_1^2/2m_1 + m_2^2 v_2^2/2m_2 = p_1^2/2m_1 + p_2^2/2m_2 + V$. (The dots indicate similar terms in y and z .)

18.41 (a) $\mu = m_1 m_2/(m_1 + m_2) = [(12.0 \text{ g/mol})/N_A] \times [(16.0 \text{ g/mol})/N_A]/[(28.0 \text{ g/mol})/N_A] = (6.86 \text{ g/mol})/N_A = 1.14 \times 10^{-23} \text{ g}$. (b) $I = \mu d^2 = (1.14 \times 10^{-26} \text{ kg}) \times (1.13 \times 10^{-10} \text{ m})^2 = 1.45 \times 10^{-46} \text{ kg m}^2$. (c) $E_{\text{rot}} = J(J+1)\hbar^2/2I$. $\hbar^2/2I = (6.626 \times 10^{-34} \text{ J s})^2/8\pi^2(1.45 \times 10^{-46} \text{ kg m}^2) = 3.83 \times 10^{-23} \text{ J}$. For $J = 0, 1, 2, 3$, we have $E_{\text{rot}} = 0, 7.66 \times 10^{-23} \text{ J}, 23.0 \times 10^{-23} \text{ J}, 46.0 \times 10^{-23} \text{ J}$, respectively. The levels are $(2J+1)$ -fold

degenerate, so the degeneracies are 1, 3, 5, 7. (d) For $J = 0$ to 1, $\Delta E = 7.66 \times 10^{-23} J - 0 = 7.66 \times 10^{-23} J = h\nu = (6.626 \times 10^{-34} J s)\nu$ and $\nu = 1.16 \times 10^{11} s^{-1}$. For $J = 1$ to 2, $\Delta E = (23.0 - 7.66)10^{-23} J = h\nu$ and $\nu = 2.32 \times 10^{11} s^{-1}$.

18.42 $\langle x^2 \rangle \approx \int_0^a \phi^* x^2 \phi dx / \int_0^a \phi^* \phi dx$, where the denominator is required because ϕ is not normalized. $\int_0^a \phi^* x^2 \phi dx = \int_0^a x(a-x)x^2x(a-x) dx = \int_0^a (a^2 x^4 - 2ax^5 + x^6) dx = a^7/5 - a^7/3 + a^7/7 = a^7/105$. Also, $\int_0^a \phi^* \phi dx = \int_0^a x^2(a-x)^2 dx = \int_0^a (a^2 x^2 - 2ax^3 + x^4) dx = a^5/3 - a^5/2 + a^5/5 = a^5/30$. Hence $\langle x^2 \rangle \approx (a^7/105) \div (a^5/30) = 2a^2/7 = 0.2857a^2$. The true value is found by setting $n = 1$ in Prob. 18.29c to give $\langle x^2 \rangle = a^2(1/3 - 1/2\pi^2) = 0.2827a^2$. The error is 1.1%.

18.43 (a) $\int_0^a \phi^* \phi dx = \int_0^a x^2(a-x)^2 x^2(a-x)^2 dx = \int_0^a (a^4 x^4 - 4a^3 x^5 + 6a^2 x^6 - 4ax^7 + x^8) dx = a^9/5 - 2a^9/3 + 6a^9/7 - a^9/2 + a^9/9 = a^9/630$. We have $\hat{H}\phi = -(\hbar^2/2m)(d^2/dx^2)(x^2 a^2 - 2ax^3 + x^4) = -(\hbar^2/2m)(2a^2 - 12ax + 12x^2)$. So $\int_0^a \phi^* \hat{H}\phi dx = -(\hbar^2/m) \int_0^a x^2(a-x)^2(a^2 - 6ax + 6x^2) dx = -(\hbar^2/m) \int_0^a (a^4 x^2 - 8a^3 x^3 + 19a^2 x^4 - 18ax^5 + 6x^6) dx = -(\hbar^2/m)(a^7/3 - 2a^7 + 19a^7/5 - 3a^7 + 6a^7/7) = \hbar^2 a^7/105m = h^2 a^7/420\pi^2 m$. Then $\int \phi^* \hat{H}\phi dx / \int \phi^* \phi dx = (h^2 a^7/420\pi^2 m)(630/a^9) = (3/2\pi^2)(h^2/ma^2) = 0.152h^2/ma^2 \approx E_{gs}$. The true E_{gs} is $h^2/8ma^2 = 0.125h^2/ma^2$. The error is 22%. (b) It is discontinuous at $x = a$, since $\phi = 0$ out-

side the box.

18.44 $\int \psi_{gs}^{(0)*} \hat{H} \psi_{gs}^{(0)} d\tau =$
 $(\alpha/\pi)^{1/2} \int_{-\infty}^{\infty} e^{-\alpha x^2/2} c x^4 e^{-\alpha x^2/2} dx =$
 $c(\alpha/\pi)^{1/2} \int_{-\infty}^{\infty} x^4 e^{-\alpha x^2} dx = 2c(\alpha/\pi)^{1/2} \int_0^{\infty} x^4 e^{-\alpha x^2} dx =$
 $2c(\alpha/\pi)^{1/2} (4! \pi^{1/2} / 2^5 2! \alpha^{5/2}) = 3c/4\alpha^2$, where we used integrals 1 and 3 (with $n = 2$) in Table 15.1. We then have $E_{gs} \approx E_{gs}^{(0)} + 3c/4\alpha^2 = \frac{1}{2}h\nu + 3ch^2/64\pi^4\nu^2 m^2$.

18.45 (a) If $Nx(a-x)$ is normalized, then
 $\int_0^a |N|^2 x^2 (a-x)^2 dx = 1 = |N|^2 \int_0^a (x^2 a^2 - 2ax^3 + x^4) dx =$
 $|N|^2 (a^5/3 - a^5/2 + a^5/5) = |N|^2 a^5/30 = 1$ and $|N| = 30^{1/2} a^{-5/2}$,
 so a normalized form is $30^{1/2} a^{-5/2} x(a-x) =$
 $30^{1/2} a^{-1/2} (x/a)(1-x/a)$. (b) For the ground state, $\psi =$
 $(2/a)^{1/2} \sin(\pi x/a)$. At $x/a = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6$
 we get $\psi = 0, (2/a)^{1/2}(0.309) = 0.437/a^{1/2}, 0.831/a^{1/2}, 1.144/a^{1/2},$
 $1.345/a^{1/2}, 1.414/a^{1/2}, 1.345/a^{1/2}$. The corresponding values of
 the function in (a) are $0, 0.493/a^{1/2}, 0.876/a^{1/2}, 1.150/a^{1/2},$
 $1.315/a^{1/2}, 1.369/a^{1/2}, 1.315/a^{1/2}$.

18.46 Since $|\psi|^2 dx$ is a probability and probabilities are dimensionless, $|\psi|^2$ has units of length^{-1} and ψ has units of $\text{length}^{-1/2}$. The SI units of ψ are $\text{m}^{-1/2}$.

18.47 The blackbody function (18.1) depends on the combinations of constants h/c^2 and h/k . In 1900, c was known reasonably accurately, so by fitting the observed blackbody curves Planck obtained values for both h and k . Use

of $R = N_A k$ then gave N_A . Use of $\mathcal{F} = N_A e$ then gave e .

18.48 (a) $E = n^2 h^2 / 8ma^2$ and doubling a multiplies E by $\frac{1}{4}$.

(b) $E = J(J + 1) \hbar^2 / 2I = J(J + 1) \hbar^2 / 2\mu d^2$ and doubling d multiplies E by $\frac{1}{4}$. (c) $E = h\nu = h(1/2\pi)(k/m)^{\frac{1}{2}}$ and doubling m multiplies E by $1/\sqrt{2}$.

18.49 (a) T. (b) T. The future state is predicted by integrating the time-dependent Schrödinger equation.

(c) T. (d) T. (e) T. This is the definition of operator addition. (f) F. (g) F. "Sum must be replaced by "product" to make the statement true. (h) T. (i) F. (j) F.

<p><u>Reminder</u>: Don't use the solutions manual to avoid working problems.</p>

CHAPTER 19

19.1 $V = Q_1'Q_2'/r = Q_1Q_2/4\pi\epsilon_0 r$. (a) $V =$
 $(-4.80 \times 10^{-10} \text{ statC})^2/(3.0 \times 10^{-8} \text{ cm}) = 7.7 \times 10^{-12} \text{ erg} =$
 $(7.7 \times 10^{-12} \text{ erg})(1 \text{ eV}/1.602 \times 10^{-12} \text{ erg}) = 4.8 \text{ eV}$. In SI
units, $V = (-1.602 \times 10^{-19} \text{ C})^2/$
 $4\pi(8.854 \times 10^{-12} \text{ C}^2/\text{N}\cdot\text{m}^2)(3.0 \times 10^{-10} \text{ m}) = 7.7 \times 10^{-19} \text{ J}$.

(b) Let the electrons be numbered 1 and 2 and let the proton be p. Then $V = V_{12} + V_{1p} + V_{2p} =$
 $(-4.80 \times 10^{-10} \text{ statC})^2/(3.0 \times 10^{-8} \text{ cm})$
 $- (4.80 \times 10^{-10} \text{ statC})^2/(4.0 \times 10^{-8} \text{ cm})$
 $- (4.80 \times 10^{-10} \text{ statC})^2/(5.0 \times 10^{-8} \text{ cm})$
 $= -2.7 \times 10^{-12} \text{ erg} = -1.7 \text{ eV}$.

19.2 $E = (100 \text{ eV})(1.602 \times 10^{-19} \text{ J})/(1 \text{ eV}) = 1.602 \times 10^{-17} \text{ J}$.
 $J = p^2/2m$, so $p = [2(9.11 \times 10^{-31} \text{ kg})(1.602 \times 10^{-17} \text{ J})]^{1/2} =$
 $5.40 \times 10^{-24} \text{ kg m/s}$. $\lambda = h/p = (6.626 \times 10^{-34} \text{ J s})/$
 $(5.40 \times 10^{-24} \text{ kg m/s}) = 1.23 \times 10^{-10} \text{ m} = 1.23 \text{ \AA}$.

19.3 $m = Q \div (Q/m) = (4.5 \times 10^{-17} \text{ C})/(6.0 \times 10^8 \text{ C/g}) =$
 $7.5 \times 10^{-26} \text{ g}$.

19.4 Q/m decreases at high v due to the relativistic increase of mass with speed.

19.5 $V = 4\pi r^3/3$, so $V_{\text{nuc}}/V_{\text{atom}} = r_{\text{nuc}}^3/r_{\text{atom}}^3 =$
 $(10^{-12} \text{ cm})^3/(10^{-8} \text{ cm})^3 = 1 \times 10^{-12}$.

19.6 $\bar{V} = M/\rho = (197 \text{ g/mole})/(19.3 \text{ g/cm}^3) = 10.2 \text{ cm}^3/\text{mol}$.

$$v_{\text{atom}} = (10.2 \text{ cm}^3/\text{mole}) / (6.02 \times 10^{23}/\text{mole}) = 1.69 \times 10^{-23} \text{ cm}^3$$

$$\text{cm}^3 = \ell^3 \text{ and } \ell = 2.57 \times 10^{-8} \text{ cm} = 2.6 \text{ \AA}.$$

19.7 (a) 0, 1, 2, 3, 4. (b) -5, -4, -3, -2, -1, 0, 1, 2, 3, 4, 5.

19.8 (a) The only $n = 1$ state is $1s_0$, so the degeneracy is 1 (i.e., nondegenerate), if spin is not considered.

(b) The states $2s$, $2p_1$, $2p_0$, $2p_{-1}$ have the same energy, so the degeneracy is 4. (c) The states $3s$, $3p_1$, $3p_0$, $3p_{-1}$, $3d_2$, $3d_1$, $3d_0$, $3d_{-1}$, $3d_{-2}$ have the same energy and the degeneracy is 9. (The general formula is n^2 .)

19.9 These are hydrogenlike species, so $E = -(Z^2/n^2) \times (13.60 \text{ eV})$. The ionization energy IE is $-E$ for the ground state, $n = 1$. (a) $\text{IE} = 2^2(13.60 \text{ eV}) = 54.4 \text{ eV}$ and the ionization potential IP is 54.4 V. (b) $\text{IE} = 3^2(13.60 \text{ eV}) = 122.4 \text{ eV}$ and $\text{IP} = 122.4 \text{ V}$.

19.10 $\Delta E = -(13.60 \text{ eV})(1.602 \times 10^{-12} \text{ erg/1 eV}) \times (1/3^2 - 1/2^2) = 3.026 \times 10^{-12} \text{ erg} = h\nu$ and $\nu = (3.026 \times 10^{-12} \text{ erg}) / (6.626 \times 10^{-27} \text{ erg s}) = 4.567 \times 10^{14}/\text{s}$.
 $\lambda = c/\nu = (2.9979 \times 10^{10} \text{ cm/s}) / (4.567 \times 10^{14}/\text{s}) = 6564 \text{ \AA}.$

19.11 For a hydrogen atom, $\mu = m_e m_p / (m_e + m_p) = \frac{(9.1095 \times 10^{-28} \text{ g})(1.67265 \times 10^{-24} \text{ g})}{(9.1095 \times 10^{-28} \text{ g} + 1.67265 \times 10^{-24} \text{ g})} = 9.1045 \times 10^{-28} \text{ g}$

We have $a = \hbar^2 / \mu e'^2 = (6.6262 \times 10^{-27} \text{ erg} \cdot \text{s})^2 /$

$$4\pi^2(9.1045 \times 10^{-28} \text{ g})(4.8032 \times 10^{-10} \text{ statC})^2 = 5.295 \times 10^{-9} \text{ cm} = 0.5295 \text{ \AA}.$$

19.12 This is a hydrogenlike species, so its energy levels are given by Eq. (19.16) as $E = -(Z^2/n^2)(e'^2/2a) = -(Z^2/n^2)(\mu e'^4/2\hbar^2)$. Let m_e be the electron mass; the positron has mass m_e . So $\mu_{\text{positronium}} = m_e^2/(m_e + m_e) = m_e/2$, as compared to $\mu \approx m_e$ for an H atom. Since E is proportional to μ , each positronium energy level is half the corresponding H-atom energy. The positronium ionization potential is thus $\frac{1}{2}(13.6 \text{ V}) = 6.8 \text{ V}$.

19.13 Using Table 19.1 and Eq. (19.25), $\langle r \rangle = \int \psi^* r \psi d\tau = \pi^{-1}(Z/a)^3 \int_0^{2\pi} \int_0^\pi \int_0^\infty e^{-Zr/a} r e^{-Zr/a} r^2 \sin \theta dr d\theta d\phi = (Z^3/\pi a^3) \int_0^\infty r^3 e^{-2Zr/a} dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi$. A table of integrals gives $\int z^3 e^{bz} dz = e^{bz}(z^3/b - 3z^2/b^2 + 6z/b^3 - 6/b^4)$, so $\int_0^\infty r^3 e^{-2Zr/a} dr = 6/(-2Z/a)^4 = 3a^4/8Z^4$, since $e^{-2Zr/a}$ vanishes at $r = \infty$. (This result also follows from the definite integral $\int_0^\infty z^n e^{-bz} dz = n!/b^{n+1}$ found in most tables.) Then $\langle r \rangle = (Z^3/\pi a^3)(3a^4/8Z^4)(2)(2\pi) = 3a/2Z$.

19.14 Let θ be the angle between the positive z axis and an angular-momentum vector. For $m = +1$ in Fig. 19.5, $\cos \theta = L_z/|\vec{L}| = \hbar/\sqrt{2}\hbar = 1/\sqrt{2} = 0.7071$ and $\theta = 45^\circ$. For $m = 0$, $\theta = 90^\circ$. For $m = -1$, $\theta = 180^\circ - 45^\circ = 135^\circ$.

19.15 (a) $L = rp \sin \beta$, where β is the angle between \vec{r} and \vec{p} . For circular motion, the velocity vector \vec{v} is perpendi-

cular to the radius, and so is $\vec{p} = m\vec{v}$; thus $\beta = 90^\circ$ and $\sin \beta = 1$. Since $p = mv$, we get $L = mvr$. (b) The \vec{L} vector is perpendicular to both \vec{r} and \vec{p} and \vec{r} and \vec{p} lie in the plane of the circular motion. Hence \vec{L} is perpendicular to the plane of the circular orbit.

19.16 (a) From Sec. 19.3, $|\vec{L}| = [\ell(\ell + 1)]^{\frac{1}{2}}\hbar = 0$, since $\ell = 0$ for the 1s state. (b) From Sec. 18.3, Bohr had $|\vec{L}| = mvr = nh/2\pi = h/2\pi$ for the ground state. The Bohr theory had the wrong value of $|\vec{L}|$.

19.17 $|\vec{L}| = [\ell(\ell + 1)]^{\frac{1}{2}}\hbar = [1(2)]^{\frac{1}{2}}\hbar = \sqrt{2}\hbar = \sqrt{2}(6.626 \times 10^{-34} \text{ J s})/2\pi = 1.491 \times 10^{-34} \text{ J s}.$

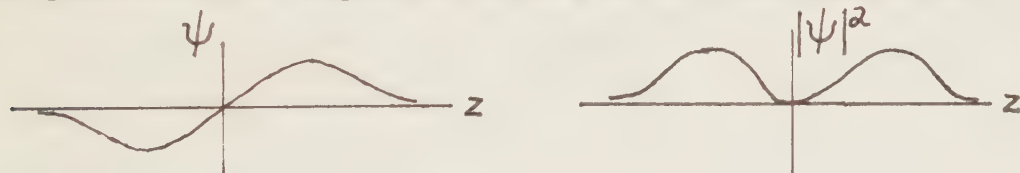
19.18 $e^{i\phi} = 1 + i\phi + (i\phi)^2/2! + (i\phi)^3/3! + (i\phi)^4/4! + (i\phi)^5/5! + \dots = 1 + i\phi - \phi^2/2! - i\phi^3/3! + \phi^4/4! + i\phi^5/5! + \dots$. Also, $\cos \phi + i \sin \phi = (1 - \phi^2/2! + \phi^4/4! - \dots) + i(\phi - \phi^3/3! + \phi^5/5! - \dots) = 1 + i\phi - \phi^2/2! - i\phi^3/3! + \phi^4/4! + i\phi^5/5! + \dots = e^{i\phi}$.

19.19 $2p_x = 2^{-\frac{1}{2}}(2p_1 + 2p_{-1}) = 2^{-\frac{1}{2}}(1/8\pi^{\frac{1}{2}})(Z/a)^{5/2} \times e^{-Zr/2a} r \sin \theta (e^{i\phi} + e^{-i\phi})$. We have $e^{i\phi} + e^{-i\phi} = \cos \phi + i \sin \phi + \cos (-\phi) + i \sin (-\phi) = \cos \phi + i \sin \phi + \cos \phi - i \sin \phi = 2 \cos \phi$, so $2p_x = (2^{\frac{1}{2}}/2^3 \pi^{\frac{1}{2}})(Z/a)^{5/2} e^{-Zr/2a} r \sin \theta \cos \phi = \pi^{-\frac{1}{2}}(Z/2a)^{5/2} x e^{-Zr/2a}$, where Eq. (19.9) was used. Also, $2p_y = (2p_1 - 2p_{-1})/i\sqrt{2} = (2^{-\frac{1}{2}}/i)(1/8\pi^{\frac{1}{2}})(Z/a)^{5/2} \times e^{-Zr/2a} r \sin \theta (e^{i\phi} - e^{-i\phi})$. We have $e^{i\phi} - e^{-i\phi} = \cos \phi + i \sin \phi - (\cos \phi - i \sin \phi) = 2i \sin \phi$, so $2p_y =$

$$(2^{\frac{1}{2}}/2^3\pi^{\frac{1}{2}})(Z/a)^{5/2}e^{-Zr/2a} r \sin \theta \sin \phi = \pi^{-\frac{1}{2}}(Z/2a)^{5/2}y e^{-Zr/2a}.$$

19.20 (a) $a_1 + ib_1 = a_2 + ib_2$. We must have $a_1 = a_2$ and $b_1 = b_2$. (b) $(2\pi)^{-\frac{1}{2}}e^{im\phi} = (2\pi)^{-\frac{1}{2}}e^{im(\phi+2\pi)} = (2\pi)^{-\frac{1}{2}}e^{im\phi}e^{2\pi mi}$, so $1 = e^{2\pi mi} = \cos(2\pi m) + i \sin(2\pi m)$, where (19.23) was used. Equating the real parts and the imaginary parts of this last equation [as shown in part (a)], we have $\cos(2\pi m) = 1$ and $\sin(2\pi m) = 0$. The cosine function equals 1 only for angles of 0, $\pm 2\pi$, $\pm 4\pi$, $\pm 6\pi$, ... and the sine vanishes at these angles. Therefore $2\pi m = 0, \pm 2\pi, \pm 4\pi, \dots$ and $m = 0, \pm 1, \pm 2, \dots$.

19.21 ψ_{2p_z} has the form bze^{-dr} ; b and d are constants. Along the z axis, $x = 0 = y$ and $r = (x^2 + y^2 + z^2)^{\frac{1}{2}} = (z^2)^{\frac{1}{2}} = |z|$. Thus $\psi_{2p_z} = bze^{-d|z|}$ along the z axis. Near $z = 0$, $e^{-d|z|} \approx 1$ and $\psi_{2p_z} \approx bz$ (a straight line through the origin). For large values of $|z|$, the exponential causes ψ to fall to zero. Also, $|\psi_{2p_z}|^2 = |b|^2 z^2 e^{-2d|z|}$ along the z axis. $|\psi|^2$ is parabolic near the origin and is positive for negative values of z . The graphs are:



19.22 $0.9 = \int_0^{r_{1s}} \int_0^\pi \int_0^{2\pi} |\psi_{1s}|^2 r^2 \sin \theta \, dr \, d\theta \, d\phi = (1/\pi a^3) \int_0^{r_{1s}} \int_0^\pi \int_0^{2\pi} e^{-2r/a} r^2 \sin \theta \, dr \, d\theta \, d\phi$, where we set

Z equal to 1. A table of integrals gives $\int e^{br} r^2 dr = e^{br} (r^2/b - 2r/b^2 + 2/b^3)$, so $\int_0^{r_{1s}} e^{-2r/a} r^2 dr = e^{-2r_{1s}/a} (\frac{1}{2} a r_{1s}^2 + \frac{1}{2} a^2 r_{1s} + \frac{1}{4} a^3) + \frac{1}{4} a^3$. Also, $\int_0^\pi \sin \theta d\theta = -\cos \theta \big|_0^\pi = 2$ and $\int_0^{2\pi} d\phi = 2\pi$. So $0.9 = e^{-2r_{1s}/a} (2r_{1s}^2/a^2 + 2r_{1s}/a + 1) + 1$. Let $w = r_{1s}/a$. We want to solve $e^{-2w} (2w^2 + 2w + 1) = 0.1$. For $w = 0, 1, 2, 3$, the left side of this equation equals 1, 0.6767, 0.2381,

0.0620. The root thus lies between 2 and 3. Further trial and error gives $w = 2.66$. So $r_{1s} = 2.66a = 2.66(0.5295 \text{ \AA}) = 1.41 \text{ \AA}$. (b) $0.9 = (1/32\pi a^3) \int_0^{r_{2s}} (2 - r/a)^2 r^2 e^{-r/a} dr \times \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi = e^{-r_{2s}/a} [-r_{2s}^2/2a^2 - r_{2s}/a - 1 - r_{2s}^4/8a^4] + 1$, where a table of integrals was used. Let $v \equiv r_{2s}/a$. We must solve $e^{-v} (4v^2 + 8v + 8 + v^4) = 0.8$. Trial and error gives $v = 9.125$ and $r_{2s} = 9.125a = 4.83 \text{ \AA}$.

19.23 (a) We have: $\langle r \rangle = \int \psi_{2p_z}^* r \psi_{2p_z} d\tau = (Z^5/32\pi a^5) \int_0^\infty \int_0^\pi \int_0^{2\pi} r e^{-Zr/2a} \cos \theta r e^{-Zr/2a} \cos \theta \times r^2 \sin \theta dr d\theta d\phi = (Z^5/32\pi a^5) \int_0^\infty r^5 e^{-Zr/a} dr \int_0^\pi \cos^2 \theta \sin \theta d\theta \int_0^{2\pi} d\phi$. A table of definite integrals gives $\int_0^\infty r^n e^{-br} dr = n!/b^{n+1}$ for $b > 0$ and n a positive integer. So $\int_0^\infty r^5 e^{-Zr/a} dr = 5! a^6/Z^6$. Let $t = \cos \theta$; then $dt = -\sin \theta d\theta$ and $\int_0^\pi \cos^2 \theta \sin \theta d\theta = -\int_1^{-1} t^2 dt = 2/3$. So $\langle r \rangle = (Z^5/32\pi a^5)(120a^6/Z^6)(2/3)(2\pi) = 5a/Z$. (b) The $2p_z$ and $2p_x$ orbitals have the same shape and the same size and differ only in spatial orientation. Since r does

not depend on spatial orientation, $\langle r \rangle$ must be the same for the $2p_x$ and $2p_z$ states. (c) $\langle r \rangle_{2p_x} = \int \psi_{2p_x}^* r \psi_{2p_x} d\tau = (Z^5/32\pi a^5) \int_0^\infty r^5 e^{-Zr/a} dr \int_0^{2\pi} \cos^2 \phi d\phi \int_0^\pi \sin^3 \theta d\theta$. The r integral was found in (a). A table of integrals gives $\int \cos^2 \phi d\phi = \frac{1}{2}\phi + \frac{1}{4}\sin 2\phi$ and $\int \sin^3 \theta d\theta = -\frac{2}{3}\cos \theta - \frac{1}{3}\cos \theta \sin^2 \theta$ and we find $\langle r \rangle_{2p_x} = (Z^5/32\pi a^5)(120a^6/Z^6) \times (\pi)(4/3) = 5a/Z$.

19.24 Equations (19.26) and (19.21) give the ground-state H-atom radial distribution function as $R_{1s}^2 r^2 = 4(Z/a)^3 r^2 e^{-2Zr/a}$. The maximum is found by setting the derivative equal to zero: $0 = 4(Z/a)^3 [2re^{-2Zr/a} - (2Zr^2/a)e^{-2Zr/a}]$ and $r = a/Z$. (The root $r=0$ is a minimum.)

19.25 Let $c = 2.00 \text{ \AA}$. To find the desired probability, we integrate $\psi^* \psi d\tau$ over the volume of a sphere of radius c . The angles go over their full ranges and r goes from 0 to c . Table 19.1 and Eq. (19.25) give the probability as $(1/\pi a^3) \int_0^c \int_0^\pi \int_0^{2\pi} e^{-2r/a} r^2 \sin \theta dr d\theta d\phi = (1/\pi a^3) \int_0^c r^2 e^{-2r/a} dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi$. The radial integral has the same form as the radial integral in Prob.

19.22 except that r_{1s} is replaced by c . Therefore, $\int_0^c r^2 e^{-2r/a} dr = -e^{-2c/a} (\frac{1}{2}ac^2 + \frac{1}{2}a^2c + \frac{1}{4}a^3) + \frac{1}{4}a^3$. The θ and ϕ integrals are given in Prob. 19.22, and the desired probability is $-e^{-2c/a} (2c^2/a^2 + 2c/a + 1) + 1$. We have $c/a = (2.00 \text{ \AA})/(0.5295 \text{ \AA}) = 3.777$, and the probability is $1 - e^{-2(3.777)} [2(3.777)^2 + 2(3.777) + 1] = 0.981$.

$$\underline{19.26} \quad \int_0^{2\pi} |\Phi|^2 d\phi = \int_0^{2\pi} \Phi^* \Phi d\phi = \\ (1/2\pi) \int_0^{2\pi} e^{-im\phi} e^{im\phi} d\phi = (1/2\pi) \int_0^{2\pi} d\phi = 1.$$

$$\underline{19.27} \quad \partial e^{-Zr/a}/\partial x = (\partial e^{-Zr/a}/\partial r)(\partial r/\partial x). \text{ We have } r = \\ (x^2 + y^2 + z^2)^{1/2} \text{ and } \partial r/\partial x = \frac{1}{2}(x^2 + y^2 + z^2)^{-1/2}(2x) = x/r.$$

$$\text{So } \partial e^{-Zr/a}/\partial x = -(Zx/ra)e^{-Zr/a}. \quad \partial^2 e^{-Zr/a}/\partial x^2 =$$

$$(\partial/\partial x)(-Zxe^{-Zr/a}/ra) = -Ze^{-Zr/a}/ra -$$

$$x[(\partial/\partial r)(Ze^{-Zr/a}/ra)](\partial r/\partial x) = -Ze^{-Zr/a}/ra +$$

$$(x^2 Z^2/r^2 a^2)e^{-Zr/a} + (Zx^2/ar^3)e^{-Zr/a}. \text{ Similar equations}$$

$$\text{hold for } \partial^2/\partial y^2 \text{ and } \partial^2/\partial z^2 \text{ of } e^{-Zr/a}. \text{ Then}$$

$$(\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2)e^{-Zr/a} = -3Ze^{-Zr/a}/ra +$$

$$[(x^2 + y^2 + z^2)Z^2/r^2 a^2]e^{-Zr/a} + [Z(x^2 + y^2 + z^2)/ar^3]e^{-Zr/a}$$

$$= -3Ze^{-Zr/a}/ra + (Z^2/a^2)e^{-Zr/a} + (Z/ra)e^{-Zr/a} =$$

$$-2Ze^{-Zr/a}/ra + (Z^2/a^2)e^{-Zr/a} = -2\mu e'^2 Ze^{-Zr/a}/r\hbar^2 +$$

$$(Z^2/a^2)e^{-Zr/a}, \text{ where (19.16) was used. The Hamiltonian op-}$$

$$\text{erator is (19.8); we have } \hat{H}\psi_{1s} =$$

$$-(\hbar^2/2\mu)(\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2)[\pi^{-1/2}(Z/a)^{3/2}e^{-Zr/a}] -$$

$$(Ze'^2/r)[\pi^{-1/2}(Z/a)^{3/2}e^{-Zr/a}] = -(Ze'^2/r)\pi^{-1/2}(Z/a)^{3/2}e^{-Zr/a}$$

$$- \pi^{-1/2}(Z/a)^{3/2}(\hbar^2/2\mu)[-2\mu e'^2 Ze^{-Zr/a}/r\hbar^2 + (Z^2/a^2)e^{-Zr/a}] =$$

$$-(\hbar^2 Z^2/2\mu a^2)\pi^{-1/2}(Z/a)^{3/2}e^{-Zr/a} =$$

$$-(Z^2 e'^2/2a)[\pi^{-1/2}(Z/a)^{3/2}e^{-Zr/a}] = E_{1s}\psi_{1s}.$$

$$\underline{19.28} \quad \langle v \rangle = \langle -Ze'^2/r \rangle = -Ze'^2 \int \psi_{1s}^* r^{-1} \psi_{1s} d\tau =$$

$$-(Z^4 e'^2/a^3 \pi) \int_0^\infty \int_0^\pi \int_0^{2\pi} e^{-Zr/a} r^{-1} e^{-Zr/a} r^2 \sin \theta dr d\theta d\phi$$

$$= -(Z^4 e'^2/a^3 \pi) \int_0^\infty r e^{-2Zr/a} dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi. \text{ Using}$$

$$\text{either the definite integral } \int_0^\infty r^n e^{-br} dr = n!/b^{n+1} \text{ or the}$$

indefinite integral $\int r e^{-br} dr = -e^{-br}(r/b + 1/b^2)$, we get $\int_0^\infty r e^{-2Zr/a} dr = a^2/4Z^2$. Then $\langle V \rangle = -(Z^4 e'^2/a^3 \pi)(a^2/4Z^2)2(2\pi) = -Z^2 e'^2/a$ for the ground state.

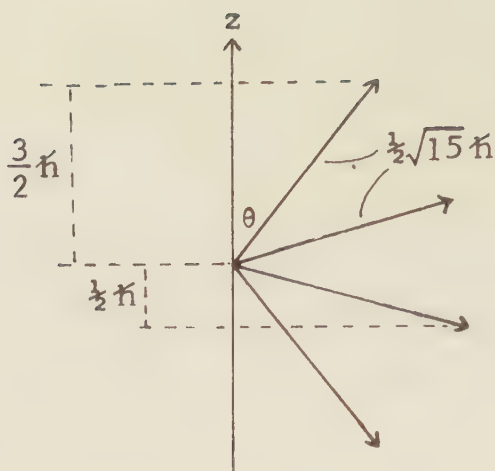
19.29 Let θ be the angle between the z axis and a spin vector. For $m_s = +\frac{1}{2}$, we have $\cos \theta = \frac{1}{2}\hbar/\sqrt{3/4}\hbar = 1/\sqrt{3} = 0.57735$ and $\theta = 54.7^\circ$. For $m_s = -\frac{1}{2}$, $\theta = 180^\circ - 54.7^\circ = 125.3^\circ$.

19.30 (a) Electronic orbital angular momentum; $|\vec{L}| = [l(l+1)]^{\frac{1}{2}}\hbar$. (b) z component of electronic orbital angular momentum; $L_z = m\hbar$. (c) Electronic spin angular momentum; $|\vec{S}| = [s(s+1)]^{\frac{1}{2}}\hbar$. (d) z component of electronic spin angular momentum; $S_z = m_s\hbar$.

19.31 (a) Neither, since $f(2)g(1) \neq \pm f(1)g(2)$. (b) Symmetric, since $g(2)g(1) = g(1)g(2)$. (c) Antisymmetric, since $-f(2)g(1) - g(2)f(1) = -[f(1)g(2) - g(1)f(2)]$. (d) Symmetric. (e) Antisymmetric.

19.32 The true ground-state energy of He is -79.0 eV (see p. 634 in the text). The variational value -86.7 eV is less than the true E_{gs} ; this violates the variation theorem (18.76), so there must be an error in the calculation.

19.33 (a) For $s = 3/2$, Eq. (19.27) gives $m_s = 3/2, 1/2, -1/2$, and $-3/2$. The possible z components of the spin are $m_s\hbar$. The length of the spin vector is $\sqrt{s(s+1)}\hbar = \frac{1}{2}\sqrt{15}\hbar$. The possible orientations are



$$\begin{aligned}
 \text{(b) } \cos \theta &= \\
 1.5\hbar / \frac{1}{2}\sqrt{15}\hbar &= \\
 0.7746 \text{ and} \\
 \theta &= 39.2^\circ.
 \end{aligned}$$

19.34 There is one electron, so $S = s = \frac{1}{2}$ and $2S + 1 = 2$; also, $L = l$. (a) 2S . (b) 2P . (c) 2D .

19.35 $2S + 1 = 4$, so $S = 3/2$. The code letter F means $L = 3$.

19.36 (a) Total electronic orbital angular momentum; $|\vec{L}| = [L(L + 1)]^{1/2}\hbar$. (b) Total electronic spin angular momentum; $|\vec{S}| = [S(S + 1)]^{1/2}\hbar$. (c) z component of total electronic spin angular momentum; $S_z = M_S\hbar$.

19.37 Let the electrons be numbered 1, 2, and 3. The nuclear charge is $3e'$. As was done with He in Eq. (19.28), we use the electron mass m in the Hamiltonian. Then $\hat{H} = -(\hbar^2/2m)\nabla_1^2 - (\hbar^2/2m)\nabla_2^2 - (\hbar^2/2m)\nabla_3^2 - 3e'^2/r_1 - 3e'^2/r_2 - 3e'^2/r_3 + e'^2/r_{12} + e'^2/r_{13} + e'^2/r_{23}$, where r_1 is the distance between electron 1 and the nucleus.

19.38 Let f and g denote the $n = 1$ and $n = 2$ spatial functions, i.e., $f = (2/a)^{1/2} \sin(\pi x/a)$ and $g =$

$(2/a)^{\frac{1}{2}} \sin(2\pi x/a)$. With interelectronic repulsion ignored, the spatial wave function is a product of one-electron spatial functions. Analogous to Eqs. (19.37) and (19.38), we form the linear combinations $2^{-\frac{1}{2}}[f(1)g(2) + f(2)g(1)]$ and $2^{-\frac{1}{2}}[f(1)g(2) - f(2)g(1)]$ that don't distinguish between the electrons. To satisfy the Pauli principle, the symmetric spatial function must be combined with the anti-symmetric two-electron spin function (19.33) and the anti-symmetric spatial function must be combined with one of the symmetric spin functions. The approximate wave functions are therefore

$$2^{-\frac{1}{2}}[f(1)g(2) + f(2)g(1)]2^{-\frac{1}{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

$$2^{-\frac{1}{2}}[f(1)g(2) - f(2)g(1)]\alpha(1)\alpha(2)$$

$$2^{-\frac{1}{2}}[f(1)g(2) - f(2)g(1)]\beta(1)\beta(2)$$

$$2^{-\frac{1}{2}}[f(1)g(2) + f(2)g(1)]2^{-\frac{1}{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

The first wave function has $S = 0$. The second, third and fourth have $S = 1$ and have the same energy as one another (since they have the same spatial factor). According to Hund's rule, the $S = 1$ functions lie lower.

19.39 The ground-state configuration is $1s^2 2s^2$. To make the approximate wave function antisymmetric, we use a Slater determinant. Analogous to Eq. (19.45), we have

$$\psi_{gs} \approx N \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) & 2s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) & 2s(2)\beta(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) & 2s(3)\beta(3) \\ 1s(4)\alpha(4) & 1s(4)\beta(4) & 2s(4)\alpha(4) & 2s(4)\beta(4) \end{vmatrix}$$

where N is a normalization constant (equal to $1/\sqrt{24}$).

19.40 H ($1s$), Li ($1s^2 2s$), B ($1s^2 2s^2 2p$), C ($1s^2 2s^2 2p^2$), N ($1s^2 2s^2 2p^3$), O ($1s^2 2s^2 2p^4$), and F ($1s^2 2s^2 2p^5$) all have one or more unpaired electrons and so have $S \neq 0$ and have paramagnetic ground states. He ($1s^2$), Be ($1s^2 2s^2$), and Ne ($1s^2 2s^2 2p^6$) have all electrons paired, have $S = 0$ and $L = 0$ and do not have paramagnetic ground states. (Ne has two $2p$ electrons with $m = +1$, two $2p$ electrons with $m = 0$, and two $2p$ electrons with $m = -1$, and so has total orbital angular-momentum quantum number $L = 0$.)

19.41 We want the energy needed for ${}_{18}\text{Ar}^{17+} \rightarrow \text{Ar}^{18+}$. The ion Ar^{17+} has one electron and so is a hydrogenlike species. From Eq. (19.20) with $n = 1$, the ionization potential is $(18)^2(13.6 \text{ V}) = 4406 \text{ V}$.

19.42 $\epsilon = -(Z_{\text{eff}}^2/n^2)(13.6 \text{ eV})$. (a) In Li, the first ionization potential is for removal of a $2s$ electron, so $5.4 \text{ eV} = (Z_{\text{eff}}^2/2^2)(13.6 \text{ eV})$ and $Z_{\text{eff}} = 1.26$. (b) $9.3 \text{ eV} = (Z_{\text{eff}}^2/2^2)(13.6 \text{ eV})$ and $Z_{\text{eff}} = 1.65$. (The increase over Li is due to the poor screening of one $2s$ electron by the other.)

19.43 (a) If $s = 3/2$, the m_s values are $3/2, 1/2, -1/2, -3/2$. For $s = 3/2$, the electrons are still fermions and the Pauli exclusion principle still holds. The four values of m_s mean that 4 electrons (instead of 2) can go in each orbital. The $1s, 2s$, and $2p$ subshells would therefore hold

4, 4, and 12 electrons (double their capacities for $s = \frac{1}{2}$). The ground-state configurations are $1s^3$, $1s^4 2s^4 2p$, and $1s^4 2s^4 2p^9$. (b) For $s = 1$, the electrons would be bosons and there would be no restriction on the number of electrons in a spin-orbital. The ground-state configurations would therefore be $1s^3$, $1s^9$, and $1s^{17}$.

19.44 (a) The outer electron in K is further from the nucleus, so Na has the higher ionization potential. (b) The ineffective screening of one 4s electron by the other makes Z_{eff} greater in Ca than in K, so Ca has the higher ionization potential. (c) Cl. (d) Kr.

19.45 For $Z = 10$, the figure gives $\sqrt{\epsilon/\epsilon_H} = 8, 2.2$, and 1.6 . Since $\epsilon_H = -13.6$ eV, we get $\epsilon_{1s} \approx -870$ eV, $\epsilon_{2s} \approx -66$ eV, and $\epsilon_{2p} \approx -35$ eV. Substitution in $\epsilon = -(Z_{\text{eff}}^2/n^2)(13.6 \text{ eV})$ gives $Z_{\text{eff},1s} \approx 8$, $Z_{\text{eff},2s} \approx 4.4$, $Z_{\text{eff},2p} \approx 3.2$.

19.46 Nitrogen, with 3 unpaired electrons.

19.47 Ionization energy data on p. 645 show that $\Delta E = 5.1$ eV for $\text{Na} \rightarrow \text{Na}^+ + e^-$, so $E(\text{Na}^+ + e^-) > E(\text{Na})$ and $E(\text{Na}^+ + 2e^-) > E(\text{Na} + e^-)$. Electron affinity data give $\Delta E = -0.5$ eV for $\text{Na} + e^- \rightarrow \text{Na}^-$, so $E(\text{Na}^-) < E(\text{Na} + e^-)$. The lowest-energy (most stable) system is Na^- ; the highest-energy system is $\text{Na}^+ + 2e^-$.

19.48 (a) Sr; (b) F; (c) K; (d) C; (e) Cl^- . Cl^- and Ar are isoelectronic and the higher Z in Ar means a smaller size.

$$19.49 \int_0^{2\pi} \int_0^\pi \int_0^a r^2 \sin \theta \, dr \, d\theta \, d\phi = \int_0^{2\pi} d\phi \int_0^\pi \sin \theta \, d\theta \times \int_0^a r^2 \, dr = 2\pi(2)(a^3/3) = \frac{4}{3}\pi a^3.$$

19.50 (a) E is proportional to $-Z^2$, so $E_H > E_{\text{He}^+}$. (b)

The ionization energy of K^+ . (c) The energy-level spacing for these one-electron species is proportional to Z^2 , so ν is proportional to Z^2 . Thus $\nu_{\text{He}^+} > \nu_H$ and $\lambda_H > \lambda_{\text{He}^+}$.

(d) These quantities are equal.

19.51 (a) Particle in a box; rigid rotor. (b) Harmonic oscillator. (c) Hydrogenlike atom.

$$19.52 \text{ (a) } \nabla_1^2(cf) = (\partial^2/\partial x_1^2 + \partial^2/\partial y_1^2 + \partial^2/\partial z_1^2)(cf) = (\partial^2/\partial x_1^2)(cf) + (\partial^2/\partial y_1^2)(cf) + (\partial^2/\partial z_1^2)(cf) = c(\partial^2 f/\partial x_1^2) + c(\partial^2 f/\partial y_1^2) + c(\partial^2 f/\partial z_1^2) = c(\partial^2/\partial x_1^2 + \partial^2/\partial y_1^2 + \partial^2/\partial z_1^2)f = c\nabla_1^2 f, \text{ where the definition of the sum of operators was used. Similar equations hold for } \nabla_2^2(cf), \text{ etc. Then } \hat{H}(cf) = [-(\hbar^2/2m_1)\nabla_1^2 - \dots - (\hbar^2/2m_n)\nabla_n^2 + V](cf) = -(\hbar^2/2m_1)\nabla_1^2(cf) - \dots - (\hbar^2/2m_n)\nabla_n^2(cf) + Vcf = c[-(\hbar^2/2m_1)\nabla_1^2 f - \dots$$

$$-(\hbar^2/2m_n)\nabla_n^2 f + Vf] = c\hat{H}f, \text{ where the definition of the sum of operators was used. We have } \nabla_1^2(f + g) = (\partial^2/\partial x_1^2 + \partial^2/\partial y_1^2 + \partial^2/\partial z_1^2)(f + g) = (\partial^2/\partial x_1^2)(f + g) + (\partial^2/\partial y_1^2)(f + g) + (\partial^2/\partial z_1^2)(f + g) = \partial^2 f/\partial x_1^2 + \partial^2 g/\partial x_1^2 + \partial^2 f/\partial y_1^2 + \partial^2 g/\partial y_1^2 + \partial^2 f/\partial z_1^2 + \partial^2 g/\partial z_1^2 = (\partial^2/\partial x_1^2 + \partial^2/\partial y_1^2 + \partial^2/\partial z_1^2)f + (\partial^2/\partial x_1^2 + \partial^2/\partial y_1^2 + \partial^2/\partial z_1^2)g = \nabla_1^2 f + \nabla_1^2 g. \text{ Then } \hat{H}(f + g) = -(\hbar^2/2m_1)\nabla_1^2(f + g) - \dots - (\hbar^2/2m_n)\nabla_n^2(f + g) + V(f + g) = -(\hbar^2/2m_1)\nabla_1^2 f - \dots$$

$$- (\hbar^2/2m_n)\nabla_n^2 f + V_f - (\hbar^2/2m_1)\nabla_1^2 g - \dots - (\hbar^2/2m_n)\nabla_n^2 g + V_g$$

$$= \hat{H}f + \hat{H}g. \quad (\underline{b}) \text{ Let } \psi_a \text{ and } \psi_b \text{ be eigenfunctions of } \hat{H}$$

with the same eigenvalue E_a , that is, $\hat{H}\psi_a = E_a\psi_a$ and

$$\hat{H}\psi_b = E_a\psi_b. \text{ Using the two properties of } \hat{H} \text{ proved in (a),}$$

$$\text{we have } \hat{H}(c_1\psi_a + c_2\psi_b) = \hat{H}(c_1\psi_a) + \hat{H}(c_2\psi_b) = c_1\hat{H}\psi_a +$$

$$c_2\hat{H}\psi_b = c_1E_a\psi_a + c_2E_a\psi_b = E_a(c_1\psi_a + c_2\psi_b), \text{ so } c_1\psi_a +$$

$c_2\psi_b$ is an eigenfunction of \hat{H} with eigenvalue E_a .

$$\underline{19.53} \quad (\underline{a}) \quad d\tau = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(0.0010 \text{ \AA})^3 = 4.19 \times 10^{-9} \text{ \AA}^3.$$

$$|\psi|^2 = (1/\pi a^3)e^{-2r/a} = [\pi(0.5295 \text{ \AA})^3]^{-1} = 2.14 \text{ \AA}^{-3}.$$

$$|\psi|^2 d\tau = 9.0 \times 10^{-9}. \quad (\underline{b}) \quad |\psi|^2 = (1/\pi a^3)e^{-2(0.50 \text{ \AA}/a)} =$$

$$0.324. \quad d\tau = 4.19 \times 10^{-9} \text{ \AA}^3. \quad |\psi|^2 d\tau = 1.4 \times 10^{-9}. \quad (\underline{c})$$

$$|\psi|^2 = 1.35 \times 10^{-8} \text{ and } |\psi|^2 d\tau = 5.7 \times 10^{-17}.$$

$$\underline{19.54} \quad (\underline{a}) \quad d\tau = dx \text{ and } -\infty \leq x \leq \infty. \quad (\underline{b}) \quad d\tau = dx dy dz.$$

x , y , and z each range from $-\infty$ to ∞ , but since $|\psi|^2 = 0$

outside the box, we need integrate over only the region

$$0 \leq x \leq a, \quad 0 \leq y \leq b, \quad 0 \leq z \leq c. \quad (\underline{c}) \quad d\tau = r^2 \sin \theta dr d\theta d\phi.$$

$$0 \leq r \leq \infty, \quad 0 \leq \theta \leq \pi, \quad 0 \leq \phi \leq 2\pi.$$

$$\underline{19.55} \quad \text{Yes. The gravitational force is far smaller than}$$

the electrostatic force and so can be neglected.

$$|F_{\text{grav}}|/|F_{\text{el}}| = (Gm_e m_p/r^2)/(e^2/4\pi\epsilon_0 r^2) = 4\pi\epsilon_0 Gm_e m_p/e^2 =$$

$$4\pi(8.85 \times 10^{-12} \text{ C}^2/\text{N}\cdot\text{m}^2)(6.67 \times 10^{-11} \text{ m}^3/\text{s}^2\cdot\text{kg}) \times$$

$$(9.1 \times 10^{-31} \text{ kg})(1.67 \times 10^{-27} \text{ kg})/(1.6 \times 10^{-19} \text{ C})^2 = 4 \times 10^{-40}.$$

$$\underline{19.56} \quad (\underline{a}) \quad F; \psi_{1s} \neq 0 \text{ at } r=0. \quad (\underline{b}) \quad T. \quad (\underline{c}) \quad F. \quad (\underline{d}) \quad F. \quad (\underline{e}) \quad F. \quad (\underline{f}) \quad F; \text{ this}$$

is true only for identical fermions. $(\underline{g}) \quad F. \quad (\underline{h}) \quad F. \quad (\underline{i}) \quad F. \quad (\underline{j}) \quad F;$

only well-behaved solutions are possible stationary states. $(\underline{k}) \quad T.$

$(\underline{l}) \quad F;$ this is true only if the states have the same energy.

CHAPTER 20

20.1 The table of bond radii on p. 653 in the text gives the following estimates. (a) $0.30 \text{ \AA} + 0.77 \text{ \AA} = 1.07 \text{ \AA}$ for CH, $0.77 \text{ \AA} + 0.66 \text{ \AA} = 1.43 \text{ \AA}$ for CO, and $0.66 \text{ \AA} + 0.30 \text{ \AA} = 0.96 \text{ \AA}$ for OH. (b) $0.30 \text{ \AA} + 0.77 \text{ \AA} = 1.07 \text{ \AA}$ for HC and $0.60 \text{ \AA} + 0.55 \text{ \AA} = 1.15 \text{ \AA}$ for CN.

20.2 Each BF bond has some double-bond character, as shown by the Lewis structure $\text{F}=\text{B} \begin{array}{l} \nearrow \text{F:} \\ \searrow \text{F:} \end{array}$ and two others.

20.3 (a) $\Delta H_{298}^{\circ} \approx \Delta H_{\text{at},298,\text{re}}^{\circ} - \Delta H_{\text{at},298,\text{pr}}^{\circ} = [2(415) + 812 + 2(436)] \text{ kJ/mol} - [344 + 6(415)] \text{ kJ/mol} = -320 \text{ kJ/mol}$. The true value is $[-84.68 - 226.73 - 2(0)] \text{ kJ/mol} = -311.4 \text{ kJ/mol}$. (b) $\Delta H_{298}^{\circ} \approx [946 + 3(436) - 2(3)391] \text{ kJ/mol} = -92 \text{ kJ/mol}$. In truth, $\Delta H_{298}^{\circ} = 2(-46.1) \text{ kJ/mol} = -92.2 \text{ kJ/mol}$.

20.4 We assume tetrahedral angles. As noted in Sec. 20.1, the vector sum of three CH moments in a CH_3 group equals the moment of one CH bond. The H_3CF dipole moment is therefore the sum of the moments $\overset{+}{\text{H}}-\overset{-}{\text{C}}$ and $\overset{+}{\text{C}}-\overset{-}{\text{F}}$. We have $1.85 \text{ D} = 0.4 \text{ D} + p'_{\text{CF}}$ and $p'_{\text{CF}} = 1.45 \text{ D}$. Similarly, $1.62 \text{ D} = 0.4 \text{ D} + p'_{\text{CI}}$ and $p'_{\text{CI}} = 1.2 \text{ D}$.

20.5 (a) The net moment of the CH_3 group equals the CH moment and the dipole moment is the sum of the moments $\overset{+}{\text{H}}-\overset{-}{\text{C}}$ and $\overset{+}{\text{C}}-\overset{-}{\text{Cl}}$. So $p' \approx 0.4 \text{ D} + 1.5 \text{ D} = 1.9 \text{ D}$. (b) $p' \approx$

$0.4 \text{ D} + 1.5 \text{ D} = 1.9 \text{ D}$. (c) $p'_y \approx 0.4 \text{ D} + 1.5 \text{ D} = 1.9 \text{ D}$.

(Here, agreement with experiment is quite poor.) (d)

$$\begin{array}{c}
 \text{Cl} \quad \text{y} \\
 \diagdown \quad | \\
 \text{C} = \text{C} \quad \text{H} \\
 \diagup \quad | \\
 \text{Cl} \quad \text{H}
 \end{array}
 \quad \begin{array}{c}
 \theta \\
 \text{---x}
 \end{array}
 \quad p'_x \approx 2p'_{\text{ClC}} \cos \theta + 2p'_{\text{CH}} \cos \theta =$$

$$2(1.5 \text{ D}) \cos 60^\circ + 2(0.4 \text{ D}) \cos 60^\circ = 1.9 \text{ D}. \quad p'_y = 0.$$

Hence $p' \approx 1.9 \text{ D}$.

20.6 The moments listed on p. 654 of the text give the H_3CCN moment as the sum of the $\text{H}-\text{C}$ and $\text{C}\equiv\text{N}$ bond moments, namely, as $p' = 0.4 \text{ D} + 3.5 \text{ D} = 3.9 \text{ D}$. If we now assume the polarity $\text{H}-\text{C}$, then the H_3C moment is oppositely directed from the CN moment, and we would have $3.9 \text{ D} = -0.4 \text{ D} + p'_{\text{C}\equiv\text{N}}$ and $p'_{\text{C}\equiv\text{N}} = 4.3 \text{ D}$ (instead of 3.5 D).

20.7 (a) $\Delta_{\text{CH}}/(\text{kJ/mol}) = 415 - \frac{1}{2}(344 + 436) = 25$.

$|x_{\text{C}} - x_{\text{H}}| = 0.102(25)^{\frac{1}{2}} = 0.5$ (compared to 0.3 in Table

20.2). (b) $\Delta_{\text{CO}}/(\text{kJ/mol}) = 350 - \frac{1}{2}(344 + 143) = 106\frac{1}{2}$.

$|x_{\text{C}} - x_{\text{O}}| = 0.102(106)^{\frac{1}{2}} = 1.05$ (compared to 0.9 in Table

20.2). (c) $\Delta_{\text{CCl}}/(\text{kJ/mol}) = 328 - \frac{1}{2}(344 + 243) = 34\frac{1}{2}$.

$|x_{\text{C}} - x_{\text{Cl}}| = 0.102(34\frac{1}{2})^{\frac{1}{2}} = 0.6$ (compared with 0.7 in

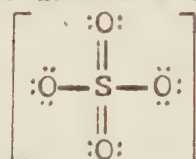
Table 20.2.

20.8 (a) $\text{H}-\ddot{\text{O}}-\overset{\text{:}\ddot{\text{O}}\text{:}}{\underset{\text{:}\ddot{\text{O}}\text{:}}{\text{S}}}-\ddot{\text{O}}-\text{H}$ (b) In the dot formula of (a),

the S has $\frac{1}{2}(8) = 4$ valence electrons, as compared to 6 valence electrons in a free S atom. The formal charge on S is $+2$ for this dot formula. This is an unlikely value for a nonmetallic element. (c) $\text{F}-\overset{\text{:}\ddot{\text{F}}\text{:}}{\underset{\text{:}\ddot{\text{F}}\text{:}}{\text{S}}}-\text{F}$ (d) The SF_6 dot

formula shows that S can share as many as 12 valence electrons. (This is due to the presence of 3d orbitals on S.)

A dot formula for H_2SO_4 that gives S a zero formal charge is $\text{H}-\ddot{\text{O}}-\overset{\text{:O:}}{\parallel}{\text{S}}-\ddot{\text{O}}-\text{H}$. Here S has $\frac{1}{2}(12) = 6$ valence electrons, as in a free S atom. (e) A dot formula for SO_4^{2-} that gives S a zero formal charge is



In addition, there are other resonance structures in which the double bonds and single bonds are permuted. Each sulfur-oxygen bond is intermediate between a single bond and a double bond.

20.9 $\text{:C}\equiv\text{O:}$ The carbon has $2 + \frac{1}{2}(6) = 5$ valence electrons, as compared to 4 in the free C atom. The formal charge on C is -1. (This formal charge opposes the greater electronegativity of O and produces a dipole moment with the polarity $\overset{+}{\text{C}}\overset{-}{\text{O}}$.)

20.10 (a) Because of the electronegativity difference between H and Cl, we expect the H—Cl bond energy to be larger than the average of the H—H and Cl—Cl bond energies, so ΔH° is negative. (b) $\Delta H^\circ < 0$, for reasons similar to those in (a).

20.11 (a) $\text{KF} \xrightarrow{1} \text{K}^+ + \text{F}^- \xrightarrow{2} \text{K} + \text{F}$. According to the model, the energy needed to dissociate KF to $\text{K}^+ + \text{F}^-$ is $\Delta E_1 \approx e'^2/R_e = (4.803 \times 10^{-10} \text{ statC})^2 / (2.17 \times 10^{-8} \text{ cm}) = 1.06_3 \times$

10^{-11} erg = 6.63 eV. The energy change for step 2 is $\Delta E_2 = -4.34 \text{ eV} + 3.40 \text{ eV} = -0.94 \text{ eV}$. The net ΔE is $6.63 \text{ eV} - 0.94 \text{ eV} = 5.69 \text{ eV}$. (b) According to the model, $p' \approx e'R_e = (4.80 \times 10^{-10} \text{ statC})(2.17 \times 10^{-8} \text{ cm}) = 10.4 \text{ D}$. (c) Both compounds are essentially completely ionic with charges of +1 and -1 on the cation and anion. The larger size of Cl^- as compared to F^- makes R_e greater in KCl and gives KCl the greater dipole moment (which is approximately $e'R_e$).

20.12 (a) At R_e , $\partial E_e / \partial R = 0 = -12B/R^{13} + e'^2/R^2$ and $B = e'^2 R_e^{11} / 12$. (b) At equilibrium, the electronic energy is $E_{e,\text{eq}} = B/R_e^{12} - e'^2/R_e = e'^2 R_e^{11} / 12 R_e^{12} - e'^2/R_e = -11e'^2 / 12 R_e = -11(4.803 \times 10^{-10} \text{ statC})^2 / 12(2.36 \times 10^{-8} \text{ cm}) = -8.96 \times 10^{-12} \text{ erg} = -5.59 \text{ eV}$. According to the model, it requires 5.59 eV to dissociate the NaCl molecule to $\text{Na}^+ + \text{Cl}^-$. ΔE for $\text{Na}^+ + \text{Cl}^- \rightarrow \text{Na} + \text{Cl}$ is $-5.14 \text{ eV} + 3.61 \text{ eV} = -1.53 \text{ eV}$ (where data was taken from p. 659 in the text). The model gives D_e of NaCl as $5.59 \text{ eV} - 1.53 \text{ eV} = 4.06 \text{ eV}$. (c) The Pauli repulsion decreases D_e . Since 4.06 eV is less than the true D_e , the function B/R^{12} overestimates the Pauli repulsion. For $E_e = A/R^m - e'^2/R$, we have at R_e , $\partial E_e / \partial R = 0 = -mA/R^{m+1} + e'^2/R^2$ and $A = e'^2 R_e^{m-1} / m$. So $E_{e,\text{eq}} = A/R_e^m - e'^2/R_e = e'^2 R_e^{m-1} / m R_e^m - e'^2/R_e = -(1 - 1/m)e'^2/R_e$. Then $4.25 \text{ eV} = (1 - 1/m)e'^2/R_e - 5.14 \text{ eV} + 3.61 \text{ eV}$. We have $e'^2/R_e = (4.803 \times 10^{-10} \text{ statC})^2 / (2.36 \times 10^{-8} \text{ cm}) = 9.77 \times 10^{-12} \text{ erg} = 6.10 \text{ eV}$, so $1 - 1/m = 0.948$ and $m = 19$.

20.13 The box size is small enough to be considered "infinitesimal." The probability is $|\psi|^2 dV \approx (2 + 2S)^{-1} \times (1s_A + 1s_B)^2 (10^{-6} \text{ \AA}^3)$, where $S = e^{-R/a_0} (1 + R/a_0 + R^2/3a_0^2)$. At the equilibrium separation of $R = 1.06 \text{ \AA} = 2.00 a_0$, we find $S = e^{-2} (1 + 2 + 4/3) = 0.586$ and $(2 + 2S)^{-1} = 0.315$.

(a) At nucleus A, $r_A = 0$ and $r_B = R = 2.00 a_0$, so $1s_A = \pi^{-1/2} (1/a_0)^{3/2} e^0 = 1.466 \text{ \AA}^{-3/2}$ and $1s_B = \pi^{-1/2} (1/a_0)^{3/2} e^{-2.00} = 0.198 \text{ \AA}^{-3/2}$. Then $|\psi|^2 dV \approx 0.315 (1.466 + 0.198)^2 \times \text{ \AA}^{-3} (10^{-6} \text{ \AA}^3) = 8.7 \times 10^{-7}$.

(b) At the midpoint of the internuclear axis, $r_A = r_B = R/2 = 1.00 a_0$, $1s_A = 1s_B = \pi^{-1/2} (1/a_0)^{3/2} e^{-1.00} = 0.539 \text{ \AA}^{-3/2}$ and $|\psi|^2 dV \approx 0.315 \times (0.539 + 0.539)^2 (10^{-6}) = 3.7 \times 10^{-7}$.

(c) $r_A = R/3 = 2a_0/3$, $r_B = 2R/3 = 4a_0/3$, $1s_A = 0.753 \text{ \AA}^{-3/2}$, $1s_B = 0.386 \text{ \AA}^{-3/2}$, $|\psi|^2 dV \approx 4.1 \times 10^{-7}$.

20.14 The MO electron configuration is $(\sigma_g 1s)^2 (\sigma_u^* 1s)^2$. To achieve antisymmetry, we use a Slater determinant. Analogous to Eqs. (19.45) and (20.20) and the Be wave function in Prob. 19.39, we write

$$N \begin{vmatrix} \sigma_g 1s(1)\alpha(1) & \sigma_g 1s(1)\beta(1) & \sigma_u^* 1s(1)\alpha(1) & \sigma_u^* 1s(1)\beta(1) \\ \sigma_g 1s(2)\alpha(2) & \sigma_g 1s(2)\beta(2) & \sigma_u^* 1s(2)\alpha(2) & \sigma_u^* 1s(2)\beta(2) \\ \sigma_g 1s(3)\alpha(3) & \sigma_g 1s(3)\beta(3) & \sigma_u^* 1s(3)\alpha(3) & \sigma_u^* 1s(3)\beta(3) \\ \sigma_g 1s(4)\alpha(4) & \sigma_g 1s(4)\beta(4) & \sigma_u^* 1s(4)\alpha(4) & \sigma_u^* 1s(4)\beta(4) \end{vmatrix}$$

where N is a normalization constant.

20.15 We use the homonuclear diatomic MOs in Fig. 20.8.

(a) $(\sigma_g 1s)^2(\sigma_u^* 1s)$. (b) $(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2$. (c) $(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2$. (d) $(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2 - (\sigma_u^* 2s)^2(\pi_u 2p)^4$. (e) $(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p)^4 - (\sigma_g 2p)^2$. He_2^+ has an unpaired electron and so is paramagnetic. All the others have filled subshells and are not paramagnetic. (f) (e) with $(\pi_g^* 2p)^4$ added.

20.16 (a) $\frac{1}{2}(2 - 1) = \frac{1}{2}$. (b) $\frac{1}{2}(4 - 2) = 1$. (c) $\frac{1}{2}(4 - 4) = 0$. (d) $\frac{1}{2}(8 - 4) = 2$. (e) $\frac{1}{2}(10 - 4) = 3$ (in agreement with the dot formula $:\text{N}\equiv\text{N}:)$. (f) 1.

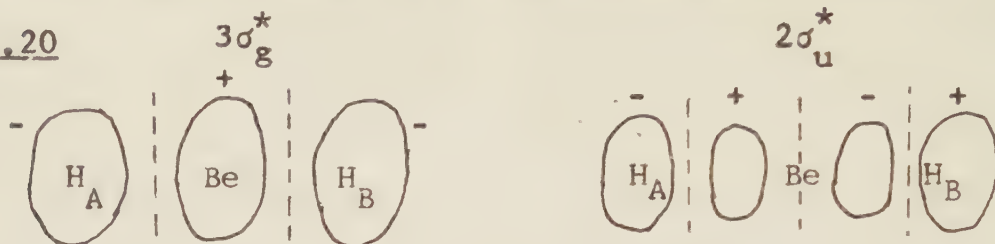
20.17 (a) The N_2 MO configuration is given in Prob. 20.15e. The highest occupied N_2 MO is a bonding MO, so N_2^+ has one less bonding electron than N_2 . Therefore N_2 has the higher D_e . (b) The O_2 MO configuration is shown in Fig. 20.10. The highest-occupied subshell, $\pi_g^* 2p$, is half-filled and is antibonding. Therefore O_2^+ has one fewer antibonding electron than O_2 and has two fewer antibonding electrons than O_2^- , so O_2^+ has the highest D_e .

20.18 $(\hat{H} + c)\psi = \hat{H}\psi + c\psi = E\psi + c\psi = (E + c)\psi$, where the definition of the sum of operators was used.

20.19 (a) We feed the valence electrons into the MOs of Fig. 20.13b where $n = 2$ and $n' = 2$. NCl has $5 + 7 = 12$ valence electrons and has the valence-electron configuration $(\sigma s)^2(\sigma^* s)^2(\pi p)^4(\sigma p)^2(\pi^* p)^2$. NCl^+ and NCl^- have 11 and 13 electrons, respectively, and have the configurations $(\sigma s)^2(\sigma^* s)^2(\pi p)^4(\sigma p)^2(\pi^* p)$ and $(\sigma s)^2(\sigma^* s)^2(\pi p)^4(\sigma p)^2(\pi^* p)^3$,

respectively. (b) $\frac{1}{2}(8 - 4) = 2$ for NCl (which is similar to O_2); $\frac{1}{2}(8 - 3) = 2.5$ for NCl^+ ; $\frac{1}{2}(8 - 5) = 1.5$ for NCl^- . (c) Each of these species has a partly filled π^* subshell, so each has $S \neq 0$ and each is paramagnetic.

20.20



20.21 (a) g , σ . (b) g , δ . (c) g , δ . (d) g , π .

20.22 (a) σ , since it has no nodal planes that contain the internuclear (z) axis. (b) π , since it has one nodal plane containing the internuclear axis. (c) π . (d) σ . (e) σ (see Fig. 19.6). (f) δ , since it has two nodal planes containing the internuclear axis. (g) δ . (h) π . (i) π .

20.23 (a) $\text{H}_\text{A}1s$, $\text{H}_\text{B}1s$, $\text{Cl}s$, $\text{C}2s$, $\text{C}2p_x$, $\text{C}2p_y$, $\text{C}2p_z$, $\text{O}1s$, $\text{O}2s$, $\text{O}2p_x$, $\text{O}2p_y$, $\text{O}2p_z$. (b) The dot formula $\begin{array}{c} \text{H} \\ \diagdown \\ \text{C}=\ddot{\text{O}} \\ \diagup \\ \text{H} \end{array}$ suggests the

following description of the occupied localized MOs. We use sp^2 hybrid AOs on C to form the CH bonds and the σ bond of the double bond. These sp^2 hybrids are formed from $\text{C}2s$ and the in-plane p orbitals $\text{C}2p_y$ and $\text{C}2p_z$. The bonding σ MO between H_A and C is a linear combination of $\text{H}_\text{A}1s$, $\text{C}2s$, $\text{C}2p_y$, and $\text{C}2p_z$. The bonding σ MO between H_B and C is a linear combination of $\text{H}_\text{B}1s$, $\text{C}2s$, $\text{C}2p_y$, and $\text{C}2p_z$. As we did with carbon, we form in-plane sp^2 hybrids on oxygen,

using $O2s$, $O2p_y$, and $O2p_z$; these hybrids go to form the σ bond of the double bond and the lone-pair AOs on oxygen. Overlap between $C2p_x$ and $O2p_x$ forms the π bond of the CO double bond. The σ bond of the CO double bond is formed by overlap of those sp^2 hybrids on C and O that point along the z (CO) axis; the $C2p_y$ and $O2p_y$ AOs do not contribute to these sp^2 hybrids—the $C2p_y$ and $O2p_y$ AOs each have one nodal plane containing the z axis and cannot contribute to the CO σ MO. Therefore the CO localized σ bonding MO is a linear combination of $C2s$, $C2p_z$, $O2s$, and $O2p_z$. The lone-pair localized MOs on O are formed from the $O2s$, $O2p_y$, and $O2p_z$ AOs. There is an inner-shell localized MO on C that is essentially identical to the $C1s$ AO and an inner-shell localized MO on O that is identical to $O1s$.



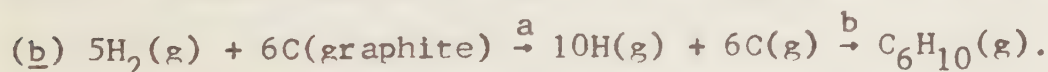
Appendix data give $\Delta H_{a,298}^\circ = [6(217.96) + 6(716.68) - 3(0) - 6(0)] \text{ kJ/mol} = 5607.8 \text{ kJ/mol}$. Viewing C_6H_6 as containing three CC single bonds and three CC double bonds, we use the bond energies on p. 653 in the text to get

$$\Delta H_{b,298}^\circ \approx -[6(415) + 3(344) + 3(615)] \text{ kJ/mol} =$$

$$-5367 \text{ kJ/mol.} \quad \text{Then } \Delta H_{f,298}^\circ = \Delta H_{a,298}^\circ + \Delta H_{b,298}^\circ \approx 241$$

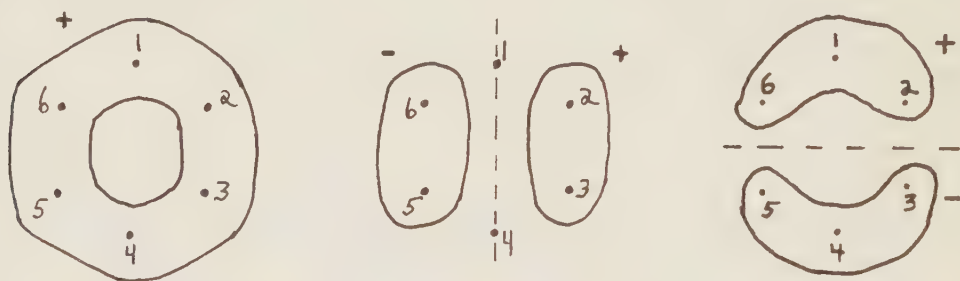
kJ/mol. The Appendix gives the experimental value as

83 kJ/mol, so benzene is far more stable than it would be if it were composed of isolated single and double bonds.



Appendix data give $\Delta H_{a,298}^{\circ} = [10(217.96) + 6(716.68) - 5(0) - 6(0)] \text{ kJ/mol} = 6479.7 \text{ kJ/mol}$. The bond-energy table gives $\Delta H_{b,298}^{\circ} \approx -[10(415) + 5(344) + 615] \text{ kJ/mol} = -6485 \text{ kJ/mol}$. Then $\Delta H_{f,298}^{\circ} = \Delta H_{a,298}^{\circ} + \Delta H_{b,298}^{\circ} \approx -5.3 \text{ kJ/mol}$. The Appendix gives the experimental value as -5.4 kJ/mol .

20.25 (a) The following sketches show a view from above the molecular plane. The dashed lines denote nodal planes perpendicular to the molecular plane. The molecular plane is a nodal plane for each MO. The lobes below the molecular plane have signs opposite those of corresponding lobes above the plane.



(b) The MO $p_1 + p_2 + p_3 + p_4 + p_5 + p_6$ has the fewest nodes and builds up the most electron probability density between the nuclei; this MO is lowest in energy.

20.26 Let $f \equiv (2s + 2p_z)/\sqrt{2}$. Along the z axis we have $x = 0$, $y = 0$, $r = (x^2 + y^2 + z^2)^{1/2} = (z^2)^{1/2} = |z|$ and $f = 2^{-1/2}(\frac{1}{4})(2\pi)^{-1/2}[a^{-3/2}(|z|/a - 2)e^{-|z|/2a} + a^{-5/2}ze^{-|z|/2a}] = (1/8\pi^{1/2}a^{3/2})e^{-|w|/2}(w + |w| - 2)$, where $w \equiv z/a$. We have $1/8\pi^{1/2}a^{3/2} = 0.183 \text{ \AA}^{-3/2}$ and we find

f	-0.050	-0.082	-0.135	-0.222	-0.366	-0.143	0
z/a	-4	-3	-2	-1	0	$\frac{1}{2}$	1
f	0.086	0.135	0.163	0.149	0.120	0.091	0.066
z/a	$1\frac{1}{2}$	2	3	4	5	6	7

The graph shows a sharp negative peak at $z/a = 0$ and a broad positive region for $z/a > 1$.

20.27 (a) The TeBr_2 Lewis dot formula has four electron pairs around Te and two lone pairs on Te. The geometry is bent with bond angle somewhat less than $109\frac{1}{2}^\circ$. (b) Two reasonable dot formulas are $[:\ddot{\text{I}}-\ddot{\text{I}}=\ddot{\text{I}}:]^-$ with "4" pairs on I and $[:\ddot{\text{I}}-\ddot{\text{I}}-\ddot{\text{I}}:]^-$ with five pairs on I. For the first structure, the ion would be bent with angle somewhat less than $109\frac{1}{2}^\circ$. For the second, the ion would be linear (see Fig. 20.26c). (In actuality, I_3^- has bond angle 180° .) (c) Hg has electron configuration $\dots 5d^{10}6s^2$ and has 2 valence electrons. So Hg has two pairs, and HgCl_2 is linear. (d) With 3 pairs on Sn, SnCl_2 is bent with angle a bit less than 120° . (e) With 5 pairs on Xe, XeF_2 is linear. (f) The dot formula $[:\ddot{\text{O}}-\ddot{\text{Cl}}-\ddot{\text{O}}:]^-$ has four pairs on Cl, so the ion is bent with angle somewhat less than $109\frac{1}{2}^\circ$.

20.28 (a) With 5 pairs on Br, BrF_3 is T-shaped (Fig. 20.26b). (b) Three pairs on Ga. Trigonal planar. (c) 4 pairs on O. Pyramidal with angles a bit less than $109\frac{1}{2}^\circ$. (d) Four pairs on P. Pyramidal with angles a bit

less than $109\frac{1}{2}^\circ$.

20.29 (a) 4 pairs on Sn. Tetrahedral. (b) 5 pairs on Se. Seesaw shape. (c) 6 pairs on Xe. Square planar. (d) 4 pairs on B. Tetrahedral. (e) 6 pairs on Br. Square planar.

20.30 (a) 5 pairs on As. Trigonal bipyramidal. (b) 6 pairs on Br. Square-based pyramid (Fig. 20.27). (c) 6 pairs on Sn. Octahedral.

20.31 Each multiple bond is counted as one pair. (a) "3" pairs on O. Bent, with angle close to 120° . (b) "3" pairs on N. Trigonal planar. (c) "3" pairs on S. Trigonal planar. (d) "3" pairs on S. Angle close to 120° . (e) "4" pairs on S. Approximately tetrahedral. (f) "4" pairs on S. Pyramidal with angles close to $109\frac{1}{2}^\circ$. (g) "4" pairs on I. Pyramidal, angles close to $109\frac{1}{2}^\circ$. (h) "5" pairs on S. Trigonal bipyramidal. (i) "4" pairs on Xe. Pyramidal with angles close to $109\frac{1}{2}^\circ$. (j) "6" pairs on Xe. Square-based pyramid.

20.32 There are 2 pi electrons in each double bond, plus the lone pair on N, for a total of $2k + 4$ pi electrons. These fill the lowest $k + 2$ pi MO's and the transition is from $n = k + 2$ to $n = k + 3$. There are $2k + 2$ conjugated bonds and addition of an extra bond length at each end gives a box length of $(2k + 4)(1.40 \text{ \AA}) = a$. Then $\Delta E = (h^2/8ma^2)[(k+3)^2 - (k+2)^2] = (2k+5)(h^2/8ma^2)$. $\Delta E = h\nu = hc/\lambda$ and $\lambda = hc/\Delta E = 8ma^2c/(2k+5)h =$

$$\frac{8m(2k+4)^2(1.40 \text{ \AA})^2c/(2k+5)h}{(2k+4)^2(1.40)^2(10^{-10} \text{ m})^2(3.00 \times 10^8 \text{ m/s})/(2k+5)(6.63 \times 10^{-34} \text{ J s})} = 64.6 \text{ nm } (2k+4)^2/(2k+5).$$

20.33 (a) $\approx 400 \text{ kJ/mol}$; (b) $= \frac{3}{2}RT \approx 4 \text{ kJ/mol}$; (c) $\approx 12 \text{ kJ/mol}$; (d) $\approx 600 \text{ kJ/mol}$; (e) $= 1300 \text{ kJ/mol}$, which corresponds to 13.6 eV/molecule . So (b) < (c) < (a) < (d) < (e).

20.34 (a) T. (b) F. (c) F. (d) F. (e) F. (f) F. (g) T. (h) T.

CHAPTER 21

21.1 $E = (1.00 \text{ eV})(1.602 \times 10^{-19} \text{ J/eV})$

$$= 1.602 \times 10^{-19} \text{ J} = h\nu, \text{ so } \nu = (1.602 \times 10^{-19} \text{ J}) / (6.626 \times 10^{-34} \text{ J s}) = 2.42 \times 10^{14} \text{ s}^{-1}. \quad \lambda = c/\nu = (2.998 \times 10^{10} \text{ cm/s}) / (2.42 \times 10^{14} / \text{s}) = 1.24 \times 10^{-4} \text{ cm}.$$

$$\sigma = 1/\lambda = (1.24 \times 10^{-4} \text{ cm})^{-1} = 8.06 \times 10^3 \text{ cm}^{-1}.$$

21.2 $c_{\text{H}_2\text{O}} = c/n_{\text{H}_2\text{O}} = (2.998 \times 10^{10} \text{ cm/s})/1.33 = 2.25 \times 10^{10} \text{ cm/s}$. The frequency is unchanged in water and $\lambda_{\text{H}_2\text{O}} = c_{\text{H}_2\text{O}}/\nu = c_{\text{H}_2\text{O}}\lambda_{\text{vac}}/c = \lambda_{\text{vac}}/n_{\text{H}_2\text{O}} = (5893 \text{ \AA})/1.33 = 4430 \text{ \AA}$.

$$\nu = \nu_{\text{vac}} = c/\lambda_{\text{vac}} = (2.9979 \times 10^8 \text{ m/s}) / (5893 \times 10^{-10} \text{ m}) = 5.087 \times 10^{14} \text{ Hz}.$$

21.3 Using identities before Eq. (21.6), we get $p_{mn} = (2Q/a)^{1/2} \int_0^a \{x \cos [(m-n)\pi x/a] - x \cos [(m+n)\pi x/a]\} dx$

$$= \frac{Q}{a} \left[\frac{a^2}{(m-n)^2\pi^2} \cos \frac{(m-n)\pi x}{a} + \frac{xa}{(m-n)\pi} \sin \frac{(m-n)\pi x}{a} - \frac{a^2}{(m+n)^2\pi^2} \cos \frac{(m+n)\pi x}{a} - \frac{xa}{(m+n)\pi} \sin \frac{(m+n)\pi x}{a} \right] \Big|_0^a$$

which reduces to Eq. (21.6), since $\sin j\pi = 0$ for j an integer and $\cos 0 = 1$.

21.4 $\nu_{\text{light}} = \Delta E/h = [(\nu_2 + \frac{1}{2})h\nu_{\text{vib}} - (\nu_1 + \frac{1}{2})h\nu_{\text{vib}}]/h = (\nu_2 - \nu_1)\nu_{\text{vib}} = \nu_{\text{vib}}$.

21.5 (a) $\hat{p} = Qx$, since this is a one-particle, one-dimensional system. $Q \int \psi_0^* x \psi_1 dx = Q(\alpha/\pi)^{1/2} (4\alpha^3/\pi)^{1/2} \times$

$\int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = Q \alpha (2/\pi)^{\frac{1}{2}} 2(2!) \pi^{\frac{1}{2}} / 2^3 1! \alpha^{3/2} = Q/(2\alpha)^{\frac{1}{2}}$, where integrals 1 and 3 of Table 15.1 were used. (b) $Q(\alpha/\pi)^{\frac{1}{2}} \times (\alpha/4\pi)^{\frac{1}{2}} \int_{-\infty}^{\infty} (2\alpha x^3 - x) e^{-\alpha x^2} dx = 0$, where integral 4 was used. (c) $Q(\alpha/\pi)^{\frac{1}{2}} (\alpha/9\pi)^{\frac{1}{2}} \int_{-\infty}^{\infty} (2\alpha^{3/2} x^4 - 3\alpha^{\frac{1}{2}} x^2) e^{-\alpha x^2} dx = Q(\alpha/3\pi)^{\frac{1}{2}} [2\alpha^{3/2} 2(4!) \pi^{\frac{1}{2}} / 2^5 2! \alpha^{5/2} - 3\alpha^{\frac{1}{2}} 2(2!) \pi^{\frac{1}{2}} / 2^3 1! \alpha^{3/2}] = 0$. The results (a)-(c) are consistent with $\Delta v = \pm 1$.

21.6 Since E increases as $n^2 + n$, the spacing between levels increases as n increases. Therefore the lowest-frequency absorption is due to the transition from $n = 1$ to $n = 3$. We have $\nu_{\text{lowest}} = 80 \text{ GHz} = \Delta E/h = [b(3)(5) - b(1)(3)]/h = 12b/h$ and $b = (80 \text{ GHz})h/12$. The next-lowest absorption frequency is that from $n = 2$ to $n = 4$ and its frequency is $\nu = \Delta E/h = [4(6)b - 2(4)b]/h = 16b/h = 16(80 \text{ GHz})h(12)^{-1}/h = (16/12)(80 \text{ GHz}) = 107 \text{ GHz}$.

21.7 (a) $\nu = \Delta E/h = (h^2/8ma^2)(n_2^2 - n_1^2)/h = (h/8ma^2) \times (n_2^2 - n_1^2) = (6.626 \times 10^{-34} \text{ J s})(n_2^2 - n_1^2) / 8(9.109 \times 10^{-31} \text{ kg})(2.00 \times 10^{-10} \text{ m})^2 = (2.273 \times 10^{15}/\text{s})(n_2^2 - n_1^2)$. The selection rule is that Δn is odd, so the lowest frequencies result from $n = 1 \rightarrow 2$, $n = 1 \rightarrow 4$, and $n = 1$ to 6. The frequencies are $(2.273 \times 10^{15}/\text{s})(4 - 1) = 6.82 \times 10^{15} \text{ Hz}$, $3.41 \times 10^{16} \text{ Hz}$, and $7.96 \times 10^{16} \text{ Hz}$. (b) The smallest values of $n_2^2 - n_1^2$ with $n_2 - n_1$ odd are for $n = 1 \rightarrow 2$, $n = 2 \rightarrow 3$, and $n = 3 \rightarrow 4$. We get $6.82 \times 10^{15} \text{ Hz}$, $1.14 \times 10^{16} \text{ Hz}$, and $1.59 \times 10^{16} \text{ Hz}$.

21.8 $T = 10^{-A}$. For $A = 0.1$, $T = 10^{-0.1} = 0.79$ and 21% is

absorbed. For $A = 1$, $T = 0.10$ and 90% is absorbed. For $A = 10$, $T = 10^{-10}$ and 99.99999999% is absorbed.

21.9 $c = n/V = P/RT$ and $T = I_{\lambda}/I_{\lambda,0} = 10^{-\epsilon_{\lambda} c_B \ell} = 10^{-\epsilon_{\lambda} P_B \ell / RT}$. (a) $\epsilon_{\lambda} P_B \ell / RT = (10^4 \text{ dm}^3/\text{mol-cm}) \times [(10/760) \text{ atm}](1.0 \text{ cm}) / (0.08206 \text{ dm}^3\text{-atm/mol-K})(298 \text{ K}) = 5.3_8$. $T = 10^{-5.38} = 4.2 \times 10^{-6}$. (b) $T = 10^{-53.8} = 1.6 \times 10^{-54}$.

21.10 $T = I_{\lambda}/I_{\lambda,0} = 10^{-\epsilon_{\lambda} c_B \ell}$. (a) $\epsilon_{\lambda} c_B \ell = (150 \text{ dm}^3/\text{mol-cm})(10^{-3} \text{ mol/dm}^3)(1.0 \text{ cm}) = 0.15$ and $T = 10^{-0.15} = 0.71$. (b) $T = 10^{-1.5} = 0.03_2$.

21.11 $A = \log(I_0/I) = \log(T^{-1}) = \log(1/0.083) = 1.08_1$. $c = (0.080 \text{ g/cm}^3)(1 \text{ mol}/14600 \text{ g})(10^3 \text{ cm}^3/1 \text{ dm}^3) = 0.0055 \text{ mol/dm}^3$. $T = I/I_0 = 10^{-\epsilon c \ell}$ and $\epsilon = -(1/c\ell) \log T = -(0.0055 \text{ mol/dm}^3)^{-1}(0.010 \text{ cm})^{-1} \log 0.083 = 2.0 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.

21.12 $A_2/A_1 = [\log(I_{\lambda,0}/I_{\lambda})_2] / [\log(I_{\lambda,0}/I_{\lambda})_1] = \epsilon_{\lambda} c_{B,2} \ell_2 / \epsilon_{\lambda} c_{B,1} \ell_1 = c_{B,2}/c_{B,1} = 2$. So $\log(I_{\lambda,0}/I_{\lambda})_2 = 2 \log(1/0.60) = 0.444$ and $I_{\lambda,0}/I_{\lambda} = 2.78$. We have $T = 1/2.78 = 0.36$ and 36% of the light is transmitted.

21.13 Let the subscripts 3 and 4 denote $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$, respectively. Use of $A = (\epsilon_3 c_3 + \epsilon_4 c_4) \ell$ and $c_3 + c_4 = 1.00 \times 10^{-3} \text{ mol/dm}^3$ gives $0.701 = [(800 \text{ dm}^3/\text{mol-cm})c_3 + (320 \text{ dm}^3/\text{mol-cm})(0.00100 \text{ mol/dm}^3 - c_3)](1.00 \text{ cm})$. We find $c_3 = 7.94 \times 10^{-4} \text{ mol/dm}^3$. Then $c_3/c_{3,0} = 0.000794/$

0.00100 = 0.794. The % reacted is 20.6%.

21.14 Division of Eq. (21.25) by hc gives $D_0/hc = D_e/hc - \frac{1}{2}\tilde{\nu}_e + \frac{1}{4}\tilde{\nu}_e x_e$. (a) $D_0/hc = [79890 - \frac{1}{2}(2359) + \frac{1}{4}(14)] \text{ cm}^{-1} = 78714 \text{ cm}^{-1}$; $D_0 = (78714 \text{ cm}^{-1})(6.6261 \times 10^{-27} \text{ erg s}) \times (2.9979 \times 10^{10} \text{ cm/s}) = 1.5636 \times 10^{-11} \text{ erg} = 9.759 \text{ eV}$. (b) $D_0/hc = [90544 - \frac{1}{2}(2170) + \frac{1}{4}(13)] \text{ cm}^{-1} = 89462 \text{ cm}^{-1}$; $D_0 = 1.7771 \times 10^{-11} \text{ erg} = 11.092 \text{ eV}$.

21.15 (a) D_e is the depth of the electronic energy curve E_e and k_e equals $E_e''(R_e)$. In the Born-Oppenheimer approximation, $E_e(R)$ is found by solving the electronic Schrödinger equation (20.8) in which the nuclei are fixed; the nuclear masses do not occur in (20.8) and (20.7). Hence, $E_e(R)$ is the same for ${}^2\text{H}^{35}\text{Cl}$ and ${}^1\text{H}^{35}\text{Cl}$, which have the same nuclear charges. From Eq. (21.25), D_0 differs from D_e by the zero-point vibrational energy. The vibrational frequency ν_e equals $(1/2\pi)(k/\mu)^{1/2}$. The reduced mass μ differs substantially for ${}^2\text{H}^{35}\text{Cl}$ and ${}^1\text{H}^{35}\text{Cl}$, so their ν_e 's differ and their D_0 's differ. (b) For ${}^1\text{H}^{35}\text{Cl}$, $D_0/hc = D_e/hc - \frac{1}{2}\tilde{\nu}_e + \frac{1}{4}\tilde{\nu}_e x_e = [37240 - \frac{1}{2}(2990.9) + \frac{1}{4}(52.8)] \text{ cm}^{-1} = 35758 \text{ cm}^{-1}$; $D_0 = 7.103_1 \times 10^{-12} \text{ erg} = 4.433_4 \text{ eV}$. From Eqs. (21.23) and (18.69) and Table 21.2: $\nu_{e,\text{DCl}}/\nu_{e,\text{HCl}} = (\mu_{\text{HCl}}/\mu_{\text{DCl}})^{1/2}$; $\mu_{\text{HCl}} = 1.00782(34.969)(\text{g/mol})/35.977N_A = (0.97959 \text{ g/mol})/N_A$; $\mu_{\text{DCl}} = (1.9044 \text{ g/mol})/N_A$. So $\tilde{\nu}_{e,\text{DCl}} = (2990.9 \text{ cm}^{-1})(0.97959/1.9044)^{1/2} = 2145.1 \text{ cm}^{-1}$. Also, $D_{e,\text{DCl}} = D_{e,\text{HCl}}$. For ${}^2\text{H}^{35}\text{Cl}$ we then have $D_0/hc = [37240 - \frac{1}{2}(2145)]$

$+ \frac{1}{2}(53)] \text{ cm}^{-1} = 36181 \text{ cm}^{-1}$ and $D_0 = 7.187 \times 10^{-12} \text{ erg} = 4.486 \text{ eV}$ (where we neglected the change in $v_e x_e$).

21.16 $\frac{1}{2}h\nu_e = \frac{1}{2}kA^2$. But $v_e = (1/2\pi)(k/\mu)^{\frac{1}{2}}$, so $k = 4\pi^2\mu\nu_e^2$; $\frac{1}{2}h\nu_e = 2\pi^2\mu\nu_e^2 A^2$ and $A = (h/4\pi^2\mu\nu_e)^{\frac{1}{2}}$. For H^{35}Cl , $\mu = (1.0)(35.0)\text{g}/(36.0)(6.02 \times 10^{23}) = 1.6 \times 10^{-24} \text{ g}$ and $\nu_e = (2.998 \times 10^{10} \text{ cm/s})(2991 \text{ cm}^{-1}) = 9.0 \times 10^{13} \text{ s}^{-1}$, so $A = [(6.63 \times 10^{-34} \text{ J s})/4\pi^2(1.6 \times 10^{-27} \text{ kg})(9.0 \times 10^{13}/\text{s})]^{\frac{1}{2}} = 1.1 \times 10^{-11} \text{ m} = 0.11 \text{ \AA}$. For $^{14}\text{N}_2$, $\mu = 14(14)\text{g}/28N_A = 1.16 \times 10^{-23} \text{ g}$, $\nu_e = 7.1 \times 10^{13} \text{ s}^{-1}$ and $A = 0.045 \text{ \AA}$.

21.17 From Eqs. (21.31), (21.33), and (21.15): $\nu_{J \rightarrow J+1} = 2(J+1)B_0 = 2B_0 = 2h/8\pi^2 I_0 = h/4\pi^2 \mu R_0^2$ and $R_0 = (h/\mu\nu)^{\frac{1}{2}}/2\pi$.

(a) Use of Table 21.2 of atomic masses gives $\mu = m_1 m_2 / (m_1 + m_2) = (1.0078250)(78.91834)\text{g}/(79.92616_5)(6.02214 \times 10^{23}) = 1.652431 \times 10^{-24} \text{ g}$ for $^1\text{H}^{79}\text{Br}$ and $\mu = 1.652945 \times 10^{-24} \text{ g}$ for $^1\text{H}^{81}\text{Br}$. For $^1\text{H}^{79}\text{Br}$, $R_0 = (1/2\pi) \times [(6.62608 \times 10^{-34} \text{ J s})/(1.652431 \times 10^{-27} \text{ kg})(500.7216 \times 10^9/\text{s})]^{\frac{1}{2}} = 1.424258 \text{ \AA}$. For $^1\text{H}^{81}\text{Br}$, we get $R_0 = 1.424258 \text{ \AA}$. (b) For $J = 1$ to 2 , $\nu = 2(J+1)B_0 = 4B_0 = 2\nu_{J=0 \rightarrow 1} = 2(500.7216 \text{ GHz}) = 1001.4432 \text{ GHz}$ with centrifugal distortion neglected.

(c) For the $J = 0$ to 1 transition, $\nu_{\text{DBr}}/\nu_{\text{HBr}} = 2B_{0,\text{DBr}}/2B_{0,\text{HBr}} = \mu_{\text{HBr}}/\mu_{\text{DBr}}$, since R_0 is essentially unchanged on isotopic substitution. $\mu_{\text{DBr}} = (2.014102)(78.91834)\text{g}/(80.93244_2)(6.02214 \times 10^{23}) = 3.261264 \times 10^{-24} \text{ g}$.

$\mu_{\text{HBr}}/\mu_{\text{DBr}} = 1.652431/3.261264 = 0.506684$ and $\nu_{\text{DBr}} = 0.506684(500.7216 \text{ GHz}) = 253.708 \text{ Hz}$.

21.18 From Eq. (21.31), $\nu_{J \rightarrow J+1} = 2B_0(J+1)$, so $B_0(^{39}\text{K}^{37}\text{Cl}) = (22410 \text{ MHz})/2(3) = 3735 \text{ MHz}$. (a) $\nu = 2(3735 \text{ MHz})_1 = 7470 \text{ MHz}$. (b) The reasoning in Prob. 21.15a shows that R_e for the two isotopic species is the same; further, R_0 should differ only very slightly for the two species (see, for example, Prob. 21.17). Equations (21.33) and (21.15) then give $B_0(^{39}\text{K}^{35}\text{Cl})/B_0(^{39}\text{K}^{37}\text{Cl}) = I_0(^{39}\text{K}^{37}\text{Cl})/I_0(^{39}\text{K}^{35}\text{Cl}) = \mu(^{39}\text{K}^{37}\text{Cl})/\mu(^{39}\text{K}^{35}\text{Cl}) = 18.9693/18.4292 = 1.02931$, where the reduced masses were found from $m_A m_B / (m_A + m_B)$ and Table 21.2. Then $B_0(^{39}\text{K}^{35}\text{Cl}) = 1.02931(3735 \text{ MHz}) = 3844\frac{1}{2} \text{ MHz}$ and $\nu_{J=0 \rightarrow 1} = 2(3844\frac{1}{2} \text{ MHz}) = 7689 \text{ MHz}$ for $^{39}\text{K}^{35}\text{Cl}$.

21.19 The equation preceding (21.37) is $\sigma = \sigma_{\text{origin}} + \tilde{B}_e J'(J' + 1) - \tilde{B}_e J''(J'' + 1)$. For P branch lines, $J' = J'' - 1$ and $J'(J' + 1) - J''(J'' + 1) = (J'' - 1)J'' - J''(J'' + 1) = -2J''$, so $\sigma_P = \sigma_{\text{origin}} - 2\tilde{B}_e J''$.

21.20 Eq. (21.39) multiplied out gives $\sigma_R = \sigma_{\text{origin}} + 2\tilde{B}_e(J'' + 1) - \tilde{\alpha}_e v'(J''^2 + 3J'' + 2) + \tilde{\alpha}_e v''(J''^2 + J'') - \tilde{\alpha}_e(J'' + 1)$. With centrifugal distortion neglected, Eq. (21.26) gives $\sigma_R = (E_{J''+1, v'} - E_{J'', v''})/hc = \tilde{\nu}_e(v' + \frac{1}{2}) - \tilde{\nu}_e x_e(v' + \frac{1}{2})^2 + \tilde{B}_e(J'' + 1)(J'' + 2) - \tilde{\alpha}_e(v' + \frac{1}{2})(J'' + 1)(J'' + 2) - \tilde{\nu}_e(v'' + \frac{1}{2}) + \tilde{\nu}_e x_e(v'' + \frac{1}{2})^2 - \tilde{B}_e J''(J'' + 1) + \tilde{\alpha}_e(v'' + \frac{1}{2})J''(J'' + 1) = \tilde{\nu}_e(v' - v'') - \tilde{\nu}_e x_e(v'^2 + v' - v''^2 - v'') + \tilde{B}_e(2J'' + 2) + \tilde{\alpha}_e v''(J''^2 + J'') - \tilde{\alpha}_e v'(J''^2 + 3J'' + 2) - \tilde{\alpha}_e(J'' + 1)$, which Eq. (21.34) shows to be the same as the above multiplied-out form of Eq.

(21.39), verifying (21.39). When multiplied out, (21.40) is $\sigma_P = \sigma_{\text{origin}} - 2B_e J'' + \tilde{\alpha}_e v'(J'' - J''^2) + \tilde{\alpha}_e v''(J'' + J''^2) + \tilde{\alpha}_e J''$. Then $\sigma_P = (E_{J''-1, v'} - E_{J'', v''})/hc$ and use of (21.26) leads to the multiplied-out form of (21.40).

21.21 $v_e = (1/2\pi)(k_e/\mu)^{1/2}$ and $k_e = 4\pi^2 \nu_e^2 \mu = 4\pi^2 c^2 \tilde{\nu}_e^2 \mu = 4\pi^2 (2.998 \times 10^{10} \text{ cm/s})^2 (1580 \text{ cm}^{-1})^2 (15.99491) \text{ g} / 2(6.0221 \times 10^{23}) = 1.176 \times 10^6 \text{ dyn/cm} = 11.76 \text{ mdyn/\AA} = 1176 \text{ N/m}$, where we used $\mu = m_A m_A / (m_A + m_A) = m_A / 2$.

21.22 (a) From Eq. (21.34), $\sigma_{\text{origin}}(0 \rightarrow 1) = \tilde{\nu}_e - 2\tilde{\nu}_e x_e$ and $\sigma_{\text{origin}}(0 \rightarrow 2) = 2\tilde{\nu}_e - 6\tilde{\nu}_e x_e$. Hence $3\sigma_{\text{origin}}(0 \rightarrow 1) - \sigma_{\text{origin}}(0 \rightarrow 2) = \tilde{\nu}_e = 3(2886.0 \text{ cm}^{-1}) - 5668.0 \text{ cm}^{-1} = 2990.0 \text{ cm}^{-1}$. Then $\tilde{\nu}_e x_e = \frac{1}{2}[\tilde{\nu}_e - \sigma_{\text{origin}}(0 \rightarrow 1)] = \frac{1}{2}(2990.0 - 2886.0) \text{ cm}^{-1} = 52.0 \text{ cm}^{-1}$. (b) From (21.34), $\sigma_{\text{origin}}(0 \rightarrow 6) = 6(2990.0 \text{ cm}^{-1}) - 42(52.0 \text{ cm}^{-1}) = 15756 \text{ cm}^{-1}$.

21.23 With centrifugal distortion neglected, the $v = 0$ vibration-rotation levels are given by Eq. (21.26) as

$$E_{\text{vib-rot}} = \frac{1}{2}h\nu_e - \frac{1}{4}h\nu_e x_e + hB_e J(J+1) - \frac{1}{2}h\alpha_e J(J+1).$$

For $J = 0$, $E_{\text{vib-rot}}(0) = \frac{1}{2}h\nu_e - \frac{1}{4}h\nu_e x_e$. We have $E_{\text{vib-rot}}(J) - E_{\text{vib-rot}}(0) = h(B_e - \frac{1}{2}\alpha_e)J(J+1) = (\tilde{B}_e - \frac{1}{2}\tilde{\alpha}_e)hcJ(J+1)$. $(\tilde{B}_e - \frac{1}{2}\tilde{\alpha}_e)hc/kT = [10.594 - \frac{1}{2}(0.31)] \text{ cm}^{-1} \times (6.6261 \times 10^{-27} \text{ erg s})(2.9979 \times 10^{10} \text{ cm/s}) / (1.3807 \times 10^{-16} \text{ erg/K})(300 \text{ K}) = 0.05006_4$. The degeneracy of each level is $2J + 1$, so the Boltzmann distribution law gives the relative populations as $N_J/N_0 = (2J + 1)e^{-\Delta E/kT}$

$$= (2J + 1) \exp [-(\tilde{B}_e - \frac{1}{2}\tilde{\alpha}_e)hcJ(J + 1)/kT] =$$

$(2J + 1)e^{-0.050064J(J + 1)}$. We find (cf. Fig. 21.11):

J	0	1	2	3	4	5	6
N_J/N_0	1	2.714	3.703	3.839	3.307	2.450	1.588

21.24 B_e —rotational constant; α_e —vibration-rotation interaction; D —centrifugal distortion; $v_e x_e$ —anharmonicity.

21.25 (a) From Fig. 20.10 O_2 has 4 more bonding electrons than antibonding electrons, O_2^+ has 5 net bonding electrons, and O_2^- has 3 net bonding electrons. Therefore O_2^+ has the strongest bond and the largest k_e and O_2^- has the smallest k_e . (b) Use of Fig. 20.8 shows that N_2 has 6 net bonding electrons and N_2^+ has 5 net bonding electrons, so N_2 has the stronger bond, the larger k_e and the larger v_e since $v_e = (1/2\pi)(k_e/\mu)^{1/2}$. (c) N_2 has a triple bond and O_2 a double bond. The N_2 bond is stronger and N_2 has the larger k_e . (d) $E_{\text{rot}} = J(J + 1)\hbar^2/2I$, where $I = \mu R_e^2$. An Na atom is heavier and larger than an Li atom, so Na_2 has the larger μ and the larger R_e . So $E_{\text{rot}, J=1}$ is greater for Li_2 .

21.26 (a) A C_2 axis and two symmetry planes. (b) A C_3 axis (through the CCl bond) and three symmetry planes (each one containing C, Cl, and one F). (c) The molecule is square planar. A C_4 axis perpendicular to the molecular plane; an S_4 axis and a C_2 axis, each coincident with the C_4 axis; a symmetry plane coincident with the molecular

plane; four symmetry planes perpendicular to the molecular plane; four C_2 axes in the molecular plane (two pass through pairs of opposite F's and two lie between the F's); a center of symmetry. (d) The structure is trigonal bipyramidal. A C_3 axis; an S_3 axis coincident with the C_3 axis; a (horizontal) plane of symmetry containing the equatorial Cl's; three planes of symmetry that each contain the two axial Cl's; three C_2 axes, each lying in the horizontal symmetry plane. (e) The VSEPR method shows the structure is a square-based pyramid. A C_4 axis and four symmetry planes. (f) A C_6 axis that is also an S_6 axis, an S_3 axis, a C_3 axis, and a C_2 axis; a center of symmetry; seven symmetry planes, six perpendicular to the molecular plane and one coincident with it; six C_2 axes lying in the molecular plane. (g) A C_2 axis perpendicular to the molecular plane; a center of symmetry; two C_2 axes in the molecular plane; three symmetry planes—one coincident with the molecular plane and two perpendicular to it. See Prob. 21.28c. (h) A C_∞ axis through the nuclei and an infinite number of symmetry planes that each contain the C_∞ axis. (i) A C_∞ axis (which is also an S_∞ axis), an infinite number of symmetry planes through this axis, a symmetry plane perpendicular to this axis, a center of symmetry, an infinite number of C_2 axes perpendicular to the molecular axis.

21.27 (a) The symmetry elements (Prob. 21.26a) are a C_2

axis and two symmetry planes, which we call σ_a and σ_b . The symmetry operations are \hat{E} , \hat{C}_2 , $\hat{\sigma}_a$, $\hat{\sigma}_b$. (b) \hat{E} , \hat{C}_3 , \hat{C}_3^2 , $\hat{\sigma}_a$, $\hat{\sigma}_b$, $\hat{\sigma}_c$.

21.28 (a) Moves a nucleus at x, y, z to $-x, -y, z$. (b) From x, y, z to $x, y, -z$. (c) The \hat{S}_2 rotation about the z axis consists of a \hat{C}_2 rotation about z followed by reflection in the xy plane. From the answers to (a) and (b) this moves a point at x, y, z to $-x, -y, -z$. We see that $\hat{S}_2 = \hat{i}$.

21.29 (a) The three principal axes intersect at the B nucleus (which is the center of mass). One principal axis is perpendicular to the molecular plane (and coincides with the C_3 axis). The other two principal axes lie in the molecular plane; one of these can be taken to coincide with a BF bond, and the other is perpendicular to this one. (As in XeF_4 , the orientation of the principal axes is not unique.) (b) The three principal axes intersect at the center of mass, which lies on the C_2 axis. One principal axis coincides with the C_2 axis. The second lies in the molecular plane and is perpendicular to the C_2 axis. The third is perpendicular to the molecular plane. (c) The three principal axes intersect at the C nucleus. One principal axis coincides with the molecular axis (which is a C_∞ axis); the other two can be taken as any two axes through the C that are perpendicular to the molecular axis and perpendicular to each other.

21.30 (a) SF_6 has more than one noncoincident C_4 axis and is a spherical top. (b) IF_5 (which is a square-based pyramid) has one C_4 axis and is a symmetric top. (c) One C_2 axis. Asymmetric top. (d) One C_3 axis. Symmetric top.

(e) One C_6 axis. Symmetric top. (f) One C_∞ axis. Symmetric top. (g) One C_3 axis. Symmetric top.

21.31 The molecule is a symmetric top with $I_a \neq I_b = I_c$. From Eq. (21.45), $E_{\text{rot}}/h = BJ(J+1) + (A-B)K^2 = [\tilde{B}J(J+1) + (\tilde{A} - \tilde{B})K^2]c$. (a) For $J=0$, $K=0$ and $E_{\text{rot}}/h = 0$. For $J=1$, $K=-1, 0, 1$. For $J=1$ and $K=0$, $E_{\text{rot}}/h = 2\tilde{B}c = 2(0.05081 \text{ cm}^{-1})(2.9979 \times 10^{10} \text{ cm/s}) = 3.046 \times 10^9 \text{ s}^{-1}$. For $J=1$ and $|K|=1$, $E_{\text{rot}}/h = [2\tilde{B} + (\tilde{A} - \tilde{B})]c = (\tilde{B} + \tilde{A})c = (0.2418 \text{ cm}^{-1})c = 7.249 \times 10^9 \text{ s}^{-1}$. (b) From Eq. (21.47), $\nu = 2B(J+1) = 2\tilde{B}c(J+1) = 2\tilde{B}c, 4\tilde{B}c, \dots = 3.046 \times 10^9 \text{ s}^{-1}, 6.093 \times 10^9 \text{ s}^{-1}, \dots = 3046 \text{ MHz}, 6093 \text{ MHz}$.

21.32 (a) Let the molecule lie on the positive half of the z axis with the origin at the oxygen nucleus. Then $z_{\text{com}} = [12(1.160 \text{ \AA}) + 31.972071(2.720 \text{ \AA})]/59.966986 = 1.682 \text{ \AA}$. (b) $I_0 = \sum_i m_i r_i^2 = [(15.994915)(1.682)^2 + 12(1.682 - 1.160)^2 + 31.972071(2.720 - 1.682)^2](g \text{ \AA})^2 / (6.02214 \times 10^{23}) = 1.377_7 \times 10^{-22} \text{ g \AA}^2 = 1.377_7 \times 10^{-45} \text{ kg m}^2$. (c) $\nu_{J \rightarrow J+1} = 2(J+1)B_0$. $B_0 = h/8\pi^2 I_0 = (6.62608 \times 10^{-34} \text{ J s}) / 8\pi^2 (1.377_7 \times 10^{-45} \text{ kg m}^2) = 6.091_2 \times 10^9 \text{ s}^{-1}$. $\nu_{0 \rightarrow 1} = 2B_0 = 12.18 \text{ GHz}$; $\nu_{1 \rightarrow 2} = 4B_0 = 24.36 \text{ GHz}$; $\nu_{2 \rightarrow 3} = 6B_0 = 36.55 \text{ GHz}$.

21.33 $B_0 = \tilde{B}_0 c = (0.39021 \text{ cm}^{-1})(2.99792 \times 10^{10} \text{ cm/s}) = 1.16982 \times 10^{10} \text{ s}^{-1}$. $I_0 = h/8\pi^2 B_0 = (6.62608 \times 10^{-34} \text{ J s}) / 8\pi^2 (1.16982 \times 10^{10} \text{ s}^{-1}) = 7.1738 \times 10^{-46} \text{ kg m}^2$. The center of mass is at the carbon atom and the principal axes pass

through this atom. If d is the CO bond length, then $I_0 = \sum_i m_i r_i^2 = m_O d^2 + m_O d^2 = 2m_O d^2$, so $d = (I_0/2m_O)^{\frac{1}{2}} = [(7.1738 \times 10^{-46} \text{ kg m}^2)(6.02214 \times 10^{23})/2(15.994915 \times 10^{-3} \text{ kg})]^{\frac{1}{2}} = 1.162 \times 10^{-10} \text{ m} = 1.162 \text{ \AA}$.

21.34 (a) From the VSEPR method, SO_2 is nonlinear; $3\mathcal{N} - 6 = 9 - 6 = 3$. (b) Linear. $3\mathcal{N} - 5 = 7$. (c) $3\mathcal{N} - 6 = 9$.

21.35 We look for sets of integers i, j, k such that $3657i + 1595j + 3756k$ is slightly greater than 7252.

Systematic trial and error (best done by first setting $j = 0$ and looking for i and k values that fit, then setting $j = 1$ and looking for i and k , then setting $j = 2$, etc.) gives the $\nu_1^1 \nu_2^1 \nu_3^1$ possibilities for the 7252 cm^{-1} band as (calculated frequencies in parentheses) 200 (7314), 101 (7413), 002 (7512).

21.36 (a) $\frac{1}{2} \sum_i h\nu_i = \frac{1}{2}hc \sum_i \tilde{\nu}_i = \frac{1}{2}hc(1340 + 667 + 667 + 2349) \text{ cm}^{-1} = 4.99 \times 10^{-13} \text{ erg} = 0.311 \text{ eV}$. (b) $\frac{1}{2}hc(3657 + 1595 + 3756) \text{ cm}^{-1} = 8.95 \times 10^{-13} \text{ erg} = 0.558 \text{ eV}$.

21.37 $\nu = (1/2\pi)\sqrt{k/\mu}$. (a) The $\text{C}\equiv\text{C}$ bond is stronger and has the greater k and the greater ν . (b) $\text{C}-\text{H}$ has the smaller μ and the greater ν . (c) Bending vibrations are generally lower-frequency than stretching, so $\text{C}-\text{H}$ stretching has the greater ν .

21.38 $\tilde{\nu} = \nu/c = (1/2\pi)(k/\mu)^{\frac{1}{2}}/c$. Isotopic substitution does not affect the electrons and hence doesn't affect k .

We have $\mu = m_1 m_2 / (m_1 + m_2) \approx m_1 m_2 / m_2 = m_1$, where $m_1 = m_H$ (or m_D) and m_2 is the mass of the rest of the molecule, and we used $m_2 \gg m_1$. Therefore $\mu_{CD} \approx 2\mu_{CH}$ and $\tilde{\nu}_{CD} \approx \tilde{\nu}_{CH}/2^{\frac{1}{2}} = (2900 \text{ cm}^{-1})/2^{\frac{1}{2}} = 2050 \text{ cm}^{-1}$.

21.39 $\nu = (1/2\pi)(k/\mu)^{\frac{1}{2}}$ and $k = 4\pi^2 \nu^2 \mu = 4\pi^2 \tilde{\nu}^2 c^2 \mu$. We have $\mu_{CH} = 12(1) \text{ g} / 13(6.02 \times 10^{23}) = 1.53 \times 10^{-24} \text{ g}$, and $\mu_{CO} = 12(16) \text{ g} / 28(6.02 \times 10^{23}) = 1.14 \times 10^{-23} \text{ g}$. So $k_{CH} = 4\pi^2 (3000 \text{ cm}^{-1})^2 (3.00 \times 10^{10} \text{ cm/s})^2 (1.53 \times 10^{-24} \text{ g}) = 4.9 \times 10^5 \text{ dyn/cm} = 490 \text{ N/m}$. Also, $k_{CO} = 4\pi^2 (1750 \text{ cm}^{-1})^2 \times (3.00 \times 10^{10} \text{ cm/s})^2 (1.14 \times 10^{-23} \text{ g}) = 1.24 \times 10^6 \text{ dyn/cm} = 1240 \text{ N/m}$.

21.40 (a) The rotational levels of a linear molecule are $E_{\text{rot}} = BhJ(J+1)$ [Eq. (21.45) with $K=0$] and the pure rotational Raman selection rule is $\Delta J = \pm 2$. So $\nu_0 - \nu_{\text{scat}} = \Delta E/h = \pm(Bh/h)[(J+2)(J+3) - J(J+1)] = \pm(4J+6)B$, where $J = 0, 1, 2, \dots$. The spacing between adjacent lines is $[4(J+1) + 6]B - (4J+6)B = 4B$. (b) $4\tilde{B} = 7.99 \text{ cm}^{-1}$ and $\tilde{B} = 1.998 \text{ cm}^{-1} = 199.8 \text{ m}^{-1}$. We have $\tilde{B} = B/c = h/8\pi^2 Ic = h/8\pi^2 c\mu R^2$ and $R = (h/8\pi^2 c\mu\tilde{B})^{\frac{1}{2}}$. Also, $\mu = m_1 m_2 / (m_1 + m_2) = m_1^2 / 2m_1 = m_1/2$ and $R =$

$$\left[\frac{2(6.626 \times 10^{-34} \text{ J s})(6.022 \times 10^{23} \text{ mol}^{-1})}{8\pi^2 (2.998 \times 10^8 \text{ m/s})(0.01401 \text{ kg/mol})(199.8 \text{ m}^{-1})} \right]^{\frac{1}{2}}$$

 $= 1.098 \times 10^{-10} \text{ m} = 1.098 \text{ \AA}$ (as in Table 21.1). (c) The lowest J is 0 and $\nu_0 - \nu_{\text{scat}} = [4(0) + 6]B = 6B$. (d) ν_0

$= c/\lambda_0 = (2.9979 \times 10^8 \text{ m/s}) / (540.8 \times 10^{-9} \text{ m}) = 5.543_5 \times 10^{14} \text{ s}^{-1}$.
 $\nu_0 - \nu_{\text{scat}} = \pm 6B = \pm 6\tilde{B}c = \pm 6(199.8 \text{ m}^{-1}) \times (2.998 \times 10^8 \text{ m/s}) = \pm 0.00359 \times 10^{14} \text{ s}^{-1}$.
 $\nu_{\text{scat}} = 5.543_5 \times 10^{14} \text{ s}^{-1} \pm 0.00359 \times 10^{14} \text{ s}^{-1} = 5.547_1 \times 10^{14} \text{ s}^{-1}$ and $5.539_9 \times 10^{14} \text{ s}^{-1}$. Then $\lambda_{\text{scat}} = c/\nu_{\text{scat}} = 540.4_5 \text{ nm}$ and 541.1_5 nm .

21.41 For the Balmer series, $n_b = 2$ in Eq. (21.50); for the series limit, $n_a = \infty$ and $1/\lambda = R/4 = \frac{1}{4}(109678 \text{ cm}^{-1})$. Then $\lambda = 3.647 \times 10^{-5} \text{ cm} = 364.7 \text{ nm}$.

21.42 For the Paschen series, $n_b = 3$ in Eq. (21.50); the first three lines have $n_a = 4, 5$, and 6 . So $1/\lambda = R(1/9 - 1/16)$, $R(1/9 - 1/25)$, $R(1/9 - 1/36)$. We get $\lambda = 1.8756 \times 10^{-4} \text{ cm}$, $1.2822 \times 10^{-4} \text{ cm}$, $1.0941 \times 10^{-4} \text{ cm}$.

21.43 Li^{2+} is a hydrogenlike atom and Eq. (19.16) gives the energy levels. The Li nucleus is substantially heavier than the H nucleus, so we can take μ equal to the electron mass. So $E = -9(2\pi^2 m_e e^4 / n^2 h^2)$ and $1/\lambda = \nu/c = \Delta E/hc = 9(2\pi^2 m_e e^4 / ch^3)(1/n_b^2 - 1/n_a^2) = 9(109736 \text{ cm}^{-1})(1/1 - 1/4) = 7.4072 \times 10^5 \text{ cm}^{-1}$. Then $\lambda = 1.3500 \times 10^{-6} \text{ cm}$.

21.44 $F = BQv \sin \theta = (1.5 \text{ T})(1.60 \times 10^{-19} \text{ C}) \times (3.0 \times 10^6 \text{ m/s}) \sin \theta = (7.2 \times 10^{-13} \text{ N}) \sin \theta$. (a) $F = 0$. (b) $F = (7.2 \times 10^{-13} \text{ N}) \sin 45^\circ = 5.1 \times 10^{-13} \text{ N}$. (c) $7.2 \times 10^{-13} \text{ N}$. (d) 0 .

21.45 From the top of p. 739 in the text, $\mu = Qvr/2 =$

$$\frac{1}{2}(2.0 \times 10^{-16} \text{ C})(2.0 \times 10^5 \text{ m/s})(25 \times 10^{-10} \text{ m}) = 5.0 \times 10^{-20} \text{ J/T}.$$

21.46 (a) Equations (21.65) and (21.63) give $E = -g_N \beta_N B M_I$
 $= -1.792(5.051 \times 10^{-27} \text{ J/T})(1.50 \text{ T})M_I = -(1.358 \times 10^{-26} \text{ J})M_I.$

Since $I = 3/2$, $M_I = 3/2, 1/2, -1/2$, and $-3/2$. The energies are $-2.04 \times 10^{-26} \text{ J}$, $-0.679 \times 10^{-26} \text{ J}$, $0.679 \times 10^{-26} \text{ J}$, $2.04 \times 10^{-26} \text{ J}$. (b) $15000 \text{ G} = 1.50 \text{ T}$; energies are the same as in (a).

21.47 (a) $\nu = |g_N| \beta_N B/h = 1.792(5.051 \times 10^{-27} \text{ J/T})(1.50 \text{ T})/6.6262 \times 10^{-34} \text{ J s} = 2.049 \times 10^7/\text{s} = 20.49 \text{ MHz}$. (b) 27.32 MHz .

21.48 (a) Equations (21.67) and (21.63) give $B = h\nu/|g_N| \beta_N = (6.626 \times 10^{-34} \text{ J s})(60 \times 10^6 \text{ s}^{-1})/5.5857(5.051 \times 10^{-27} \text{ J/T}) = 1.41 \text{ T}$. (b) $(300/60)(1.41 \text{ T}) = 7.05 \text{ T}$.

21.49 $M_I = +\frac{1}{2}$ and $-\frac{1}{2}$. The energy separation between the levels is given by Eq. (21.65) as $\Delta E = |g_N| \beta_N B = 5.5857 \times (5.051 \times 10^{-27} \text{ J/T})(1.41 \text{ T}) = 3.98 \times 10^{-26} \text{ J}$. The levels are nondegenerate and the population ratio is $e^{-\Delta E/kT} = \exp [-(3.98 \times 10^{-26} \text{ J})/(1.381 \times 10^{-23} \text{ J/K})(298 \text{ K})] = \exp (-0.00000967) = 0.9999903$. (b) An increase in B increases the separation between energy levels, thereby producing a greater population difference between the initial and final states. Hence the absorption intensity increases.

21.50 From (21.72), $\nu_i - \nu_j = 10^{-6}(60 \times 10^6 \text{ Hz})(1.0) = 60 \text{ Hz}$.

21.51 (a) One singlet peak. (b) The CH_3 protons give a doublet of relative intensity 3; the CH proton gives a quartet of relative intensity 1. (c) One singlet. (d) The four methylene protons give a quartet of relative intensity 2; the six methyl protons give a triplet of relative intensity 3. (e) The $(\text{CH}_3)_2$ protons give a doublet of relative intensity 6; the CH proton gives a septet of relative intensity 1. (f) Two equal-intensity singlet peaks. The CH_3 groups are not equivalent and don't split each other. (g) Three quartet peaks of equal intensity. In each of the three quartets, the 4 lines have equal intensity but only two of the 3 spacings are equal.

21.52 All peaks are singlets. (a) One peak. (b) Two peaks of equal intensity. (c) One peak. (d) Two peaks of equal intensity. (e) Two peaks with 2:1 intensity ratio. (f) Three equal-intensity peaks. (g) Two peaks of equal intensity.

21.53 In Fig. 21.37, 100 Hz corresponds to a length of 28 mm and J corresponds to a length of $2\frac{1}{4}$ mm, so $J = (2\frac{1}{4}/28)(100 \text{ Hz}) = 8 \text{ Hz}$.

21.54 (a) Unchanged; see Eq. (21.70) and the following paragraph. (b) Each ν and the difference between the ν 's is multiplied by 10; see Eqs. (21.68) and (21.72). (c) Unchanged, as noted after (21.73).

21.55 From Eq. (21.69), $\sigma_i = 1 - h\nu_{\text{spec}}/|g_i|\beta_N B_{0,i}$. So $\delta_i = 10^6(\sigma_{\text{ref}} - \sigma_i) = 10^6(-h\nu_{\text{spec}}/|g_i|\beta_N)(1/B_{0,\text{ref}} - 1/B_{0,i})$

$$= 10^6 B_0 (B_{0,\text{ref}} - B_{0,i}) / B_{0,\text{ref}} B_{0,i}. \text{ Since } \sigma_i \ll 1, \text{ we have } B_{0,i} \approx h\nu_{\text{spec}} / |g_i| \beta_N = B_0, \text{ and } \delta_i = 10^6 (B_{0,\text{ref}} - B_{0,i}) / B_{0,\text{ref}}.$$

21.56 Substitution of Eq. (21.55) into $B' = B(4\pi/\mu_0)^{\frac{1}{2}}$ followed by use of (21.54) and of $1 \text{ G} = 1 \text{ g}^{\frac{1}{2}} \text{ s}^{-1} \text{ cm}^{-\frac{1}{2}}$ gives $B' = (1 \text{ T})(10^7 \text{ T}^{-1} \text{ m}^{-1} \text{ A})^{\frac{1}{2}} = 10^{7/2} \text{ T}^{\frac{1}{2}} \text{ m}^{-\frac{1}{2}} \text{ A}^{\frac{1}{2}} = 10^{7/2} \text{ kg}^{\frac{1}{2}} \text{ s}^{-\frac{1}{2}} \text{ C}^{-\frac{1}{2}} (10^2 \text{ cm})^{-\frac{1}{2}} (\text{C s}^{-1})^{\frac{1}{2}} = 10^{7/2} 10^{3/2} \text{ g}^{\frac{1}{2}} \text{ s}^{-\frac{1}{2}} \text{ C}^{-\frac{1}{2}} 10^{-1} \text{ cm}^{-\frac{1}{2}} \text{ C}^{\frac{1}{2}} \text{ s}^{-\frac{1}{2}} = 10^4 \text{ g}^{\frac{1}{2}} \text{ s}^{-1} \text{ cm}^{-\frac{1}{2}} = 10^4 \text{ G}.$

21.57 $\nu = g\beta_e B_0/h = 2.0026(9.274 \times 10^{-24} \text{ J/T})(2.50 \text{ T}) / (6.6261 \times 10^{-34} \text{ J s}) = 7.01 \times 10^{10} \text{ s}^{-1} = 70.1 \text{ GHz}.$

21.58 There is one set of 4 equivalent protons and a second set of 4 equivalent protons, so there are $5(5) = 25$ lines.

21.59 $[\alpha] = \alpha / [\rho_B / (\text{g/cm}^3)] (1/\text{dm}) = 1.90^\circ / (0.0650)(2.00) = 14.6^\circ.$

21.60 The observed α of the mixture is the sum of the α 's of the α and β isomers: $\alpha = \alpha_\alpha + \alpha_\beta = [\alpha]_\alpha \rho_\alpha 1(\text{cm}^3/\text{dm g}) + [\alpha]_\beta \rho_\beta 1(\text{cm}^3/\text{dm g})$ (1). The total solute mass m is $m = m_\alpha + m_\beta$ and division by the solution's volume gives $\rho = \rho_\alpha + \rho_\beta$. Division of Eq. (1) by $\rho 1(\text{cm}^3/\text{dm g})$ gives $[\alpha] = [\alpha]_\alpha w_\alpha + [\alpha]_\beta w_\beta$ (2), where $w_\alpha = \rho_\alpha / (\rho_\alpha + \rho_\beta) = m_\alpha / (m_\alpha + m_\beta)$ and w_β are the mass fractions (and also the mole fractions) of the α and β iso-

mers. Equation (2) gives $52.7^\circ = w_\alpha 112.2^\circ + (1 - w_\alpha) 17.5^\circ$ and $w_\alpha = 0.372$, or 37.2% α -D-glucose.

21.61 (a) The photon energy is $h\nu = hc/\lambda = [(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m/s})/(30.4 \times 10^{-9} \text{ m})] \times (1 \text{ eV}/1.602 \times 10^{-19} \text{ J}) = 40.8 \text{ eV}$. Hence the energy used to ionize the molecule is $40.8 \text{ eV} - 31.5 \text{ eV} = 9.3 \text{ eV}$. (b) Replacement of 30.4 nm by 58.4 nm in the calculation in (a) gives a photon energy of 21.2 eV; subtraction of the 9.3 eV ionization energy gives 11.9 eV as the photoelectron energy.

21.62 As discussed in Sec. 21.15, the 17 eV band results from loss of a $\pi_u 2p$ electron. Since this is a bonding electron, the N_2^+ ion produced is more weakly bound than N_2 and has a smaller force constant k and hence has a smaller vibration frequency $\nu = (1/2\pi)(k/\mu)^{1/2}$.

21.63 (a) Two carbon peaks of equal intensity. One oxygen peak. (b) One C peak. One O peak. (c) Three C peaks of equal intensity. Two O peaks of equal intensity. (d) Three C peaks of relative intensities 2:2:1. One O peak.

21.64 $E = h\nu = hc/\lambda$. The first entry in (21.79) is $E = (6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m/s})/(200 \times 10^{-9} \text{ m}) = 9.93 \times 10^{-19} \text{ J} = 6.20 \text{ eV}$; etc. The first entry in the following line is $N_A h\nu = N_A hc/\lambda = (6.022 \times 10^{23}/\text{mole}) \times (6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m/s})/(200 \times 10^{-9} \text{ m}) = 5.98 \times 10^5 \text{ J/mol}$; etc.

21.65 The energy absorbed is $0.744(0.00155 \text{ J/s})(110 \text{ s}) = 0.1269 \text{ J}$. The number of moles of photons absorbed is $(0.1269 \text{ J})/(N_A hc/\lambda) = 4.92 \times 10^{-7} \text{ mole}$. So $\Phi = (6.80 \times 10^{-6} \text{ mole})/(4.92 \times 10^{-7} \text{ mole}) = 13.8$.

21.66 (a) $d[\text{HI}]/dt = -\phi \mathcal{I}_a - k_2[\text{H}][\text{HI}]$. The steady-state approximation for H gives $d[\text{H}]/dt = 0 = \phi \mathcal{I}_a - k_2[\text{H}][\text{HI}]$ and $k_2[\text{H}][\text{HI}] = \phi \mathcal{I}_a$. So $d[\text{HI}]/dt = -2\phi \mathcal{I}_a = -2\mathcal{I}_a$, since $\phi \approx 1$. (b) The number N of photons absorbed satisfies $4184 \text{ J} = Nh\nu = Nhc/\lambda$ and $N = (4184 \text{ J})(250 \times 10^{-9} \text{ m})/(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m/s}) = 5.27 \times 10^{21}$. The number of HI molecules decomposed is $2(5.27 \times 10^{21}) = 1.05 \times 10^{22}$.

21.67 With the inclusion of reaction (5), Eq. (21.84) becomes $r = k_2[\text{A}^*][\text{A}] - k_4[\text{A}_2] + k_5[\text{A}]^2$. Reaction (5) does not involve A^* , so (21.85) still holds and we have $r = k_2[\text{A}]\mathcal{I}_a/(k_2[\text{A}] + k_3) - k_4[\text{A}_2] + k_5[\text{A}]^2$. For the photo-stationary state, $r = 0$ and we get $[\text{A}_2] = k_5[\text{A}]^2/k_4 + k_2[\text{A}]\mathcal{I}_a/(k_4k_2[\text{A}] + k_3k_4)$. In the absence of radiation, $\mathcal{I}_a = 0$ and the last equation becomes $[\text{A}_2] = k_5[\text{A}]^2/k_4$. The concentration of A_2 is greater in the presence of radiation.

21.68 (a) HBr, H_2S , CH_3Cl , which have nonzero dipole moments. (b) HBr, CO_2 , H_2S , CH_4 , CH_3Cl , C_6H_6 , which have vibrations that change the dipole moment. (c) N_2 , HBr, CO_2 , H_2S , CH_3Cl , and C_6H_6 , which are not spherical tops.

21.69 (a) T. (b) F. It cannot change its rotational state by absorption or emission of radiation, but can change its rotational state during collisions. (c) F. Counterexamples are CH_4 and BF_3 . (d) F. The energy might be transferred to another molecule in a collision. (e) F. A counterexample is H_2O . (f) T. (g) F. This formula is only for linear and spherical-top molecules. (h) T. (i) This question is too silly to answer.

22.1 $Z = \sum_j e^{-E_j/kT}$ is dimensionless.

22.2 The Helmholtz energy A is extensive, so A_2 is 25/10 = 2.5 times A_1 . Hence $A_2/A_1 = 2.5 = (-kT \ln Z_2)/(-kT \ln Z_1) = (\ln Z_2)/(\ln Z_1)$.

22.3 $G = A + PV = -kT \ln Z + V kT (\partial \ln Z / \partial V)_{T, N_B} = kTV^2 [\partial (V^{-1} \ln Z) / \partial V]_{T, N_B}$.

22.4 Let a subscript o denote the partition function and thermodynamic properties before the constant b is added to the levels. Then $Z = \sum_j e^{-(E_j+b)/kT} = e^{-b/kT} \sum_j e^{-E_j/kT} = e^{-b/kT} Z_o$ and $\ln Z = -b/kT + \ln Z_o$. (a) $P = kT (\partial \ln Z / \partial V)_{T, N_B} = kT (\partial \ln Z_o / \partial V)_{T, N_B} = P_o$. (b) $U = kT^2 (\partial \ln Z / \partial T)_{V, N_B} = kT^2 [b/kT^2 + (\partial \ln Z_o / \partial T)_{V, N_B}] = b + U_o$. (c) $S = U/T + k \ln Z = b/T + U_o/T - kb/kT + k \ln Z_o = U_o/T + k \ln Z_o = S_o$. (d) $A = -kT \ln Z = -kT(-b/kT + \ln Z_o) = b - kT \ln Z_o = b + A_o$.

22.5 From $p_j = \exp(-\beta E_j)/Z$ [Eq. (22.15)], we have $\ln p_j = -\beta E_j - \ln Z$. So $-\sum_j p_j \ln p_j = \beta \sum_j p_j E_j + \ln Z \sum_j p_j = (kT)^{-1} U + \ln Z = S/k$, where (22.3), (22.33), and $\sum_j p_j = 1$ were used.

22.6 From page 776 of the text, the number of available molecular translational states is approximately $60(mkT/h^2)^{3/2} V = [60(10 \text{ cm}^3)/(6.6 \times 10^{-27} \text{ erg s})^3] \times$

$$\left[(20 \text{ g/mol})(1.38 \times 10^{-16} \text{ erg/K})(300 \text{ K}) / (6.0 \times 10^{23} / \text{mol}) \right]^{3/2} = 3 \times 10^{27}.$$

22.7 (a) Each dot with n_x , n_y , and n_z being positive integers corresponds to a stationary state with quantum numbers n_x , n_y , n_z . The states with $\epsilon_{tr} \leq \epsilon_{\max}$ satisfy Eq. (22.52). The distance of a dot from the origin is $r = (n_x^2 + n_y^2 + n_z^2)^{1/2}$, so the positive square root of (22.52) is $r \leq (8mV^{2/3}h^{-2}\epsilon_{\max})^{1/2}$. The region defined by this inequality is a sphere of radius $r_{\max} = (8mV^{2/3}h^{-2}\epsilon_{\max})^{1/2}$ and the number of dots in 1/8th of this sphere equals the number of quantum states with energy $\epsilon_{tr} \leq \epsilon_{\max}$; we take 1/8th of the sphere because n_x , n_y , and n_z must each be positive, which is true only in 1/8th of the sphere. (b) Fig. 24.7 shows the 4 cubes at the same altitude that share a dot, and 4 more cubes above these 4 also share this dot. The number of translational states with $\epsilon_{tr} \leq \epsilon_{\max}$ is then $\frac{1}{8} \left(\frac{4}{3} \pi r_{\max}^3 \right) = (\pi/6) [(8mV^{2/3}h^{-2} \cdot 3kT)^{1/2}]^3 = (\pi/6) (24mV^{2/3}h^{-2}kT)^{3/2}$.

22.8 $z = \sum_r e^{-\epsilon_r/kT}$ is dimensionless.

22.9 (a) We get 3,628,810. (b) $9.332621569 \times 10^{157}$, where we used $100^{100.5} = (10^2)^{100.5} = 10^{201}$. (c) Using $(10^3)^{1000.5} = 10^{1/2} 10^{3001}$ and $e^{-1000} = (e^{-100})^{10} = (3.72007597601 \times 10^{-44})^{10} = 507595.88975 \times 10^{-440}$, we get $4.0238726006 \times 10^{2567}$.

$$22.10 \quad \ln(300!) = \ln 1 + \ln 2 + \ln 3 + \cdots + \ln 300.$$

A BASIC program is

```

10 S = 0
20 FOR I = 1 TO 300
30 S = S + LOG(I)
40 NEXT I
50 PRINT S
60 END

```

One finds $\ln(300!) = 1414.905850$. Also, $N \ln N - N = 300 \ln 300 - 300 = 1411.134742$.

22.11 From Eqs. (22.51) and (22.56), $\ln Z = N_C \ln z_C - \ln N_C! + N_B \ln z_B - \ln N_B! + \cdots = N_C \ln z_C - \ln N_C! + N_B \ln z_B - N_B \ln N_B + N_B + \cdots$ and $(\partial \ln Z / \partial N_B)_{T,V,N_{C \neq B}} = \ln z_B - \ln N_B - 1 + 1 = \ln(z_B/N_B)$. Substitution in Eq. (22.41) gives $\mu_B = -RT \ln(z_B/N_B)$.

22.12 $\epsilon_x = n_x^2 h^2 / 8ma^2$ and $\Delta \epsilon_x = (h^2 / 8ma^2) [(n_x + 1)^2 - n_x^2] = (h^2 / 8ma^2) (2n_x + 1)$. From $\epsilon_x = n_x^2 h^2 / 8ma^2 = kT$ we get $n_x = a(8mkT)^{1/2} / h = [(2 \text{ cm}) / (6.6 \times 10^{-27} \text{ erg s})] \times [8(28 \text{ g} / 6.0 \times 10^{23}) (1.38 \times 10^{-16} \text{ erg/K}) (273 \text{ K})]^{1/2}$ and $n_x = 1.1 \times 10^9$. Then $\Delta \epsilon_x / kT = (h^2 / 8ma^2) (2n_x + 1) / kT = 1.8 \times 10^{-9}$.

22.13 At room temperature, $kT = (1.38 \times 10^{-23} \text{ J/K}) (298 \text{ K}) \times (1 \text{ eV} / 1.6022 \times 10^{-19} \text{ J}) = 0.026 \text{ eV}$; $kT/hc = (1.38 \times 10^{-16} \text{ erg/K}) (298 \text{ K}) / (6.63 \times 10^{-27} \text{ erg s}) (3 \times 10^{10} \text{ cm/s}) = 207 \text{ cm}^{-1}$; $RT = (1.987 \text{ cal/mol-K}) (298 \text{ K}) = 0.59 \text{ kcal/mol} = 2.5 \text{ kJ/mol}$.

22.14 With anharmonicity neglected, $\langle N_1 \rangle / \langle N_0 \rangle = \frac{e^{-(1+\frac{1}{2})h\nu_0/kT}}{e^{-\frac{1}{2}h\nu_0/kT}} = e^{-h\nu_0/kT}$. (a) $h\nu_0/kT = (6.626 \times 10^{-34} \text{ J s}) (6.98 \times 10^{13} / \text{s}) / (1.381 \times 10^{-23} \text{ J/K}) (298 \text{ K}) = 11.24$ and $\langle N_1 \rangle / \langle N_0 \rangle = e^{-11.24} = 0.000013$. (b) $\langle N_1 \rangle /$

$$\langle N_0 \rangle = e^{-3.121} = 0.044. \quad (\underline{c}) \quad e^{-1.023} = 0.36.$$

22.15 With centrifugal distortion neglected, the rotational levels are $B_0 h J(J+1)$. The degeneracy of each level is $2J+1$, and $\langle N_1 \rangle / \langle N_0 \rangle = 3e^{-2B_0 h/kT} / e^{-0} = 3e^{-2B_0 h/kT}$.
 $2B_0 h/k = 2(5.96 \times 10^{10}/s)(6.626 \times 10^{-34} \text{ J s}) /$
 $(1.381 \times 10^{-23} \text{ J/K}) = 5.72 \text{ K.} \quad (\underline{a}) \quad \langle N_1 \rangle / \langle N_0 \rangle =$
 $3e^{-(5.72 \text{ K})/(200 \text{ K})} = 2.92. \quad (\underline{b}) \quad 3e^{-(5.72 \text{ K})/(600 \text{ K})} =$
 $2.97. \quad (\underline{c}) \quad 3.$

22.16 (a) The vibrational levels are nondegenerate and $\langle N_1 \rangle / \langle N_0 \rangle = e^{-\Delta \epsilon/kT} = e^{-h\nu/kT}$. We have $\langle N_2 \rangle / \langle N_0 \rangle = e^{-2h\nu/kT} = (N_1/N_0)^2$. We find $(0.528)^2 = 0.279$, as is observed. Therefore there is an equilibrium distribution in these levels. (b) $\ln(N_1/N_0) = -h\nu/kT$ and $T = -h\nu / k \ln(N_1/N_0) = -(6.626 \times 10^{-34} \text{ J s})(6.39 \times 10^{12} \text{ s}^{-1}) /$
 $(1.381 \times 10^{-23} \text{ J/K})(\ln 0.528) = 480 \text{ K.} \quad (\underline{c}) \quad N_3/N_0 =$
 $e^{-3h\nu/kT} = (N_1/N_0)^3 = (0.340)^3 = 0.0393$. This is an approximation since anharmonicity has been neglected.

22.17 With the ± 1 neglected, (22.77) becomes $\langle N_r \rangle_{\text{BE}}^{\text{FD}} = e^{-\epsilon_r/kT} / e^{-\mu/RT}$. Use of the Prob. 22.11 result gives $-\mu/RT = \ln(z/N)$, so $e^{-\mu/RT} = e^{\ln(z/N)} = z/N$. Hence $\langle N_r \rangle_{\text{BE}}^{\text{FD}} = e^{-\epsilon_r/kT} N/z$, which is (22.69).

22.18 $\ln Z_{\text{BE}}^{\text{FD}} = -\beta \mu N/N_A + \sum_r (\pm 1) \ln [1 \pm e^{\beta(\mu/N_A - \epsilon_r)}]$, where Eqs. (1.67) and (1.68) were used. Since $1 \gg e^{\beta(\mu/N_A - \epsilon_r)}$, we can use Eq. (8.30) to expand the log and

we need include only the first term in the sum; so $\ln Z_{BE}^{FD} \approx -\beta \mu N/N_A + \sum_r (\pm 1) [\pm e^{\beta(\mu/N_A - \epsilon_r)}] = -\beta \mu N/N_A + \sum_r e^{(\mu/N_A - \epsilon_r)/kT}$. For $\langle N_r \rangle \ll 1$, the ± 1 in (22.77) can be neglected to give $\langle N_r \rangle \approx e^{\mu/N_A kT - \epsilon_r/kT}$. So $\ln Z_{BE}^{FD} \approx -\beta \mu N/N_A + \sum_r \langle N_r \rangle = -\mu N/N_A kT + N$. Use of (22.77) with the ± 1 neglected gives $\sum_r \langle N_r \rangle = N \approx \sum_r e^{\mu/N_A kT - \epsilon_r/kT}$, so $e^{\mu/N_A kT} \approx N / (\sum_r e^{-\epsilon_r/kT})$ and $\mu/N_A kT \approx \ln N - \ln (\sum_r e^{-\epsilon_r/kT})$. Hence $\ln Z_{BE}^{FD} \approx -N \ln N + N \ln \sum_r e^{-\epsilon_r/kT} + N \approx N \ln z - \ln N!$ and $Z_{BE}^{FD} \approx z^N / N!$ for $\langle N_r \rangle \ll 1$.

22.19 We have $\exp(\epsilon_{tr}/kT) = \exp(\frac{1}{2}mv_x^2/kT)\exp(\frac{1}{2}mv_y^2/kT) \times \exp(\frac{1}{2}mv_z^2/kT)$. However, because of the ± 1 term in (22.77), the population $\langle N_r \rangle_{BE}^{FD}$ (which is related to the probability of occupation of state r) is not equal to the product of separate factors for v_x , v_y , and v_z ; hence, v_x , v_y , and v_z are not statistically independent. When $\langle N_r \rangle \ll 1$ does hold, the ± 1 can be neglected and $\langle N_r \rangle$ becomes the product of factors for the three velocity components. Here, the components are statistically independent.

22.20 As explained at the end of the problem, we omit the $1/N!$ from Z . (a) $z = \sum_r e^{-\epsilon_r/kT} = e^{-0} + e^{-a/kT} = 1 + e^{-a/kT}$. $Z = z^N = (1 + e^{-a/kT})^N$. $\ln Z = N \ln (1 + e^{-a/kT})$. $U = kT^2 (\partial \ln Z / \partial T)_{V,N} = kT^2 [N e^{-a/kT} (a/kT^2) / (1 + e^{-a/kT})] = Na / (e^{a/kT} + 1)$. $C_V = (\partial U / \partial T)_V = Na^2 e^{a/kT} / kT^2 (e^{a/kT} + 1)^2$. $S = U/T + k \ln Z = Na/T (e^{a/kT} + 1) + Nk \ln (1 + e^{-a/kT})$. (b) $a/kT = 1.81$ and $z = 1 + e^{-1.81} = 1.163$. $U =$

$(6.0 \times 10^{23})(1.0 \times 10^{-20} \text{ J})/(e^{1.81} + 1) = 844 \text{ J} = 202 \text{ cal.}$
 $S = U/T + Nk \ln z = (844 \text{ J})/(400 \text{ K}) + (6.0 \times 10^{23}) \times (1.38 \times 10^{-23} \text{ J/K}) \ln 1.163 = 3.36 \text{ J/K} = 0.80 \text{ cal/K. (c)}$
 As $T \rightarrow \infty$, we have $e^{a/kT} \rightarrow 1$ and $U \rightarrow \frac{1}{2}Na$. This is because in the $T = \infty$ limit, the populations of the two levels become equal and $U(T = \infty)$ equals the average energy of the levels multiplied by the number of molecules. As $T \rightarrow \infty$, $C_V \rightarrow Na^2/4kT^2 \rightarrow 0$. At very high T , the populations of the two levels have become essentially equal, so we get no further increase in U as T increases further; hence, $C_V = (\partial U/\partial T)_V$ becomes 0. (d) As $T \rightarrow \infty$, $S \rightarrow 0 + Nk \ln 2 = Nk \ln 2$.

22.21 Equations (22.76) and (22.90) give $\langle N_v \rangle/N = e^{-v\Delta\epsilon_v/kT}/z_{\text{vib}} = e^{-0}/z_{\text{vib}} = 1/z_{\text{vib}} = (1 - e^{-h\nu/kT})$. (a)
 $1/z_{\text{vib}} = 1 - e^{-10} = 0.999955$. (b) $1 - e^{-3} = 0.950$. (c)
 $1 - e^{-2} = 0.865$. (d) $1 - e^{-1} = 0.632$. (e) 0.095.

22.22 (a) $\langle N_v \rangle/N = e^{-\epsilon_{\text{vib},v}/kT}/z_{\text{vib}} = e^{-vh\nu/kT}/(1 - e^{-\theta_{\text{vib}}/T})^{-1} = e^{-v\theta_{\text{vib}}/T}(1 - e^{-\theta_{\text{vib}}/T})$, where (22.75), (22.90), and (22.88) were used. (b) For $\theta_{\text{vib}} = 3352 \text{ K}$ and $v = 1$, $\langle N_1 \rangle/N = e^{-(3352 \text{ K})/T}(1 - e^{-(3352 \text{ K})/T})$. We find

T	0	2000	4000	6000	8000	10000	12000	15000
$\langle N_1 \rangle/N$	0	0.152	0.245	0.245	0.225	0.204	0.184	0.160

N_2 is not a harmonic oscillator, so anharmonicity and the finite number of vibrational levels make the high- T values inaccurate.

22.23 $d(\langle N_v \rangle / N) / dT = 0 = (d/dT)(e^{-v\theta_{\text{vib}}/T} - e^{-(v+1)\theta_{\text{vib}}/T})$
 $= (v\theta_{\text{vib}}/T^2)e^{-v\theta_{\text{vib}}/T} - (v+1)(\theta_{\text{vib}}/T^2)e^{-(v+1)\theta_{\text{vib}}/T} = 0$
and $v = (v+1)e^{-\theta_{\text{vib}}/T}$, so $\theta_{\text{vib}}/T = -\ln[v/(v+1)]$ and $T = \theta_{\text{vib}}/\ln[(v+1)/v] = \theta_{\text{vib}}/\ln(1 + 1/v)$. For $\theta_{\text{vib}}/T = -\ln[v/(v+1)]$, we get $\langle N_v \rangle / N = e^{v \ln[v/(v+1)]} - e^{(v+1) \ln[v/(v+1)]} = \exp\{\ln[v/(v+1)]^v\} - \exp\{\ln[v/(v+1)]^{v+1}\} = v^v/(v+1)^v - v^{v+1}/(v+1)^{v+1} = [(v+1)v^v - v^{v+1}]/(v+1)^{v+1} = v^v/(v+1)^{v+1}$.

22.24 Yes. Despite the fact that $\epsilon_r > \epsilon_s$ in Eq. (22.72), N_{ϵ_r} might exceed N_{ϵ_s} if the degeneracy g_r exceeds g_s . (For example, see Prob. 22.15.)

22.25 (a) $z = \sum_{\text{m(levels)}} g_m e^{-\epsilon_m/kT} = 1e^0 + 3e^{-100 \text{ K}/200 \text{ K}} + 5e^{-300 \text{ K}/200 \text{ K}} = 3.935$. (b) Equation (22.71) gives $\langle N(\epsilon_s) \rangle = Ng_s e^{-\epsilon_s/kT} / z$. So $\langle N_1 \rangle = (6.02 \times 10^{23})e^0 / 3.935 = 1.53 \times 10^{23}$; $\langle N_2 \rangle = (6.02 \times 10^{23})3e^{-100 \text{ K}/200 \text{ K}} / 3.935 = 2.78 \times 10^{23}$; $\langle N_3 \rangle = (6.02 \times 10^{23})5e^{-300 \text{ K}/200 \text{ K}} / 3.935 = 1.71 \times 10^{23}$. (c) As $T \rightarrow \infty$, we have $e^{-\epsilon_m/kT} \rightarrow e^{-0} = 1$ and $z \rightarrow 1 + 3 + 5 = 9$. So $\langle N_1 \rangle \rightarrow (6.02 \times 10^{23})/9 = 0.669 \times 10^{23}$, $\langle N_2 \rangle \rightarrow (6.02 \times 10^{23})3/9 = 2.01 \times 10^{23}$, and $\langle N_3 \rangle \rightarrow (6.02 \times 10^{23})5/9 = 3.35 \times 10^{23}$.

22.26 (a) $N! = 1 \cdot 2 \cdot 3 \cdots N$ and $\ln N! = \ln 1 + \ln 2 + \ln 3 + \cdots + \ln N = \sum_{x=1}^N \ln x$. (b) For large N , the main contributions to the sum come from the later terms (where x is reasonably close to N); the later terms don't vary greatly as we go from x to $x + 1$. (For example, $\ln 50 =$

3.912 and $\ln 51 = 3.932$.) So Eq. (22.79) can be used.

$$(\underline{c}) \sum_{x=1}^N \ln x \approx \int_1^N \ln x \, dx = (x \ln x - x) \Big|_1^N =$$

$$N \ln N - N + 1 \approx N \ln N - N.$$

22.27 (a) Let $\theta = \Theta_{\text{rot}}$. Then $\sigma z_{\text{rot}} =$

$$\sum_{J=0}^{\infty} (2J+1) e^{-\theta J(J+1)/T}. \quad J \text{ corresponds to } n, \quad a = 0, \text{ and}$$

$$f(J) = (2J+1) e^{-\theta(J^2+J)/T}. \quad \text{So } f(0) = 1. \text{ Differentiation}$$

$$\text{gives } f'(J) = [2 - \theta(2J+1)^2/T] e^{-\theta(J^2+J)/T}, \text{ so } f'(0) =$$

$$2 - \theta/T. \quad f''(J) = [-6\theta(2J+1)/T + \theta^2(2J+1)^3/T^2] \times$$

$$e^{-\theta(J^2+J)/T}. \quad f'''(J) = [-12\theta/T + 12\theta^2(2J+1)^2/T^2$$

$$- \theta^3(2J+1)^4/T^3] e^{-\theta(J^2+J)/T}. \quad f'''(0) = -12\theta/T + 12\theta^2/T^2 -$$

$$\theta^3/T^3. \quad f^{iv}(J) = [60(2J+1)\theta^2/T^2 - 20(2J+1)^3\theta^3/T^3 +$$

$$(2J+1)^5\theta^4/T^4] e^{-\theta(J^2+J)/T}. \quad f^{(v)}(J) = [120\theta^2/T^2$$

$$- 180(2J+1)^2\theta^3/T^3 + 30(2J+1)^4\theta^4/T^4 - (2J+1)^6\theta^5/T^5] \times$$

$$e^{-\theta(J^2+J)/T}. \quad f^{(v)}(0) = 120\theta^2/T^2 - 180\theta^3/T^3 + 30\theta^4/T^4 -$$

$$\theta^5/T^5. \quad \text{Noting that } \int_0^{\infty} (2J+1) e^{-\theta(J^2+J)/T} dJ =$$

$$\int_0^{\infty} e^{-\theta w/T} dw = T/\theta, \text{ we have } \sigma z_{\text{rot}} = T/\theta + \frac{1}{2} - (2 - \theta/T)/12$$

$$+ (-12\theta/T + 12\theta^2/T^2 - \theta^3/T^3)/720 - (120\theta^2/T^2 - 180\theta^3/T^3 +$$

$$30\theta^4/T^4 - \theta^5/T^5)/30240 + \dots \text{ and } z_{\text{rot}} = (T/\sigma \Theta_{\text{rot}})(1 +$$

$$\Theta_{\text{rot}}/3T + \Theta_{\text{rot}}^2/15T^2 + 4\Theta_{\text{rot}}^3/315T^3 + \dots). \quad (\underline{b}) \quad \Theta_{\text{rot}}/T$$

$$= 85.3/273.15 = 0.3123. \quad \text{Equation (22.85) gives } z_{\text{rot}} \approx$$

$$1/2(0.3123) = 1.601. \quad \text{Equation (22.86) gives } z_{\text{rot}} = 1.601 \times$$

$$[1 + 0.3123/3 + (0.3123)^2/15 + 4(0.3123)^3/315 + \dots] =$$

$$1.779 \text{ and the error is } \sim 10\%. \quad (\underline{c}) \quad \Theta_{\text{rot}}/T = 2.862/$$

$$273.15 = 0.01048. \quad \text{Then } z_{\text{rot}} \approx 1/2(0.01048) = 47.72 \text{ and}$$

$$z_{\text{rot}} = 47.72[1 + 0.01048/3 + (0.01048)^2/15 +$$

$4(0.01048)^3/315] = 47.72(1.0035)$ and the error is -0.35% .

22.28 $U_{\text{rot}} = nRT^2 (d \ln z_{\text{rot}}/dT) = nRT^2 (d/dT) [\ln T - \ln \sigma^{\oplus}_{\text{rot}}] = nRT$. $U_{\text{vib}} = nRT^2 d \ln z_{\text{vib}}/dT = -nRT^2 \times [d \ln (1 - e^{-h\nu/kT})/dT] = -nRT^2 e^{-h\nu/kT} (-h\nu/kT^2)/(1 - e^{-h\nu/kT}) = (nRh\nu/k)/(e^{h\nu/kT} - 1)$. $U_{\text{el}} = nRT^2 \times (d/dT) \ln g_{\text{el},0} = 0$.

22.29 As $T \rightarrow \infty$, the Taylor series for e^x shows that $e^{\oplus_{\text{vib}}/T} \rightarrow 1 + \oplus_{\text{vib}}/T$. Hence, $C_{V,\text{vib}} \rightarrow nR(\oplus_{\text{vib}}/T)^2 e^0 / (\oplus_{\text{vib}}/T)^2 = nR$.

22.30 $S_{\text{tr}} = U_{\text{tr}}/T + Nk \ln z_{\text{tr}} - Nk(\ln N - 1) = \frac{3}{2}nR + Nk[\frac{3}{2} \ln (2\pi mk/h^2) + \frac{3}{2} \ln T + \ln V] - Nk \ln N + nR = \frac{5}{2}nR + nR \ln [(2\pi mk/h^2)^{3/2} T^{3/2} (NkT/P)(1/N)] = \frac{5}{2}nR + nR \ln [(2\pi m)^{3/2} (kT)^{5/2} / h^3 P]$. $S_{\text{rot}} = U_{\text{rot}}/T + Nk \ln z_{\text{rot}} = nR + nR \ln [T/\sigma^{\oplus}_{\text{rot}}]$. $S_{\text{vib}} = U_{\text{vib}}/T + Nk \ln z_{\text{vib}} = nR \oplus_{\text{vib}}/T (e^{\oplus_{\text{vib}}/T} - 1) - nR \ln (1 - e^{-\oplus_{\text{vib}}/T})$. $S_{\text{el}} = U_{\text{el}}/T + Nk \ln z_{\text{el}} = 0 + nR \ln g_{\text{el},0} = nR \ln g_{\text{el},0}$.

22.31 $\bar{S}_{\text{tr}}/R = 2.5 + 2.5 \ln (T/K) - \ln (P/\text{bar}) + 1.5 \ln M_r + \ln [(2\pi \times 10^{-3} \text{ kg/mol})^{3/2} (1.38066 \times 10^{-23} \text{ J/K})^{5/2} K^{5/2} \times (6.02214 \times 10^{23} \text{ /mol})^{-3/2} (6.62608 \times 10^{-34} \text{ J s})^{-3} (10^5 \text{ N/m}^2)^{-1}] = 2.5 + 2.5 \ln (T/K) - \ln (P/\text{bar}) + 1.5 \ln M_r - 3.65169 = 2.5 \ln (T/K) - \ln (P/\text{bar}) + 1.5 \ln M_r - 1.1517$.

22.32 For these gases of closed-shell monatomic molecules, $S = S_{\text{tr}}$. Equation (22.108) gives $\bar{S}^{\circ}_{298}(\text{He}) = (8.3145 \text{ J/mol-K})(1.5 \ln 4.0026 + 2.5 \ln 298.15 - \ln 1 -$

1.1517) = 126.15 J/mol-K. Similarly, $\bar{S}_{298}^{\circ}(\text{Ne}) = 146.33$ J/mol-K, $\bar{S}_{298}^{\circ}(\text{Ar}) = 154.85$ J/mol-K, $\bar{S}_{298}^{\circ}(\text{Kr}) = 164.09$ J/mol-K.

22.33 For H, $g_{\text{el},0} = 2$ and Eqs. (22.107) and (22.108) give $\bar{S} = \bar{S}_{\text{tr}} + \bar{S}_{\text{el}} = (8.3145 \text{ J/mol-K})(1.5 \ln 1.0079 + 2.5 \ln 298.15 - \ln 1 - 1.1517 + \ln 2) = 114.72 \text{ J/mol-K}$.

22.34 Equations (22.94) and (22.95) give $\bar{U}_{298}^{\circ} - \bar{U}_0^{\circ} = \bar{U}_{\text{tr}} = \frac{3}{2}RT = 1.5(8.3145 \text{ J/mol-K})(298.15 \text{ K}) = 3718 \text{ J/mol}$ for each gas.

22.35 $S = (U - U_0)/T + k \ln Z$; $\ln Z = [S - (U - U_0)/T]/k$
 $= [154.8 \text{ J/K} - (3718 \text{ J})/(298.1 \text{ K})](1.3807 \times 10^{-23} \text{ J/K})^{-1}$
 $= 1.03 \times 10^{25} = 2.303 \log Z$. So $\log Z = 4.48 \times 10^{24}$ and $Z = 10^{4.48 \times 10^{24}}$ for 1 mole. $Z = z^N/N!$
and $\ln Z = N \ln z - \ln N! = N \ln z - N \ln N + N$. So $\ln z = (\ln Z + N \ln N - N)/N = (1.03 \times 10^{25})/(6.02 \times 10^{23}) + \ln(6.02 \times 10^{23}) - 1 = 70.9$ and $z = 6 \times 10^{30}$.

22.36 (a) $\tilde{\nu}_0 = \tilde{\nu}_e - 2\tilde{\nu}_e x_e = 2358.6 \text{ cm}^{-1} - 2(14.3 \text{ cm}^{-1}) = 2330.0 \text{ cm}^{-1}$. $\tilde{B}_0 = \tilde{B}_e - \frac{1}{2}\tilde{\alpha}_e = 1.998 \text{ cm}^{-1} - \frac{1}{2}(0.017 \text{ cm}^{-1}) = 1.989_5 \text{ cm}^{-1}$. $hc/k = (6.62608 \times 10^{-34} \text{ J s}) \times (2.99792 \times 10^8 \text{ m/s})/(1.38066 \times 10^{-23} \text{ J/K}) = 0.0143877 \text{ m K} = 1.43877 \text{ cm K}$. $\Theta_{\text{vib}} = \tilde{\nu}_0 hc/k = (2330.0 \text{ cm}^{-1}) \times (1.43877 \text{ cm K}) = 3352.3 \text{ K}$. $\Theta_{\text{rot}} = (1.989_5 \text{ cm}^{-1}) \times (1.43877 \text{ cm K}) = 2.862 \text{ K}$. (b) $z_{\text{tr}} = (2\pi MkT/N_A h^2)^{3/2} V$.
 $V = nRT/P = 12310 \text{ cm}^3$. $z_{\text{tr}} = (12310 \text{ cm}^3) \times$

$$[2\pi(28.0 \text{ g/mol})(1.3807 \times 10^{-16} \text{ erg/K})(300 \text{ K})/$$

$$(6.022 \times 10^{23}/\text{mol})(6.626 \times 10^{-27} \text{ erg s})^2]^{3/2} = 1.78 \times 10^{30}.$$

$$z_{\text{rot}} = T/\sigma\theta_{\text{rot}} = (300 \text{ K})/2(2.862 \text{ K}) = 52.4. \quad z_{\text{vib}} = [1 - e^{-\theta_{\text{vib}}/T}]^{-1} = [1 - e^{-3352/300}]^{-1} = 1.000014. \quad z_{\text{el}} =$$

$$g_{\text{el},0} = 1. \quad (\underline{c}) \quad V = nRT/P = 1.026 \times 10^5 \text{ cm}^3 \text{ and } z_{\text{tr}} = 3.57 \times 10^{32}; \quad z_{\text{rot}} = 437; \quad z_{\text{vib}} = 1.35. \quad z_{\text{el}} = 1.$$

22.37 (a) $\Theta_{\text{vib}} = \tilde{\nu}_0 hc/k = 5696 \text{ K}$ and $\Theta_{\text{vib}}/T = 19.104.$

$$\Theta_{\text{rot}} = \tilde{B}_0 hc/k = 29.58 \text{ K. Equations (22.105)-(22.108) give}$$

$$\text{at } P = 1 \text{ bar: } \bar{S}_{\text{tr}}^\circ = (8.3145 \text{ J/mol-K})(1.5 \ln 20.0063 +$$

$$2.5 \ln 298.15 - 1.1517) = 146.22 \text{ J/mol-K. } \bar{S}_{\text{rot}}^\circ =$$

$$(8.3145 \text{ J/mol-K})\{1 + \ln [(298.15 \text{ K})/(1(29.58 \text{ K}))]\} = 27.53$$

$$\text{J/mol-K. } \bar{S}_{\text{vib}}^\circ = (8.3145 \text{ J/mol-K})[19.104/(e^{19.104} - 1) - \ln(1 - e^{-19.104})] = 8 \times 10^{-7} \text{ J/mol-K. } \bar{S}_{\text{el}}^\circ = 0 \text{ (since}$$

$$\text{all electrons are paired). So } \bar{S}_{298}^\circ = \bar{S}_{\text{tr}}^\circ + \bar{S}_{\text{rot}}^\circ + \bar{S}_{\text{vib}}^\circ +$$

$$\bar{S}_{\text{el}}^\circ = 173.75 \text{ J/mol-K. (b) Equations (22.100)-(22.102)}$$

$$\text{give: } \bar{C}_{V,\text{tr}}^\circ = 1.5(8.3145 \text{ J/mol-K}) = 12.47 \text{ J/mol-K.}$$

$$\bar{C}_{V,\text{rot}}^\circ = 8.3145 \text{ J/mol-K. } \bar{C}_{V,\text{vib}}^\circ = (8.3145 \text{ J/mol-K}) \times (19.104)^2 e^{19.104}/(e^{19.104} - 1)^2 = 1.5 \times 10^{-5} \text{ J/mol-K. So}$$

$$\bar{C}_{V,298}^\circ = 20.79 \text{ J/mol-K. (c) } \bar{C}_P^\circ = \bar{C}_V^\circ + R = 29.10 \text{ J/mol-K.}$$

22.38 $\mu = m^2/2m = m/2 = \frac{1}{2}(126.90 \text{ g})/(6.022 \times 10^{23}) =$

$$1.0536 \times 10^{-22} \text{ g. } I = \mu R^2 = (1.0536 \times 10^{-22} \text{ g}) \times$$

$$(2.67 \times 10^{-8} \text{ cm})^2 = 7.51 \times 10^{-38} \text{ g cm}^2. \quad \Theta_{\text{rot}} = h^2/8\pi^2 Ik$$

$$= 0.0536 \text{ K. } \Theta_{\text{vib}} = h\nu_0/k = 306.9 \text{ K and } \Theta_{\text{vib}}/T = 0.6138.$$

(a) From Eqs. (22.94)-(22.98) at 500 K: $\bar{U}_{\text{tr}}^\circ = (3/2)RT =$

$1.5(8.3145 \text{ J/mol-K})(500 \text{ K}) = 6236 \text{ J/mol}$. $\bar{U}_{\text{rot}}^{\circ} = RT = 4157 \text{ J/mol}$. $\bar{U}_{\text{vib}}^{\circ} = (8.3145 \text{ J/mol-K})(306.9 \text{ K}) / (e^{0.6138} - 1) = 3011 \text{ J/mol}$. $\bar{U}_{\text{el}}^{\circ} = 0$. $\bar{U}_{500}^{\circ} - \bar{U}_0^{\circ} = 13404 \text{ J/mol}$. (b) $\bar{H}_{500}^{\circ} - \bar{U}_0^{\circ} = \bar{U}_{500}^{\circ} + RT - \bar{U}_0^{\circ} = 13404 \text{ J/mol} + (8.3145 \text{ J/mol-K})(500 \text{ K}) = 17561 \text{ J/mol}$. (c) From Eqs. (22.105)-(22.108): $\bar{S}_{\text{tr}}^{\circ} = R(1.5 \ln 253.8 + 2.5 \ln 500 - 1.1517) = 188.65 \text{ J/mol-K}$. $\bar{S}_{\text{rot}}^{\circ} = R\{1 + \ln [500/2(0.0536)]\} = 78.55 \text{ J/mol-K}$. $\bar{S}_{\text{vib}}^{\circ} = R[0.6138/(e^{0.6138} - 1) - \ln(1 - e^{-0.6138})] = 12.50 \text{ J/mol-K}$. $\bar{S}_{\text{el}}^{\circ} = 0$. So $\bar{S}_{500}^{\circ} = 279.70 \text{ J/mol-K}$. (d) $\bar{G}_{500}^{\circ} - \bar{U}_0^{\circ} = \bar{H}_{500}^{\circ} - T\bar{S}_{500}^{\circ} - \bar{U}_0^{\circ} = 17561 \text{ J/mol} - (500 \text{ K}) \times (279.70 \text{ J/mol-K}) = -122.29 \text{ kJ/mol}$.

22.39 From Fig. 21.10 the pure-rotational lines are at $2B_0, 4B_0, 6B_0, \dots$, so the separation is $2\tilde{B}_0 = 20.9 \text{ cm}^{-1}$ and $\tilde{B}_0 = 10.45 \text{ cm}^{-1}$. Also, $\tilde{\nu}_0 = 2885 \text{ cm}^{-1}$. So $\Theta_{\text{rot}}^{\circ} = \tilde{B}_0 hc/k = 15.04 \text{ K}$; $\Theta_{\text{vib}}^{\circ} = \tilde{\nu}_0 hc/k = 4151 \text{ K}$ and $\Theta_{\text{vib}}^{\circ}/T = 13.92$. We shall assume the spectral data are for the predominant species H^{35}Cl and shall calculate \bar{S}_{298}° for H^{35}Cl . At 298.15 K : $\bar{S}_{\text{tr}}^{\circ} = R(1.5 \ln 36.0 + 2.5 \ln 298.1 - \ln 1 - 1.1517) = 153.5 \text{ J/mol-K}$. $\bar{S}_{\text{rot}}^{\circ} = R\{1 + \ln [298.15/1(15.04)]\} = 33.1 \text{ J/mol-K}$. $\bar{S}_{\text{vib}}^{\circ} = R[13.92/(e^{13.92} - 1) - \ln(1 - e^{-13.92})] = 0.00011 \text{ J/mol-K}$. $\bar{S}_{\text{el}}^{\circ} = 0$. So $\bar{S}_{298}^{\circ} = 186.6 \text{ J/mol-K}$.

22.40 (a) For this relatively light diatomic molecule, only translation and rotation contribute to C_V and $\bar{C}_V^{\circ} \approx$

$\frac{3}{2}R + R = 2.5R = 20.79 \text{ J/mol-K}$. $\bar{C}_p^\circ = \bar{C}_V^\circ + R \approx 3.5R = 29.10 \text{ J/mol-K}$. The true value is 29.13 J/mol-K . (b) All gases of relatively light diatomic molecules have $\bar{C}_p^\circ \approx 3.5R = 29.1 \text{ J/mol-K}$.

22.41 $\epsilon_{el,1}/k = (0.0149 \text{ eV})(1.6022 \times 10^{-19} \text{ J/eV}) / (1.38066 \times 10^{-23} \text{ J/K}) = 172.9 \text{ K}$. $z_{el} = g_{el,0} + g_{el,1}e^{-\epsilon_{el,1}/kT} = 2 + 2e^{-(172.9 \text{ K})/T}$. At 30 K , $z_{el} = 2 + 2e^{-172.9/30} = 2.006$. At 150 K , $z_{el} = 2.63$. At 300 K , $z_{el} = 3.12$.

22.42 Using the z_{el} expression found in Prob. 22.41, we have $U_{el} = NkT^2(d \ln z_{el}/dT) = (nRT^2/z_{el})(dz_{el}/dT) = (nRT^2/z_{el})[2(173 \text{ K})T^{-2}e^{-(173 \text{ K})/T}] = nR(346 \text{ K}) \times e^{-(173 \text{ K})/T}/z_{el}$ and $\bar{U}_{el} = (2875 \text{ J/mol})e^{-(173 \text{ K})/T}/[2 + 2e^{-(173 \text{ K})/T}] = (1438 \text{ J/mol})/(e^{(173 \text{ K})/T} + 1)$. $\bar{C}_{V,el} = d\bar{U}_{el}/dT = -(1438 \text{ J/mol})[-(173 \text{ K})/T^2]e^{(173 \text{ K})/T}/(e^{(173 \text{ K})/T} + 1)^2 = (2.49 \times 10^5 \text{ J K/mol})T^{-2}e^{(173 \text{ K})/T}/(e^{(173 \text{ K})/T} + 1)^2$. We find (note the maximum in $\bar{C}_{V,el}$)

$\bar{C}_{V,el}/(\text{J/mol-K})$	0.86	2.52	3.47	3.42	2.67	2.02	1.30	0.88	0.64
T/K	30	45	60	90	120	150	200	250	300

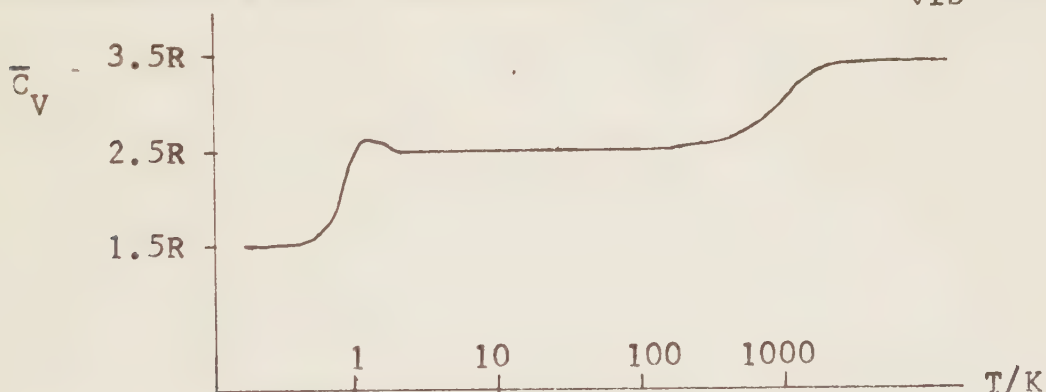
22.43 (a) $s - xs = 1 + x + x^2 + x^3 + \dots - (x + x^2 + x^3 + \dots) = 1$. So $s = 1/(1 - x)$. (b) The Taylor series for $1/(1 - x)$ about $x = 0$ is given by Eq. (8.8) as $1/(1 - x) = 1 + x + x^2 + x^3 + \dots$ for $|x| < 1$.

22.44 (a) $z_{vib} = \sum_v e^{-\epsilon_{vib,v}/kT} = \sum_{v=0}^{\infty} e^{-(v+\frac{1}{2})h\nu/kT} =$

$e^{-\frac{1}{2}h\nu/kT} \sum_{v=0}^{\infty} e^{-vh\nu/kT} = e^{-\frac{1}{2}h\nu/kT} / (1 - e^{-h\nu/kT})$, where Eq. (22.89) was used. (b) $\ln z_{\text{vib}} = -\frac{1}{2}h\nu/kT - \ln(1 - e^{-h\nu/kT})$. $U_{\text{vib}} = nRT^2(\partial \ln z_{\text{vib}}/\partial T)_V = nRT^2[\frac{1}{2}h\nu/kT^2 + e^{-h\nu/kT}(h\nu/kT^2)/(1 - e^{-h\nu/kT})] = \frac{1}{2}N h\nu + nR h\nu/k(e^{h\nu/kT} - 1)$, which differs from Eq. (22.97) by $N(\frac{1}{2}h\nu)$; this agrees with the Prob. 22.4b result.

22.45 From Eq. (22.100), $\bar{C}_{V,\text{tr}} = \frac{3}{2}R$. The translational levels are so closely spaced that this result holds at all temperatures not extremely close to 0 K. From p. 785,

Θ_{rot} is typically of order of magnitude 1 K (except for hydrides). Figure 22.9 shows that $\bar{C}_{V,\text{rot}} = R$ for T above $1.3\Theta_{\text{rot}}$. From p. 786, Θ_{vib} is typically 10^3 K. Figure 22.8 shows that $\bar{C}_{V,\text{vib}}$ is negligible below $0.1\Theta_{\text{vib}}$ and increases to R as T increases to 1 or 2 times Θ_{vib} . So:



22.46 $z_{\text{rot}} = [(298 \text{ K})/1(2.77 \text{ K})][1 + (1/3)(2.77/298) + \dots] = 107.9$. $\epsilon_{\text{rot}} = J(J+1)\hbar^2/2I = J(J+1)k\Theta_{\text{rot}}$, where (22.83) was used. (a) Use of Eq. (22.71) gives

$$[\sum_{J=0}^{16} \langle N_J \rangle]/N = z_{\text{rot}}^{-1} \sum_{J=0}^{16} (2J+1) \exp[-J(J+1)\Theta_{\text{rot}}/T] \approx$$

$$z_{\text{rot}}^{-1} \int_0^{17} (2J+1) \exp[-(J^2 + J)\Theta_{\text{rot}}/T] dJ = z_{\text{rot}}^{-1} \times$$

$$\int_0^{17^2 + 17} \exp[-(\Theta_{\text{rot}}/T)w] dw = z_{\text{rot}}^{-1} (-T/\Theta_{\text{rot}}) \times$$

$$[\exp(-306\Theta_{\text{rot}}/T) - 1] = (107.9)^{-1} (298/2.77) \times$$

$$[1 - e^{-306(2.77/298)}] = 0.93_9, \text{ which is } 94\%; \text{ we took } w \equiv$$

$$J^2 + J \text{ and } dw = 2J + 1; \text{ the sum has 17 terms, so 17 was}$$

used as the upper limit of the integral. (b) The required sum is $(107.9)^{-1} \sum_{J=0}^{16} (2J+1)e^{-(J^2 + J)(2.77/298)}$. Direct evaluation gives $0.932 = 93.2\%$. The individual percentages are 0.927, 2.73, 4.38, 5.80, 6.93, 7.71, 8.15, 8.26, 8.07, 7.63, 7.00, 6.25, 5.44, 4.61, 3.82, 3.09, and 2.44 for $J = 0, 1, 2, \dots, 16$, respectively.

A BASIC program is

```

10 S = 0
20 A = 2.77/298.1
30 FOR J = 0 TO 16
40 B = (2*J + 1)*EXP(-A*(J*J + J))/107.9
50 P = 100*B
60 PRINT "J=";J;" POP=";P
70 S = S + B
80 NEXT J
90 PRINT "SUM=";S
95 END

```

22.47 $v = (k/\mu)^{1/2}/2\pi$. N_2 and F_2 have roughly the same μ values, but N_2 has a triple bond and F_2 has a single bond, so $k_{N_2} \gg k_{F_2}$ (cf. Table 21.1). The high k_{N_2} makes v_{N_2} and Θ_{vib, N_2} high, so the vibrational contribution to $\bar{S}_{N_2}^\circ$ is negligible at room temperature. The light mass of H makes $\mu_{HF} \ll \mu_{F_2}$, so $v_{HF} \gg v_{F_2}$ and $\bar{S}_{\text{vib}, 298, HF}^\circ \ll \bar{S}_{\text{vib}, 298, F_2}^\circ$.

22.48 (a) $z_{\text{vib}} \approx \int_0^\infty e^{-v\Theta_{\text{vib}}/T} dv = -(T/\Theta_{\text{vib}}) e^{-v\Theta_{\text{vib}}/T} \Big|_0^\infty$
 T/Θ_{vib} . (b) For high T the Taylor series for e^x gives $e^{-hv/kT} \approx 1 - hv/kT$, so $z_{\text{vib}} \rightarrow 1/(hv/kT) = T/\Theta_{\text{vib}}$.

22.49 Equations (22.104) and (22.82) are not applicable at extremely low T since the translational levels are then no longer closely spaced compared to kT and the sum in z_{tr} [Eq. (22.78)] can't be replaced by an integral. Another reason is that at extremely low T , the condition $\langle N_r \rangle \ll 1$ does not hold, so Bose-Einstein or Fermi-Dirac statistics must be used.

22.50 (a) $z_{tr,N_2} \approx z_{tr,CO}$, since $m_{N_2} \approx m_{CO}$. z_{rot,N_2} and $z_{rot,CO}$ differ substantially since $\sigma_{N_2} = 2$ but $\sigma_{CO} = 1$. We have $\mu_{N_2} \approx \mu_{CO}$ and $k_{N_2} \approx k_{CO}$ for these isoelectronic triply bonded molecules, so $\nu_{N_2} \approx \nu_{CO}$ (see Table 21.1); therefore $z_{vib,N_2} \approx z_{vib,CO}$. z_{el} for each species is essentially 1. (b) From (22.64) and (22.104)-(22.107) and the results of part (a), $\bar{S}_{298,CO(g)}^\circ - \bar{S}_{298,N_2(g)}^\circ \approx \bar{S}_{298,rot,CO(g)}^\circ - \bar{S}_{298,rot,N_2(g)}^\circ \approx R \ln (\sigma_{N_2}/\sigma_{CO}) = R \ln 2 = 1.38 \text{ cal/mol-K} = 5.76 \text{ J/mol-K}$, since we expect Θ_{rot} to be approximately the same for the two species. The actual difference is 6.06 J/mol-K.

22.51 (a) Br_2 is the heaviest molecule and has the largest moment of inertia and the smallest Θ_{rot} . N_2 is the lightest molecule and also has the shortest bond length (since it has a triple bond), so N_2 has the smallest I and the largest Θ_{rot} . (b) $\nu = (1/2\pi)(k/\mu)^{1/2}$. The large μ of Br_2 makes this singly bonded species have the smallest ν and hence the smallest Θ_{vib} . The high k and small μ of $\equiv N$ makes ν_{N_2} and Θ_{vib,N_2} the largest. (c) The low

value of Θ_{rot} for Br_2 makes more of its excited rotational levels populated and makes $z_{\text{rot}, \text{Br}_2}$ largest. (d) The small v_{Br_2} and $\Theta_{\text{vib}, \text{Br}_2}$ make excited vibrational levels populated and $z_{\text{vib}, \text{Br}_2}$ is largest. (e) All these species have essentially the same $\bar{C}_{\text{V}, \text{rot}}$ at room temperature since they all have essentially attained the high-T limit $\bar{C}_{\text{V}, \text{rot}} = R$ at room temperature. (f) Br_2 , for which excited vibrational levels are accessible at room T.

22.52 z_{tr} is very roughly equal to the number of translational energy levels that have significant populations at temperature T. The particle-in-a-box translational levels have ϵ_{tr} proportional to $1/m$ (Chap. 18), so an increase in molecular mass m lowers the translational levels and allows more of them to be populated at T, thereby increasing z_{tr} and increasing \bar{S}_{tr} .

22.53 (a) At 20 K, $z_{\text{rot}} \approx T/\sigma\Theta_{\text{rot}} = (20 \text{ K})/(29.577 \text{ K}) = 0.676$. At 30 K, $z_{\text{rot}} \approx 1.014$. At 40 K, $z_{\text{rot}} \approx 1.352$. (b) $z_{\text{rot}} \approx 0.6762[1 + 1/3(0.6762) + 1/15(0.6762)^2 + 4/315(0.6762)^3] = 1.136$ at 20 K. At 30 K, $z_{\text{rot}} \approx 1.426$. At 40 K, $z_{\text{rot}} \approx 1.742$. (c) A BASIC program is

10 TH = 29.577	60 IF A < 1E-10 THEN 90
20 S = 0	70 S = S + A
30 INPUT "T=";T	80 NEXT J
40 FOR J = 0 TO 10000	90 PRINT "ZROT=";S
50 A = (2*J + 1)*EXP(-J*(J + 1)*TH/T)	95 GOTO 20
	99 END

The exact values are $z_{\text{rot}} = 1.1565$ at 20 K, $z_{\text{rot}} = 1.4312$ at 30 K, $z_{\text{rot}} = 1.7439$ at 40 K.

22.54 $S = U/T + k \ln Z = kT(\partial \ln Z / \partial T)_{V, N_B} + k \ln (z^N / N!)$
 $= kT(\partial \ln (z^N / N!) / \partial T)_{V, N_B} + Nk \ln z - k \ln N! =$
 $NkT(\partial \ln z / \partial T)_{V, N_B} + Nk \ln z - k \ln N! = (NkT/z)(\partial z / \partial T)_{V, N_B}$
 $+ Nk \ln z \sum_S e^{-\epsilon_S / kT} / z - k \ln N!.$ Use of $\partial z / \partial T =$
 $(\partial / \partial T) \sum_S e^{-\epsilon_S / kT} = (1/kT^2) \sum_S \epsilon_S e^{-\epsilon_S / kT}$ gives $S =$
 $(N/zT) \sum_S \epsilon_S e^{-\epsilon_S / kT} + (Nk/z) \ln z \sum_S e^{-\epsilon_S / kT} - k \ln N! =$
 $Nk \sum_S [(\epsilon_S / kT + \ln z)(e^{-\epsilon_S / kT} / z)] - k \ln N!.$ From (22.69),
 $x_S = e^{-\epsilon_S / kT} / z$ and $\ln x_S = -\epsilon_S / kT - \ln z$, so $S =$
 $-Nk \sum_S x_S \ln x_S - k \ln N!.$ The other condition is $\langle N_r \rangle \ll$
 1 , as in (22.49).

22.55 $\ln z_{\text{rot}} = \ln(T / \sigma \theta_{\text{rot}}) + \ln(1 + \theta_{\text{rot}} / 3T + \theta_{\text{rot}}^2 / 15T^2 +$
 $\cdots) = \ln T - \ln(\sigma \theta_{\text{rot}}) + (\theta_{\text{rot}} / 3T + \theta_{\text{rot}}^2 / 15T^2 + \cdots) -$
 $\frac{1}{2}(\theta_{\text{rot}} / 3T + \theta_{\text{rot}}^2 / 15T^2 + \cdots)^2 + \cdots = \ln T - \ln(\sigma \theta_{\text{rot}}) +$
 $\theta_{\text{rot}} / 3T + (1/15 - 1/18)(\theta_{\text{rot}}^2 / T^2) + \cdots = \ln T - \ln(\sigma \theta_{\text{rot}})$
 $+ \theta_{\text{rot}} / 3T + \theta_{\text{rot}}^2 / 90T^2 + \cdots.$ $d \ln z_{\text{rot}} / dT = 1/T - \theta_{\text{rot}} / 3T^2$
 $- \theta_{\text{rot}}^2 / 45T^3 + \cdots.$ $U_{\text{rot}} = nRT^2(d \ln z_{\text{rot}} / dT) = nRT -$
 $nR\theta_{\text{rot}} / 3 - nR\theta_{\text{rot}}^2 / 45T + \cdots.$ As $T \rightarrow \infty$, all terms after
the second go to zero and $U_{\text{rot}} \rightarrow n(RT - R\theta_{\text{rot}} / 3).$

22.56 (a) We have the original orientation plus the following: 120° and 240° rotations about the C_3 axis give 2 indistinguishable orientations; rotation about a C_2 axis followed by rotations about the C_3 axis give 3 more indistinguishable orientations. So $\sigma = 6$. (b) 2. (c) 1 (the same as for a heteronuclear diatomic). (d) 120° and 240° rotations about each of the four C_3 axes produce $2(4) = 8$

indistinguishable orientations; 180° rotations about each of the three C_2 axes (these coincide with the S_4 axes—see Fig. 21.17) produce 3 more indistinguishable orientations. Adding in the original orientation, we get $\sigma = 12$. (e) 2 (the same as for a homonuclear diatomic). (f) There are three C_2 axes and $\sigma = 4$.

22.57 $\bar{S}_{tr}^\circ = R(1.5 \ln 34.08 + 2.5 \ln 298.15 - 1.1517) = 152.87 \text{ J/mol-K}$. $\tilde{A}_0 = h/8\pi^2 c I_{a,0}$, $\tilde{B}_0 = h/8\pi^2 c I_{b,0}$, $\tilde{C}_0 =$ etc. Equation (22.109) becomes $z_{rot} = (\pi^{1/2}/\sigma)(kT/hc)^{3/2} \times (1/\tilde{A}_0 \tilde{B}_0 \tilde{C}_0)^{1/2}$. Using $\sigma = 2$, we get $z_{rot} = 125.9$. So $\bar{S}_{rot}^\circ = R(1.5 + \ln 125.9) = 52.68 \text{ J/mol-K}$. $\Theta_{vib,1}/T = (2615 \text{ cm}^{-1})hc/kT = 12.62$. $\Theta_{vib,2}/T = 5.709$. $\Theta_{vib,3}/T = 12.68$. $\bar{S}_{vib}^\circ = R[12.62/(e^{12.62} - 1) - \ln(1 - e^{-12.62}) + 5.709/(e^{5.709} - 1) - \ln(1 - e^{-5.709}) + 12.68/(e^{12.68} - 1) - \ln(1 - e^{-12.68})] = 0.186 \text{ J/mol-K}$. $\bar{S}_{el}^\circ = 0$. Adding, we get $\bar{S}_{298}^\circ = 205.74 \text{ J/mol-K}$.

22.58 $\bar{S}_{tr}^\circ = R(1.5 \ln 44.01 + 2.5 \ln 298.15 - \ln 1 - 1.1517) = 156.05 \text{ J/mol-K}$. $\Theta_{rot} = \tilde{B}_0 hc/k = 0.561 \text{ K}$. For this linear molecule, Eq. (22.105) gives $\bar{S}_{rot}^\circ = R\{1 + \ln [(298.15 \text{ K})/2(0.561 \text{ K})]\} = 54.73 \text{ J/mol-K}$. $\Theta_{vib,1}/T = (1340 \text{ cm}^{-1})hc/kT = 6.466$; $\Theta_{vib,2}/T = (667 \text{ cm}^{-1})hc/kT = 3.219$; $\Theta_{vib,3}/T = 3.219$; $\Theta_{vib,4}/T = 11.34$. Equations (22.118) and (22.106) give $\bar{S}_{vib}^\circ = R[6.466/(e^{6.466} - 1) - \ln(1 - e^{-6.466}) + 2(3.219)/(e^{3.219} - 1) - 2 \ln(1 - e^{-3.219}) + 11.34/(e^{11.34} - 1)]$

- $\ln(1 - e^{-11.34})] = 0.3616R = 3.01 \text{ J/mol-K. } \bar{S}_{e1}^{\circ} = 0.$
 $\bar{S}_{298}^{\circ} = (156.05 + 54.73 + 3.01 + 0) \text{ J/mol-K} = 213.79 \text{ J/mol-K.}$

22.59 $\bar{C}_{V, \text{tr}}^{\circ} = \frac{3}{2}R. \bar{C}_{V, \text{vib}, s}^{\circ} \rightarrow R$ at high T for each vibrational mode s. $\bar{C}_{V, \text{rot}}^{\circ} \rightarrow R$ at high T for linear molecules; $\bar{C}_{V, \text{rot}}^{\circ} \rightarrow \frac{3}{2}R$ at high T for nonlinear molecules.

(a) Linear. $3(3) - 5 = 4$ normal modes. $\bar{C}_V^{\circ} \rightarrow R(\frac{3}{2} + 4 + 1) = 6.5R = 54.04 \text{ J/mol-K. } \bar{C}_P^{\circ} = \bar{C}_V^{\circ} + R = 62.36 \text{ J/mol-K.}$

(b) Nonlinear. $3(3) - 6 = 3$ normal modes. $\bar{C}_V^{\circ} \rightarrow R(\frac{3}{2} + 3 + \frac{3}{2}) = 6R = 49.89 \text{ J/mol-K. } \bar{C}_P^{\circ} \rightarrow 58.20 \text{ J/mol-K. (c) 12}$
normal modes. $\bar{C}_V^{\circ} \rightarrow R(\frac{3}{2} + 12 + \frac{3}{2}) = 15R = 124.72 \text{ J/mol-K. } \bar{C}_P^{\circ} \rightarrow 133.03 \text{ J/mol-K.}$

22.60 Since z_{tr} is the same as for a gas of diatomic molecules, U_{tr} is given by (22.95). For a gas of linear molecules, z_{rot} is the same as for a gas of diatomics, so (22.96) gives z_{rot} . Use of Eq. (22.109) gives for a gas of nonlinear molecules: $U_{\text{rot}} = nRT^2 \frac{d \ln z_{\text{rot}}}{dT} = nRT^2 \frac{d(\frac{3}{2} \ln T + \text{const})}{dT} = \frac{3}{2}nRT.$ Equation (22.110) gives $U_{\text{vib}} = -nRT^2 \frac{d}{dT} \ln \prod_s (1 - e^{-h\nu_s/kT}) = -nRT^2 \times \frac{d}{dT} \sum_s \ln(1 - e^{-\Theta_s/T}) = -nRT^2 \sum_s [e^{-\Theta_s/T} (-\Theta_s/T^2) / (1 - e^{-\Theta_s/T})] = nR \sum_s \Theta_s / (e^{\Theta_s/T} - 1).$

22.61 $K_P^{\circ} = K_C^{\circ}$ since $\Delta n = 0.$ The quantity ΔU_0° is small since isotopic species are involved. The only major difference between the z's of an isotopic pair is the symmetry number. Since z is proportional to $1/\sigma.$ Eq. (22.125)

gives $K_P^\circ \approx \prod_B \sigma^{-\nu_B}$. (a) $\sigma(B^{35}Cl_3) = 6$, $\sigma(^{37}Cl_2) = 2$, $\sigma(B^{35}Cl_2^{37}Cl) = 2$, $\sigma(^{35}Cl^{37}Cl) = 1$. $K_P^\circ \approx 6(2)/2(1) = 6$. (b) $K_P^\circ \approx 3^2/1^3 = 27$. (c) $K_P^\circ \approx 1(2)/3(1) = 0.67$.

22.62 (a) At 0 K, there is no translational, rotational, or vibrational energy (above the zero-point energy) for the H_2 molecules; ΔU_0° is determined by the change in electronic energy and $\Delta U_0^\circ = (4.4780 \text{ eV})N_A = (4.4780 \text{ eV}) \times (1.602177 \times 10^{-19} \text{ J/eV})(6.02214 \times 10^{23}/\text{mol}) = 432.06 \text{ kJ/mol}$. (b) At 25°C, we need consider only translational and rotational contributions to \bar{U} of $H_2(g)$; the translational contribution is $\frac{3}{2}RT$ and the rotational is RT , for a total of $\frac{5}{2}RT$. The translational contribution to \bar{U} of $2H(g)$ is $2(\frac{3}{2}RT) = 3RT$. Hence $\Delta U_{298}^\circ - \Delta U_0^\circ = 3RT - \frac{5}{2}RT = \frac{1}{2}RT$. Then $\Delta H_{298}^\circ = \Delta U_{298}^\circ + \Delta n_g RT/\text{mol} = \Delta U_0^\circ + \frac{1}{2}RT + RT = \Delta U_0^\circ + \frac{3}{2}RT = 432.06 \text{ kJ/mol} + 1.5(0.0083145 \text{ kJ/mol-K})(298.15 \text{ K}) = 435.78 \text{ kJ/mol}$. The Appendix gives $2(217.965 \text{ kJ/mol}) = 435.93 \text{ kJ/mol}$.

22.63 (a) $\bar{H}_T^\circ - \bar{H}_0^\circ = \bar{U}_T^\circ + RT - \bar{U}_0^\circ = (\bar{U}_{T, \text{tr}}^\circ - \bar{U}_0^\circ) + RT = \frac{3}{2}RT + RT = \frac{5}{2}RT = 2.5(8.3145 \text{ J/mol-K})(298.15 \text{ K}) = 6.1974 \text{ kJ/mol}$. (b) $2.5RT = 20.786 \text{ kJ/mol}$. (c) $\bar{G}_T^\circ - \bar{H}_0^\circ = \bar{H}_T^\circ - T\bar{S}_T^\circ - \bar{H}_0^\circ = \bar{H}_T^\circ - \bar{H}_0^\circ - T\bar{S}_{T, \text{tr}}^\circ$. We take $\bar{H}_T^\circ - \bar{H}_0^\circ$ from (a) or (b) and use (22.108) for $\bar{S}_{T, \text{tr}}^\circ$. (Alternatively, (22.123) can be used.) $\bar{G}_{298}^\circ - \bar{H}_0^\circ = 6.1974 \text{ kJ/mol} - (298.15 \text{ K}) \times (0.0083145 \text{ kJ/mol-K})[1.5 \ln 39.948 + 2.5 \ln 298.15 - 1.1517] = -39.970 \text{ kJ/mol}$. (d) $\bar{G}_{1000}^\circ - \bar{H}_0^\circ = 20.786 \text{ kJ/mol} -$

$$180.00 \text{ kJ/mol} = -159.22 \text{ kJ/mol}.$$

22.64 From (22.123) with $\bar{H}_0^\circ = \bar{U}_0^\circ$, $z = \text{Ne}^{-(\bar{G}_T - \bar{H}_0)/RT} = (6.0221 \times 10^{23}) e^{(257.7 \text{ J/mol-K})/(8.3145 \text{ J/mol-K})} = 1.739 \times 10^{37}.$

22.65 $A - U_0 = -kT \ln Z$ and $\ln Z = -(A - U_0)/kT$. $A - U_0 = U - U_0 - TS \approx H - H_0 - TS$, since there is negligible difference between $H - H_0$ and $U - U_0$ for a solid. So $A - U_0 = [523 \text{ J/mol} - (298.15 \text{ K})(2.377 \text{ J/mol-K})](1 \text{ mol}) = -185.7 \text{ J}$. $\ln Z = (185.7 \text{ J})/kT = 4.51 \times 10^{22}.$

22.66 $S = k \ln W$ and $\Delta S = k \ln (W_{\text{final}}/W_{\text{initial}})$, so $W_{\text{final}}/W_{\text{initial}} = e^{\Delta S/k}$. $\Delta S_{\text{mix}} = -R(1.00 \text{ mol} \ln \frac{1}{2} + 1.00 \text{ mol} \ln \frac{1}{2}) = 11.53 \text{ J/K}$. So $W_{\text{final}}/W_{\text{initial}} = \exp[(11.53 \text{ J/K})/(1.381 \times 10^{-23} \text{ J/K})] = \exp(8.35 \times 10^{23})$. Let $10^y = e^{8.35 \times 10^{23}}$. Taking base-10 logs gives $y = 8.35 \times 10^{23} \log e = 3.626 \times 10^{23}$. So $W_{\text{final}}/W_{\text{initial}} = 10^{3.626 \times 10^{23}} = 10^{3.626} 10^{10^{23}} = 4200 \times 10^{10^{23}}.$

22.67 $S = k \ln W$ and $\ln W = S/k = (191.61 \text{ J/K})/(1.3807 \times 10^{-23} \text{ J/K}) = 1.388 \times 10^{25}$, where the Appendix was used.

22.68 (a) Ne. (b) Each has 2 electrons. The single +2-charged nucleus in He holds the 2 electrons more tightly than the two +1-charged nuclei in H_2 , so H_2 is more polarizable. (c) Cl_2 . (d) Each has 18 electrons. H_2S is more polarizable. (e) C_2H_6 .

22.69 From the table inside the back cover, $p' =$

$$p/(4\pi\epsilon_0)^{\frac{1}{2}} \text{ and } \alpha' = \alpha/4\pi\epsilon_0. \text{ So } v_{d-d} = -(2/3kT) \times (p_1^2 p_2^2 / 16\pi^2 \epsilon_0^2 r^6), v_{d-id} = -(p_1^2 \alpha_2 + p_2^2 \alpha_1) / 16\pi^2 \epsilon_0^2 r^6, v_{disp} \approx -[3I_1 I_2 / 2(I_1 + I_2)] \alpha_1 \alpha_2 / 16\pi^2 \epsilon_0^2 r^6.$$

22.70 $-10^{60} v_{d-d} r^6 = 2(1.60 \times 10^{-18} \text{ statC cm})^4 10^{60} / 3(1.38 \times 10^{-16} \text{ erg/K})(298 \text{ K}) = 106 \text{ erg cm}^6.$ $-10^{60} v_{d-id} r^6 = 2(1.60 \times 10^{-18} \text{ statC cm})^2 (6.48 \times 10^{-24} \text{ cm}^3) 10^{60} = 33 \text{ erg cm}^6.$ $-10^{60} v_{disp} r^6 = [3(11.3 \text{ eV})^2 / 2(22.6 \text{ eV})] \times (1.602 \times 10^{-12} \text{ erg/1 eV})(6.48 \times 10^{-24} \text{ cm}^3)^2 10^{60} = 570 \text{ erg cm}^6.$

22.71 $F = -dV/dr = 4\epsilon(12\sigma^{12}/r^{13} - 6\sigma^6/r^7) = (24\epsilon/r) \times [2(\sigma/r)^{12} - (\sigma/r)^6].$ $\epsilon = 0.013 \text{ eV} = 2.1 \times 10^{-14} \text{ erg}$ and $\sigma = 3.8 \text{ \AA}.$ (a) $F = [24(2.1 \times 10^{-14} \text{ erg}) / (8 \times 10^{-8} \text{ cm})] \times [2(3.8/8)^{12} - (3.8/8)^6] = -7.1 \times 10^{-8} \text{ dyn} = -7.1 \times 10^{-13} \text{ N}.$ (b) $-1.2 \times 10^{-6} \text{ dyn}.$ (c) $5.0 \times 10^{-4} \text{ dyn}.$

22.72 (a) $v = A/r^{12} - B/r^6.$ $0 = A/\sigma^{12} - B/\sigma^6,$ so $B\sigma^6 = A$ and $v = B\sigma^6/r^{12} - B/r^6.$ (b) $dv/dr = -12B\sigma^6/r^{13} + 6B/r^7 = 0.$ So $r_{\min}^6 = 2\sigma^6$ and $r_{\min} = 2^{1/6}\sigma.$ (c) $\epsilon = v(\infty) - v(r_{\min}) = 0 - [B\sigma^6/(2^{1/6}\sigma)^{12} - B/(2^{1/6}\sigma)^6] = B/4\sigma^6$ and $B = 4\sigma^6\epsilon.$ (d) Substitution of $\sigma = r_{\min} 2^{-1/6}$ in (22.132) gives $v = 4\epsilon(r_{\min}^{12}/4r^{12} - r_{\min}^6/2r^6) = \epsilon[(r_{\min}/r)^{12} - 2(r_{\min}/r)^6].$

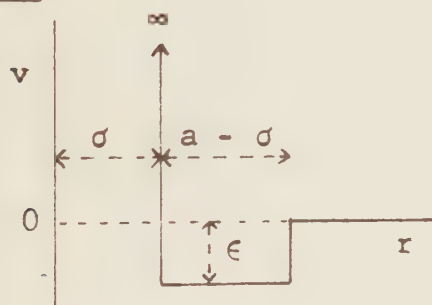
22.73 (a) $r_{\min} = 2^{1/6}\sigma = 2^{1/6}(3.5 \text{ \AA}) = 3.9 \text{ \AA}.$ (b) $r_{\min} = 2^{1/6}(8.6 \text{ \AA}) = 9.6_5 \text{ \AA}.$

22.74 (a) As noted on p. 808 of the text, for a nonpolar molecule $\epsilon \approx 1.3kT_b = 1.3(1.38 \times 10^{-16} \text{ erg/K})(27.1 \text{ K}) =$

$4.8_6 \times 10^{-15}$ erg. (b) From Sec. 8.3, $T_c \approx 1.6T_b$, so $\epsilon \approx 1.3k(T_c/1.6) = 3.4_2 \times 10^{-14}$ erg.

22.75 (a) We approximate the intermolecular potential by the Lennard-Jones potential. $F(r) = -dV/dr = -4\epsilon(-12\sigma^{12}/r^{13} + 6\sigma^6/r^7) = 24\epsilon(2\sigma^{12}/r^{13} - \sigma^6/r^7) = c/r^{13} - d/r^7$. The $F(r)$ curve has the same general appearance as the $v(r)$ curve, being 0 at $r = \infty$, negative (i.e., attractive) for large r , positive for small r , and ∞ at $r = 0$. (b) $0 = 24\epsilon(2\sigma^{12}/b^{13} - \sigma^6/b^7)$, so $2\sigma^6 = b^6$ and $b = 2^{1/6}\sigma$. [Cf. Prob. 22.72b; $F(r) = 0$ at the minimum in v .]

22.76



22.77 (a) Xe (higher M); (b) C_2H_5OH (H bonding); (c) H_2O .

22.78 (a) $v/\epsilon = 4[(\sigma/2^{1/6}\sigma)^{12} - (\sigma/2^{1/6}\sigma)^6] = 4(\frac{1}{4} - \frac{1}{2}) = -1$ (this is the minimum); (b) $4[(\sigma/1.5\sigma)^{12} - (\sigma/1.5\sigma)^6] = -0.320$; (c) -0.062 ; (d) -0.016 ; (e) -0.005 .

22.79 (a) For an ideal gas, $\mathcal{V} = 0$; for linear molecules

Eq. (22.141) becomes $Z_{\text{con}} = (4\pi)^{-N} \int_0^\pi \sin \theta_1 d\theta_1 \cdots \int_0^\pi \sin \theta_N d\theta_N \int_0^{2\pi} d\phi_1 \cdots \int_0^{2\pi} d\phi_N \int_0^a dx_1 \int_0^b dy_1 \int_0^c dz_1 \cdots \int_0^a dx_N \int_0^b dy_N \int_0^c dz_N = (4\pi)^{-N} 2^N (2\pi)^N (abc)^N = V^N$. For an

ideal gas of nonlinear molecules, $(4\pi)^{-N}$ is replaced by $(8\pi^2)^{-N} = (2\pi)^{-N}(4\pi)^{-N}$ and we have the additional integral factors $\int_0^{2\pi} d\chi_1 \cdots \int_0^{2\pi} d\chi_N = (2\pi)^N$, so we still get $Z_{\text{con}} = V^N$. (b) $P = kT(\partial \ln V^N / \partial V)_{T,N} = NkT(\partial \ln V / \partial V) = NkT/V$.

$$\begin{aligned} \underline{22.80} \quad B &= -2\pi N_A \int_0^\infty (e^{-v/kT} - 1)r^2 dr = \\ &= -2\pi N_A \left[\int_0^d (e^{-\infty/kT} - 1)r^2 dr + \int_d^\infty (e^{-0/kT} - 1)r^2 dr \right] = \\ &= -2\pi N_A \left[-\int_0^d r^2 dr + 0 \right] = 2\pi N_A d^3/3 = 4N_A \left[\frac{4}{3}\pi(d/2)^3 \right]. \end{aligned}$$

22.81 At 100 K, $\log(kT/\epsilon) = \log[(1.381 \times 10^{-23} \text{ J/K}) \times (100 \text{ K}) / (1.31 \times 10^{-21} \text{ J})] = 0.0229$. For this $\log(kT/\epsilon)$, Fig. 22.18 gives $B/\sigma^3 N_A \approx -5.4$ and $B \approx -5.4 \times (3.74 \times 10^{-8} \text{ cm})^3 (6.022 \times 10^{23} / \text{mol}) = -170 \text{ cm}^3 / \text{mol}$. At 300 K, $\log(kT/\epsilon) = 0.500$; Fig. 22.18 gives $B/\sigma^3 N_A \approx -0.1$ and $B \approx -3 \text{ cm}^3 / \text{mol}$. At 500 K, $\log(kT/\epsilon) = 0.722$; $B/\sigma^3 N_A \approx 0.5$ and $B \approx 16 \text{ cm}^3 / \text{mol}$.

$$\begin{aligned} \underline{22.82} \quad (\underline{a}) \quad B &= -2\pi N_A \int_0^\sigma (e^{-\infty} - 1)r^2 dr - 2\pi N_A \times \\ &\times \int_\sigma^a (e^{\epsilon/kT} - 1)r^2 dr - 2\pi N_A \int_a^\infty (e^0 - 1)r^2 dr = 2\pi N_A \sigma^3/3 \\ &- 2\pi N_A (e^{\epsilon/kT} - 1)(a^3 - \sigma^3)/3 + 0 = 2\pi N_A (\sigma^3 - a^3)e^{\epsilon/kT}/3 + \\ &+ 2\pi N_A a^3/3. \quad (\underline{b}) \text{ Substitution of numerical values gives} \\ B(100 \text{ K}) &= -163 \text{ cm}^3 / \text{mol}, \quad B(300 \text{ K}) = -4 \text{ cm}^3 / \text{mol}, \\ B(500 \text{ K}) &= 17 \text{ cm}^3 / \text{mol}. \quad (\underline{c}) \text{ From (8.5) and (8.6), } Z \approx \\ 1 + B^*P &= 1 + BP/RT \approx 1 - (163 \text{ cm}^3 / \text{mol})(3.0 \text{ atm}) / \\ (82.06 \text{ cm}^3 \text{-atm/mol-K})(100 \text{ K}) &= 0.94. \end{aligned}$$

$$\begin{aligned} \underline{22.83} \quad U &= kT^2(\partial \ln Z / \partial T)_{V,N} = kT^2(\partial \ln Z_{\text{id}} / \partial T)_{V,N} + \\ &+ kT^2(\partial \ln Z_{\text{con}} / \partial T)_{V,N} = U_{\text{id}} + kT^2(-N) \left[(1/\bar{V}) dB / dT + \right. \end{aligned}$$

$$\begin{aligned}
 (1/2\bar{V}^2)dC/dT + \dots] &= U_{id} - nRT^2[(1/\bar{V})dB/dT + \\
 (1/2\bar{V}^2)dC/dT + \dots]. \quad S &= U/T + k \ln Z = U_{id}/T - nRT \times \\
 [(1/\bar{V})dB/dT + (1/2\bar{V}^2)dC/dT + \dots] &+ k \ln Z_{id} + kN \ln V \\
 - Nk[(1/\bar{V})B + (1/2\bar{V}^2)C + \dots] - Nk \ln V &= S_{id} - nR \times \\
 [(1/\bar{V})(B + T dB/dT) + (1/2\bar{V}^2)(C + T dC/dT) + \dots], \\
 \text{since } S_{id} &= U_{id}/T + k \ln Z_{id}. \quad G = A + PV = -kT \ln Z + \\
 kTV(\partial \ln Z_{con}/\partial V)_{T,N} &= -kT \ln Z_{id} - kTN \ln V + kTN(B/\bar{V} + \\
 C/2\bar{V}^2 + \dots) + kTN \ln V + kTVN(1/V + B/V\bar{V} + C/V\bar{V}^2 + \\
 \dots) &= G_{id} + nRT(2B/\bar{V} + 3C/2\bar{V}^2 + \dots), \text{ since } G_{id} = \\
 A_{id} + (PV)_{id} &= -kT \ln Z_{id} + NkT.
 \end{aligned}$$

22.84 $A = -kT \ln Z$ and $A_{false} = -kT \ln Z_{false}$, so

$$\begin{aligned}
 A_{false} - A &= -kT \ln (Z_{false}/Z) = -(1.38 \times 10^{-23} \text{ J/K}) \times \\
 (298 \text{ K}) \ln 10^{(\pm 10^{15})} &= -(4.11 \times 10^{-21} \text{ J}) 2.30 \log 10^{(\pm 10^{15})} \\
 &= -9.5 \times 10^{-21} \text{ J}(\pm 10^{15}) = \pm 10^{-5} \text{ J}, \text{ which is negligible.}
 \end{aligned}$$

22.85 $\langle N_r \rangle / N = e^{-\epsilon_r/kT} / z$, so $\langle N_{gs} \rangle / N = e^{-0} / z = 1/z =$
 $1/154.1 = 0.00649.$

22.86 (a) Since A is proportional to n and $A = -kT \ln Z$, we see that $\ln Z$ is proportional to n . From (22.81), z_{tr} is proportional to V , which is proportional to n ; so z_{tr} is proportional to n . Since z_{tr} is proportional to n , z is proportional to n . (b) z_{rot} , z_{vib} , and z_{el} are independent of n . (c) None. (d) z_{rot} , z_{vib} , and z_{el} .

22.87 Every thermodynamic system in equilibrium.

$$23.1 \quad A = k e^{E_a/RT} = k e^{E_{thr}/RT} e^{\frac{1}{2}} = N_A \pi d_B^2 e^{\frac{1}{2}} (4RT/\pi M_B)^{\frac{1}{2}},$$

where Eqs. (17.69), (23.5), and (23.4) were used.

$$23.2 \quad (a) \text{ Equation (23.6) gives } A = (6.0 \times 10^{23} / \text{mole}) \pi \times (3.4 \times 10^{-10} \text{ m})^2 [8(8.314 \text{ J/mole-K})(500 \text{ K})/\pi]^{\frac{1}{2}} \times [\text{mole}/(0.030 \text{ kg}) + \text{mole}/(0.048 \text{ kg})]^{\frac{1}{2}} (2.72)^{\frac{1}{2}} = 3 \times 10^8 \text{ m}^3 \text{ s}^{-1} \text{ mole}^{-1} = 3 \times 10^{14} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}. \quad (b) 8 \times 10^{11} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1} = p(3 \times 10^{14} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}) \text{ and } p = 0.003.$$

$$23.3 \quad \langle v_{rc} \rangle = \int_0^\infty v_{rc} g(v_{rc}) dv_{rc} = 2(m_{rc}/2\pi kT)^{\frac{1}{2}} \times \int_0^\infty v_{rc} \exp(-m_{rc} v_{rc}^2 / 2kT) dv_{rc} = 2(m_{rc}/2\pi kT)^{\frac{1}{2}} \frac{1}{2} (2kT/m_{rc}) = (2kT/\pi m_{rc})^{\frac{1}{2}}.$$

$$23.4 \quad \text{The energy per molecule is } (9.6 \text{ kcal/mole})/N_A = [(9600 \text{ cal/mole})/(6.02 \times 10^{23} / \text{mole})](4.184 \text{ J/1 cal}) \times (10^7 \text{ erg/1 J}) = 6.7 \times 10^{-13} \text{ erg}.$$

23.5 (a) $D \text{---} H \text{---} H$, $d = 0.930 \text{ \AA}$ (p. 840). Let the origin be at D and let the molecular axis be the x axis. The center of mass is at $x_{cm} = \sum_i m_i x_i / m_{tot} = [2.014(0) + 1.008 d + 1.008(2d)]/4.030 = 0.698 \text{ \AA}$. The principal axes pass through the center of mass (which is on the molecular axis and 0.698 \AA away from D); one principal axis is the molecular axis; the other two are perpendicular to this axis.

$$I_{b, DH_2} = \sum_i m_i r_{b,i}^2 = N_A^{-1} [(2.014)(0.698)^2 + 1.008(0.930 - 0.698)^2 + 1.008(1.860 - 0.698)^2] (\text{g/mol}) \text{ \AA}^2 =$$

$2.397 N_A^{-1} (\text{g/mol}) \text{ \AA}^2$. (b) For H_2 , $I_{\text{H}_2} = \mu R^2 = (m_{\text{H}}^2/2m_{\text{H}})R^2 = \frac{1}{2}m_{\text{H}}R^2 = N_A^{-1} \frac{1}{2}(1.008)(0.741)^2 (\text{g/mol}) \text{ \AA}^2 = 0.2767 N_A^{-1} (\text{g/mol}) \text{ \AA}^2$. Then $I_{\text{b, DH}_2}/I_{\text{H}_2} = 2.397/0.2767 = 8.66$. Since $\sigma_{\text{H}_2} = 2$ and $\sigma_{\text{DH}_2} = 1$, the rotational-partition-function ratio is $2(8.66) = 17.3$.

23.6 (a) $z_{\text{vib, H}_2} = [1 - \exp(-h\tilde{\nu}c/kT)]^{-1}$; $h\tilde{\nu}c/kT = (6.626 \times 10^{-34} \text{ J s})(4400 \text{ cm}^{-1})(2.998 \times 10^{10} \text{ cm/s}) / (1.3807 \times 10^{-23} \text{ J/K})(450 \text{ K}) = 14.07$; $z_{\text{vib, H}_2} = (1 - e^{-14.07})^{-1} = 1.000$. The activated complex has 3 ordinary vibrations, with wave numbers 1764, 870, and 870 cm^{-1} and $z_{\text{vib}}^{\ddagger}$ is the product of factors for each of these vibrations. We have $h\tilde{\nu}_{\text{str}}c/kT = h(1764 \text{ cm}^{-1})c/kT = 5.640$, $h\tilde{\nu}_{\text{bend}}c/kT = h(870 \text{ cm}^{-1})c/kT = 2.781$. Then $z_{\text{vib}}^{\ddagger} = (1 - e^{-5.640})^{-1}(1 - e^{-2.781})^{-2} = 1.141$. From (22.81) and Table 21.2, $(z_{\text{tr}}^{\ddagger}/V) / [(z_{\text{tr, D}}/V)(z_{\text{tr, H}_2}/V)] = (m_{\text{DH}_2}/m_{\text{D}}m_{\text{H}_2})^{3/2} (h^2/2\pi kT)^{3/2} = [4.030/(2.014)(2.016)]^{3/2} \times (\text{mol}/10^{-3} \text{ kg})^{3/2} (6.022 \times 10^{23}/\text{mol})^{3/2} (6.626 \times 10^{-34} \text{ J s})^3 \times [2\pi(1.3807 \times 10^{-23} \text{ J/K})(450 \text{ K})]^{-3/2} = 5.51 \times 10^{-31} \text{ m}^3 = 5.51 \times 10^{-25} \text{ cm}^3$. (b) $N_A kT h^{-1} \exp(-\Delta\epsilon_0^{\ddagger}/kT) = (6.022 \times 10^{23}/\text{mol})(1.381 \times 10^{-23} \text{ J/K})(450 \text{ K}) \times (6.626 \times 10^{-34} \text{ J s})^{-1} \exp\{(-5.8 \times 10^{-20} \text{ J}) / [(450 \text{ K}) \times (1.381 \times 10^{-23} \text{ J/K})]\} = 5.0 \times 10^{32}/\text{mol-s}$. Then $k_r = (5.0 \times 10^{32}/\text{mol-s})(5.51 \times 10^{-25} \text{ cm}^3)(17.3)(1.141)(1) = 5.4 \times 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

23.7 Replacing 450 K by 600 K in Prob. 23.6b, we find

$N_A k T h^{-1} \exp(-\Delta \epsilon_0^\ddagger / kT) = 6.9 \times 10^{33} / \text{mol-s}$. Replacing 450 K by 600 K in Prob. 23.6a, we find $(z_{\text{tr}}^\ddagger / V) / [(z_{\text{tr},D} / V) \times (z_{\text{tr},H_2} / V)] = 3.58 \times 10^{-31} \text{ m}^3$, $z_{\text{vib},H_2} = 1.000$, $z_{\text{vib}}^\ddagger = 1.323$. So $k_r = (6.9 \times 10^{33} / \text{mol-s})(3.58 \times 10^{-25} \text{ cm}^3)(17.3) \times (1.323)(1) = 5.6 \times 10^{10} \text{ cm}^3 / \text{mol-s}$. The tunneling correction is $7.5/5.6 = 1.3$, which is less than that at 450 K; tunneling becomes less important as T increases.

23.8 $\tilde{\nu} = v/c = (1/2\pi c)(k/\mu)^{1/2}$. k is the same for H_2 and D_2 so $\tilde{\nu}_{D_2} / \tilde{\nu}_{H_2} = (\mu_{H_2} / \mu_{D_2})^{1/2} = (\frac{1}{2}m_H / \frac{1}{2}m_D)^{1/2} = (1.0078/2.0141)^{1/2} = 0.7074$ and $\tilde{\nu}_{D_2} = 3112 \text{ cm}^{-1}$. The ZPE of the activated complex is $\frac{1}{2}hc(1762 + 694 + 694)\text{cm}^{-1} = 3.13 \times 10^{-13} \text{ erg}$. The ZPE of H is 0 and that of D_2 is $\frac{1}{2}hc\tilde{\nu}_{D_2} = 3.09 \times 10^{-13} \text{ erg}$. $\Delta(\text{ZPE}) = 0.04 \times 10^{-13} \text{ erg}$. The classical barrier height is the same as that for $D + H_2$, namely, $6.7 \times 10^{-13} \text{ erg}$. So $\Delta \epsilon_0^\ddagger = 6.7_4 \times 10^{-13} \text{ erg}$. Also, $z_{\text{el},H} = 2$, $z_{\text{el},D_2} = 1$, $z_{\text{el}}^\ddagger = 2$. $z_{\text{rot}}^\ddagger / z_{\text{rot},D_2} = I^\ddagger \sigma_{D_2} / I_{D_2} \sigma^\ddagger = 2I^\ddagger / I_{D_2}$. $I_{D_2} = \mu R^2 = m_D R^2 / 2 = N_A^{-1} \frac{1}{2}(2.014)(0.741)^2 (\text{g/mol}) \text{ \AA}^2 = 0.553 N_A^{-1} (\text{g/mol}) \text{ \AA}^2$. $H \underline{d} D \underline{d} D$, $d = 0.930 \text{ \AA}$ (p.840). The procedure of Prob. 23.5a gives (with the origin at H) $x_{\text{cm}} = 1.116 \text{ \AA}$, $I^\ddagger = 2.440 (\text{g/mol}) \text{ \AA}^2$, and $z_{\text{rot}}^\ddagger / z_{\text{rot},D_2} = 8.82$. Proceeding as in Prob. 23.6a, we find $z_{\text{vib},D_2} = 1.001$, $z_{\text{vib}}^\ddagger = 1.545$, $(z_{\text{tr}}^\ddagger / V) / [(z_{\text{tr},H} / V)(z_{\text{tr},D_2} / V)] = 5.00 \times 10^{-25} \text{ cm}^3$. $N_A k T h^{-1} \exp(-\Delta \epsilon_0^\ddagger / kT) = 2.2 \times 10^{33} / \text{mol-s}$. So $k_r = (2.2 \times 10^{33} / \text{mol-s})(5.00 \times 10^{-25} \text{ cm}^3)(8.82)(1.544)(1) = 1.5 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

23.9 The Taylor series for e^x gives at high T , $e^{-h\nu_s/kT} \approx 1 - h\nu_s/kT$ and $z_{\text{vib},s} \approx 1/(h\nu_s/kT) = kT/h\nu_s$. There are f_{vib} factors in z_{vib} in Eq. (22.110), so z_{vib} is proportional to $T^{f_{\text{vib}}}$ at high T .

23.10 Let lin , nonlin , lin^\ddagger , and nonlin^\ddagger denote linear and nonlinear reactant molecules and linear and nonlinear transition states. (a) First consider the reaction between an atom and a molecule. Let the reaction be $\text{atom}_A + \text{lin}_B \rightarrow \text{lin}^\ddagger$. The ratio $z_{\text{tr}}^\ddagger/z_{\text{tr},A}z_{\text{tr},B}$ is proportional to $T^{3/2}/T^{3/2}T^{3/2} = T^{-3/2}$ for any bimolecular reaction. Also, $z_{\text{rot}}^\ddagger/z_{\text{B,rot}} \propto T/T = T^0$. Let lin_B have w atoms. Then lin_B has $3w - 5$ normal modes. Further, lin^\ddagger has $w + 1$ atoms and $3(w + 1) - 5 - 1 = 3w - 3$ "ordinary" normal modes and one anomalous mode (the "vibration" along the reaction coordinate). So lin^\ddagger has 2 more ordinary normal modes than does lin_B . Also, the vibrational frequencies of lin^\ddagger and lin_B should be of the same order of magnitude in most cases, so we expect that $z_{\text{vib}}^\ddagger/z_{\text{vib},B}$ is proportional to T^j , where $0 \leq j \leq \frac{1}{2}(f_{\text{vib}}^\ddagger - f_{\text{vib},B})$. Hence, $z_{\text{vib}}^\ddagger/z_{\text{vib},B} \propto T^c$, where $0 \leq c \leq 1$. Equation (23.23) then gives $A \propto T^1 T^{-3/2} T^0 T^c = T^{c-1/2} = T^m$, where $-1/2 \leq m \leq 1/2$. Now consider $\text{atom}_A + \text{lin}_B \rightarrow \text{nonlin}^\ddagger$. We have $z_{\text{rot}}^\ddagger/z_{\text{rot},B} \propto T^{3/2}/T = T^{1/2}$. Reasoning similar to the above shows that the species nonlin^\ddagger has 1 more ordinary normal mode than lin_B , so $z_{\text{vib}}^\ddagger/z_{\text{vib},B} \propto T^b$, where $0 \leq b \leq 1/2$. Hence, $A \propto T^1 T^{-3/2} T^{1/2} T^b = T^b = T^m$, where $0 \leq m \leq 1/2$. For $\text{atom}_A + \text{nonlin}_B \rightarrow \text{nonlin}^\ddagger$, we find similarly that $A \propto T^1 T^{-3/2} T^0 T^a = T^{a-1/2}$, where $0 \leq a \leq 1$. So $-1/2 \leq m \leq 1/2$. (b) Now let the reaction be between two mol-

ecules. First consider $\text{nonlin}_A + \text{nonlin}_B \rightarrow \text{nonlin}^\ddagger$. Let A and B have w_A and w_B atoms. Then A and B have a total of $3w_A + 3w_B - 12$ normal modes and nonlin^\ddagger has $3(w_A + w_B) - 6 - 1 = 3w_A + 3w_B - 7$ ordinary normal modes, which is 5 more than the total of A and B. So $z_{\text{vib}}^\ddagger / z_{\text{vib},A} z_{\text{vib},B} \propto T^d$, where $0 \leq d \leq 2\frac{1}{2}$. Hence, $A \propto T^1 T^{-3/2} T^{-3/2} T^d = T^{d-2} = T^m$, where $-2 \leq m \leq \frac{1}{2}$. For $\text{lin}_A + \text{nonlin}_B \rightarrow \text{nonlin}^\ddagger$, we find similarly that nonlin^\ddagger has 4 more ordinary normal modes than A + B, so $A \propto T^1 T^{-3/2} T^{-1} T^e = T^{e-1\frac{1}{2}} = T^m$, where $0 \leq e \leq 2$ and $-1\frac{1}{2} \leq m \leq \frac{1}{2}$. For $\text{lin}_A + \text{lin}_B \rightarrow \text{nonlin}^\ddagger$, nonlin^\ddagger has 3 more ordinary normal modes than A and B together, so $A \propto T^1 T^{-3/2} T^{-\frac{1}{2}} T^g = T^{g-1} = T^m$, where $0 \leq g \leq 1\frac{1}{2}$ and $-1 \leq m \leq \frac{1}{2}$.

23.11 From the example in Sec. 23.4, $\Delta\epsilon_0^\ddagger = 5.8 \times 10^{-13}$ erg $= 5.8 \times 10^{-20}$ J. So $\Delta E_0^\ddagger = (5.8 \times 10^{-20} \text{ J})(6.02 \times 10^{23} / \text{mole}) = (3.5 \times 10^4 \text{ J/mole})(1 \text{ cal}/4.184 \text{ J}) = 8.3_5 \text{ kcal/mol}$. m is the exponent of T in k_r . The example in Sec. 23.4 shows the z_{tr} ratio and the z_{rot} ratio to be proportional to $T^{-3/2}$ and T^0 , respectively. At 300 K, the z_{vib} ratio is nearly equal to 1 and its temperature dependence is essentially negligible. z_{el} is independent of T at 300 K. So Eq. (23.19) gives $k_r \propto T^1 T^{-3/2} T^0 = T^{-\frac{1}{2}}$ and $m = -\frac{1}{2}$. Then $E_a = \Delta E_0^\ddagger + mRT = 8350 \text{ cal/mol} - \frac{1}{2}R(300 \text{ K}) = 8.0 \text{ kcal/mole}$.

23.12 The activated complex A^\ddagger is an A molecule in the hole or within a distance δ beyond the hole. We have $\Delta\epsilon_0^\ddagger = 0$. Also, z_{vib} , z_{rot} , and z_{el} are the same for A and A^\ddagger . The volume factor in z_{tr}^\ddagger is $\mathcal{A}\delta$, where \mathcal{A} is the hole

area; also, z_{tr}^\ddagger contains an extra factor of $\frac{1}{2}$ since A^\ddagger is moving only forward along the reaction coordinate (which is the direction perpendicular to the hole). Equations (23.16), (23.18), and (22.81) give $r = \delta^{-1}(2kT/\pi m)^{\frac{1}{2}} \times (z_{tr}^\ddagger/z_{tr,A})[A] = \delta^{-1}(2RT/\pi M)^{\frac{1}{2}} \frac{1}{2}(2\pi mkT/h^2)^{3/2} \mathcal{A} \delta \times [(2\pi mkT/h^2)^{3/2} V]^{-1}[A] = (RT/2\pi M)^{\frac{1}{2}} P \mathcal{A}/VRT$, since $[A] = P/RT$. So $J = rV = -dn_A/dt = P \mathcal{A}/(2\pi MRT)^{\frac{1}{2}}$.

23.13 From Sec. 21.9, $\tilde{\nu}_{CH} \approx 3000 \text{ cm}^{-1}$ and (see p. 843) $\exp[-\Delta(\Delta\epsilon_0^\ddagger)/kT] = \exp[-0.146(6.63 \times 10^{-34} \text{ J s})(300000 \text{ m}^{-1}) \times (3.0 \times 10^8 \text{ m/s})/(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})] = 0.122 = 1/8.2$. As T increases, the exponential comes closer to 1 and the isotope effect decreases.

23.14 $\nu = (1/2\pi)(k/\mu)^{\frac{1}{2}}$. $\nu_{CT}/\nu_{CH} = (\mu_{CH}/\mu_{CT})^{\frac{1}{2}} \approx (m_H/m_T)^{\frac{1}{2}} = (1/3)^{\frac{1}{2}}$ and $\nu_{CT} = \nu_{CH}/\sqrt{3}$. The ZPE of the reactant is lowered by $\frac{1}{2}h(\nu_{CH} - \nu_{CT}) = \frac{1}{2}h\nu_{CH}(1 - 1/\sqrt{3}) = 0.211h\nu_{CH}$ and the ZPE of the activated complex is unaffected. Replacement of 0.146 with 0.211 in Prob. 23.13 shows k_r is multiplied by $0.048 = 1/21$.

23.15 The rate-determining step doesn't involve breaking the Ar—H bond, so (a) and (c) are ruled out.

23.16 (a) $\Delta H_C^{\circ\ddagger} = \Delta H^{\circ\ddagger} = E_a - nRT = 2500 \text{ cal/mol} - 2(1.987 \text{ cal/mol-K})(270 \text{ K}) = 1.4_3 \text{ kcal/mole}$. From Eq. (23.35), $\Delta S_C^{\circ\ddagger} = R\{\ln [Ah(c^\circ)^{n-1}/kT] - n\} = R\{\ln [(6 \times 10^8 \text{ dm}^3/\text{mol-s})(6.6 \times 10^{-34} \text{ J s})(\text{mol/dm}^3)/(1.38 \times 10^{-23} \text{ J/K})(270 \text{ K})] - 2\} = -22.1 \text{ cal/mol-K}$. $\Delta G_C^{\circ\ddagger} =$

$(1.4_3 \text{ kcal/mol}) - (270 \text{ K})(-0.0221 \text{ kcal/mol-K}) = 7.4 \text{ kcal/mol}$. (b) The equations used in (a) give $\Delta H_c^{\circ\ddagger} = 40.3 \text{ kcal/mol}$, $\Delta S_c^{\circ\ddagger} = -23.2 \text{ cal/mol-K}$, and $\Delta G_c^{\circ\ddagger} = 103.0 \text{ kcal/mol}$.

23.17 (a) Equation (23.44) gives $\log(k_r/k_r^\infty) = 1.02(-6) \times [I^{1/2}/(1 + I^{1/2}) - 0.30I]$. For $I = 10^{-3}$, $\log(k_r/k_r^\infty) = -0.1858$ and $k_r/k_r^\infty = 0.65$. For $I = 10^{-2}$, $k_r/k_r^\infty = 0.29$. For $I = 10^{-1}$, $k_r/k_r^\infty = 0.052$. (b) Replacement of the factor -6 by +6 gives $k_r/k_r^\infty = 1.53, 3.4_5$, and 19.4 for $I = 10^{-3}, 10^{-2}, 10^{-1}$.

23.18 The slope of a plot of $\log(k_r/k^\circ)$ vs. $I^{1/2}/(1 + I^{1/2}) - 0.30I$ is $1.02z_C z_B$. The data are

$\log(k_r/k^\circ)$	-0.979	-0.951	-0.928	-0.900	-0.854
$I^{1/2}/(1 + I^{1/2}) - 0.30I$	0.0464	0.0559	0.0724	0.0817	0.0966

The straight-line fit is at best only fair; the slope is $2.3_7 = 1.02z_C z_B$ and $z_C z_B = 2.3 \approx 2$.

23.19 Equation (23.49) gives $\Delta S^{\circ\ddagger}/R = \ln(Ahc^\circ/kTe) = \ln 0.000118 = -9.0_5$. So $\Delta S^{\circ\ddagger} = R(-9.0_5) = -18.0 \text{ cal/mol-K}$. From (23.48), $\Delta H^{\circ\ddagger} = E_a - RT = 15700 \text{ cal/mol} - R(300 \text{ K}) = 15.1 \text{ kcal/mol}$. $\Delta G^{\circ\ddagger} = \Delta H^{\circ\ddagger} - T \Delta S^{\circ\ddagger} = (15.1 \text{ kcal/mol}) - (300 \text{ K})(-0.0180 \text{ kcal/mol-K}) = 20.5 \text{ kcal/mol}$.

23.20 We get $[C]_{R=r_B+r_C} = [C][1 - k_{\text{chem}}/(k_{\text{diff}} + k_{\text{chem}})]$. For diffusion-controlled reactions, $k_{\text{chem}} \gg k_{\text{diff}}$ and $[C]_{R=r_B+r_C}/[C] = 1 - 1/(1 + k_{\text{diff}}/k_{\text{chem}}) \approx 1 - (1 - k_{\text{diff}}/k_{\text{chem}}) = k_{\text{diff}}/k_{\text{chem}}$, where Eq. (8.8) was used. For chemically controlled reactions, $k_{\text{chem}} \ll k_{\text{diff}}$

and $[C]_{R=r_B+r_C} \approx [C]$.

23.21 1. A unimolecular reaction in the falloff region.
2. A diffusion-controlled reaction. 3. A photochemical reaction.
4. A laser-illuminated reaction. 5. A reaction with a very low E_a (see p. 820).

23.22 In the unimolecular decomposition of C_2H_5Cl , the transition state of Fig. 23.17b has two reactant bonds partially weakened and an equal number of new bonds partially formed; moreover, the transition state and the reactant have similar sizes. Thus the degree of disorder in the activated complex is similar to that in the reactant molecule, and we expect $\Delta S_c^{\circ\ddagger}$ to be close to zero for this and similar decompositions. In the C_2H_6 decomposition (p. 848) and similar decompositions, the bond elongation in the transition state produces a "disordered" transition state, and we expect $\Delta S_c^{\circ\ddagger} \gg 0$ here.

CHAPTER 24

24.1 (a) Metallic; (b) molecular; (c) covalent; (d) ionic; (e) molecular; (f) ionic; (g) metallic.

24.2 (a) For $\text{C}(\text{graphite}) \rightarrow \text{C}(\text{g})$, $E_{\text{c},298} = \Delta H_{298}^{\circ} = (716.7 - 0) \text{ kJ/mol} = 716.7 \text{ kJ/mol}$. (b) For $\text{SiC}(\text{c}) \rightarrow \text{Si}(\text{g}) + \text{C}(\text{g})$, $E_{\text{c},298} = (455.6 + 716.7 + 65.3) \text{ kJ/mol} = 1237.6 \text{ kJ/mol}$. (c) For $\text{SiO}_2(\text{c}) \rightarrow \text{Si}(\text{g}) + 2 \text{O}(\text{g})$, $E_{\text{c},298} = [455.6 + 2(249.2) - (-910.9)] \text{ kJ/mol} = 1864.9 \text{ kJ/mol}$.

24.3 $E_{\text{c}} = (411.15 + 107.32 + 121.68) \text{ kJ/mol} + (6.022 \times 10^{23} / \text{mol})(5.139 - 3.614) \text{ eV} (1.6022 \times 10^{-19} \text{ J/1 eV}) \times (1 \text{ kJ} / 1000 \text{ J}) = 787.3 \text{ kJ/mol}$.

24.4 (a) I_2 (greater M); (b) NH_3 (H bonding); (c) SiO_2 (covalent solid); (d) MgO (greater ionic charges).

24.5 For $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$, $E_{\text{c},298} = \Delta H_{298}^{\circ} = 44.0 \text{ kJ/mol}$.

24.6 $E_{\text{Coul}} = -(4.803 \times 10^{-10} \text{ statC})^2 (1.74756) \times (6.022 \times 10^{23} / \text{mol}) (2.798 \times 10^{-8} \text{ cm})^{-1} (1 \text{ J} / 10^7 \text{ ergs}) = -867.7 \text{ kJ/mol}$.

24.7 $n = 1 + 18(2.798 \times 10^{-8} \text{ cm})^4 / (3.7 \times 10^{-12} \text{ cm}^2 / \text{dyn}) (4.803 \times 10^{-10} \text{ statC})^2 1.74756 = 8.4$.

24.8 (a) From (24.11) with $e'^2 = e^2 / 4\pi\epsilon_0$ and with R_0 at 0 K approximated by R_0 at 25°C , we have $n \approx 1 + 18 \times (3.299 \times 10^{-10} \text{ m})^4 4\pi(8.854 \times 10^{-12} \text{ C}^2 / \text{N}\cdot\text{m}^2) (10^5 \text{ Pa}) / (5.5 \times 10^{-6}) (1.602 \times 10^{-19} \text{ C})^2 1.74756 \approx 10.6$. From (24.9),

$$E_c \approx (1.602 \times 10^{-19} \text{ C})^2 1.74756 (6.022 \times 10^{23} / \text{mol}) (1 - 1/10.6) / 4\pi (8.854 \times 10^{-12} \text{ C}^2 / \text{N-m}^2) (3.299 \times 10^{-10} \text{ m}) = 666 \text{ kJ/mol}.$$

(b) From Fig. 24.16, the nearest-neighbor distance R_0 is one-half the length d of the diagonal of the unit cell. As in Fig. 15.1 and Eq. (15.1), $d^2 = a^2 + a^2 + a^2$ and $d = 3^{\frac{1}{2}}a$, where a is the edge length. So $R_0 = \frac{1}{2}(3^{\frac{1}{2}})a = \frac{1}{2}(3^{\frac{1}{2}})(4.123 \times 10^{-10} \text{ m}) = 3.571 \times 10^{-10} \text{ m}$. Fig. 24.16 shows that there is one CsCl ion pair per unit cell, so the molar volume is $\bar{V}_0 = N_A a^3 = N_A (2R_0/3^{\frac{1}{2}})^3 = 8R_0^3 N_A / 3^{3/2}$ and Eq. (24.10) becomes $n = 1 + 8(3^{\frac{1}{2}})R_0^4 / \kappa e'^2 \mathcal{M} \approx 1 + 8(3^{\frac{1}{2}}) \times (3.571 \times 10^{-10} \text{ m})^4 4\pi (8.854 \times 10^{-12} \text{ C}^2 / \text{N-m}^2) (10^5 \text{ Pa}) / (6 \times 10^{-6}) (1.602 \times 10^{-19} \text{ C})^2 1.762675 \approx 10.2$. Equation (24.9) becomes $E_c \approx (1.602 \times 10^{-19} \text{ C})^2 1.762675 (6.022 \times 10^{23} / \text{mol}) \times (1 - 1/10.2) / 4\pi (8.854 \times 10^{-12} \text{ C}^2 / \text{N-m}^2) (3.571 \times 10^{-10} \text{ m}) = 620 \text{ kJ/mol}$. In both (a) and (b), the theoretical value is less than the experimental value due to neglect of the dispersion energy.

24.9 (a) $(\partial^2 \bar{U} / \partial \bar{V}^2)_T = T(\partial^2 P / \partial \bar{V} \partial T) - (\partial P / \partial \bar{V})_T$. As $T \rightarrow 0$, the first term on the right side of this equation goes to zero and $(\partial^2 \bar{U} / \partial \bar{V}^2)_T \rightarrow -(\partial P / \partial \bar{V})_T = 1/\kappa \bar{V}$, where $\kappa \equiv -\bar{V}^{-1}(\partial \bar{V} / \partial P)_T$ was used. (b) Use of $\bar{V}^{1/3} = c^{1/3} R$ and $\bar{V}_0^{1/3} = c^{1/3} R_0$ in (24.8) gives the desired equation for $-E_p$; differentiation of this equation gives $-\partial^2 E_p / \partial \bar{V}^2 = e'^2 \mathcal{M} N_A R_0^{-1} [(-\frac{1}{3})(-\frac{4}{3})\bar{V}_0^{-1/3} \bar{V}^{-7/3} - n^{-1}(-\frac{n}{3})(-\frac{n}{3} - 1)\bar{V}_0^{-n/3} \bar{V}^{-n/3-2}]$. Setting $\bar{V} = \bar{V}_0$, we get $-\partial^2 E_p / \partial \bar{V}^2|_{R=R_0} = e'^2 \mathcal{M} N_A R_0^{-1} \bar{V}_0^{-2} \times$

$(1 - n)/9$. Substitution of this result into the 0-K equations $\partial^2 E_p / \partial \bar{V}^2|_{R=R_0} = \partial^2 \bar{U} / \partial \bar{V}^2|_{R=R_0} = 1/\kappa \bar{V}_0$ gives $e'^2 \mathcal{M}_{N_A R_0^{-1} \bar{V}_0^{-2}} (n - 1)/9 = 1/\kappa \bar{V}_0$; solving for n , we get (24.10).

24.10 A given positive ion has two negative ions at a distance R , two positive ions at $2R$, two negative ions at $3R$, two positive ions at $4R$, etc. The potential energy of interaction between one positive ion and all the other ions is $e'^2(-2/R + 2/2R - 2/3R + 2/4R - \dots) = -e'^2 \mathcal{M}/R$, where $\mathcal{M} = 2(1 - 1/2 + 1/3 - 1/4 + 1/5 - \dots)$. By symmetry, the potential energy of interaction between a given negative ion and all the other ions is $-e'^2 \mathcal{M}/R$. Multiplication of $-2e'^2 \mathcal{M}/R$ by N_A and division by 2 (to avoid counting each interionic interaction twice) gives $E_{\text{Coul}} = -e'^2 \mathcal{M} N_A / R$, as in Eq. (24.2). Equation (8.30) with $x = 2$ gives $\ln 2 = 1 - 1/2 + 1/3 - 1/4 + \dots$, so $\mathcal{M} = 2 \ln 2 = 1.38629$.

24.11 (a) $-E_c = (6.022 \times 10^{23} / \text{mol})(118 \text{ K}) \times (1.381 \times 10^{-23} \text{ J/mol-K}) \times [24.264(3.50 \text{ \AA}/3.75 \text{ \AA})^{12} - 28.908(3.50 \text{ \AA}/3.75 \text{ \AA})^6]$ and $E_c = 8.3 \text{ kJ/mol}$. **(b)** At equilibrium, $\partial E_p / \partial R = -\partial E_c / \partial R = 0 = N_0 e' [-12(24.264)\sigma^{12}/R^{13} + 6(28.908)\sigma^6/R^7]$; so $R_0^6 = [12(24.264)/6(28.908)]\sigma^6$ and $R_0/\sigma = 1.09$. The experimental value is $R_0/\sigma = (3.75 \text{ \AA})/(3.50 \text{ \AA}) = 1.07$.

24.12 $E_c \approx -24(6.022 \times 10^{23} / \text{mol})(0.0101 \text{ eV}) \times (1.602 \times 10^{-19} \text{ J/eV})[(3.50/3.75)^{12} - (3.50/3.75)^6] =$

$$5240 \text{ J/mol} = 1.25 \text{ kcal/mol}.$$

24.13 (a) Each of the 8 points at the corners is shared with a total of 8 unit cells. The point within the unit cell is not shared. So each unit cell has $8/8 + 1 = 2$ lattice points. (b) $8/8 + 2/2 = 2$.

24.14 (a) The unit cell has $8/8 + 6/2 = 4$ lattice points. There is one basis group at each lattice point, so each unit cell has 4 basis groups. (b) Each unit cell has $8/8 = 1$ lattice point and therefore has 1 basis group.

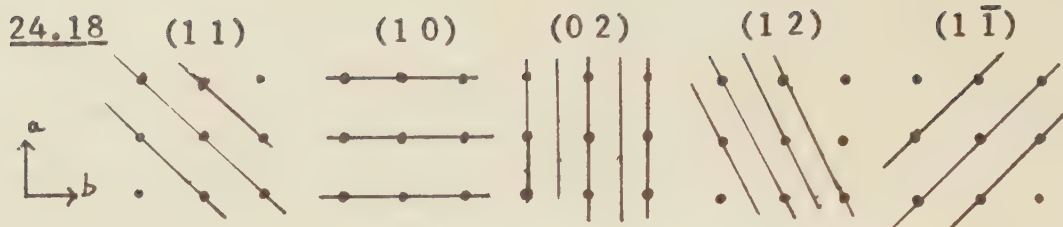
24.15 An orthorhombic lattice has 90° angles and Eq.

(24.12) gives $Z = \rho abc N_A / M = (2.93 \text{ g/cm}^3)(4.94 \times 10^{-8} \text{ cm}) \times (7.94 \times 10^{-8} \text{ cm})(5.72 \times 10^{-8} \text{ cm})(6.022 \times 10^{23} / \text{mol}) / (100.09 \text{ g/mol}) = 3.96 \approx 4$. There are 4 formula units and hence 4 Ca^{2+} ions per unit cell.

24.16 A tetragonal lattice has 90° angles and has $a = b$.

Equation (24.12) gives $\rho = MZ / abc N_A = (79.899 \text{ g/mol})2 / (4.594 \times 10^{-8} \text{ cm})^2 (2.959 \times 10^{-8} \text{ cm})(6.0220 \times 10^{23} / \text{mol}) = 4.249 \text{ g/cm}^3$.

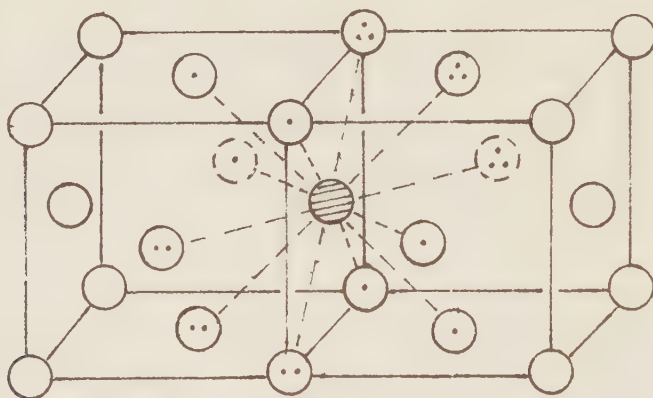
24.17 The c intercepts are all at ∞ , so the Miller l index is 0 in each case. With origin at the leftmost dot in the third row from the bottom, the leftmost p_2 plane intercepts the a axis at 1 and the b axis at $-\frac{1}{2}$. The reciprocals of these intercepts give the Miller indices as $(1\bar{2}0)$. With origin at the sixth dot in the bottom row, the s_3 surface intersects the a axis at 1 and is parallel to the b axis (intercept at ∞). The reciprocals give (100) as the Miller indices. (The p_2 planes can also be called $(\bar{1}20)$.)



24.19 A body-centered lattice has $8/8 + 1 = 2$ lattice points per unit cell. There is one basis group per lattice point, so there are 2 basis groups per unit cell. The basis therefore has $16/2 = 8$ molecules of COCl_2 .

24.20 For a spherical atom of radius r inscribed in a cubic unit cell of edge length $2r$, the atom's volume is $\frac{4}{3}\pi r^3$ and the unit cell's volume is $(2r)^3 = 8r^3$. The percentage of occupied space is $(\frac{4}{3}\pi r^3 / 8r^3) 100\% = (\pi/6) 100\% = 52.4\%$ and there is 47.6% empty space.

24.21



The shaded atom touches the six atoms that have a single dot; all seven of these atoms lie in the (1 1 1) plane. The shaded atom also touches the three atoms with two dots [which lie below the (1 1 1) plane of the shaded atom] and touches the three atoms with three dots [which lie above

the (111) plane of the shaded atom]. (The two atoms drawn with broken circles lie on the back faces of the unit cells.)

24.22 A cubic unit cell has right angles and has $a = b = c$, so Eq. (24.12) gives $\rho = MZ/abcN_A = (58.10 \text{ g/mol}) 4 / a^3 (6.022 \times 10^{23} / \text{mol}) = 2.48 \text{ g/cm}^3$. We get $a = 5.38 \times 10^{-8} \text{ cm} = 5.38 \text{ \AA}$. As is clear from Fig. 24.15b, the nearest-neighbor distance is $\frac{1}{2}a = 2.69 \text{ \AA}$.

24.23 The CsCl space lattice is simple cubic with $Z = 1$; Eq. (24.12) gives $a^3 = MZ/\rho N_A = (212.8 \text{ g/mol}) 1 / (4.44 \text{ g/cm}^3) (6.022 \times 10^{23} / \text{mol}) = 7.96 \times 10^{-23} \text{ cm}^3$, so $a = 4.30 \text{ \AA}$. From Fig. 24.16a, the nearest-neighbor distance is half the length of the diagonal of the cubic unit cell, which is $\frac{1}{2}\sqrt{3} a = 3.72 \text{ \AA}$.

24.24 From Fig. 24.17 and the associated discussion, the lattice is face-centered cubic with $a = b = c$; there are 8 F^- ions and $8/8 + 6/2 = 4 \text{ Ca}^{2+}$ ions per unit cell, so $Z = 4$. Equation (24.12) gives $a^3 = MZ/\rho N_A = (78.08 \text{ g/mol}) 4 / (3.18 \text{ g/cm}^3) (6.022 \times 10^{23} / \text{mol}) = 1.63 \times 10^{-22} \text{ cm}^3$ and $a = 5.46 \text{ \AA}$.

24.25 The lattice is face-centered cubic with 90° angles and $a = b = c$. Equation (24.12) gives $a = (MZ/\rho N_A)^{1/3} = [(12.011 \text{ g/mol}) 8 / (3.51 \text{ g/cm}^3) (6.022 \times 10^{23} / \text{mol})]^{1/3} = 3.569 \text{ \AA}$. Nearest-neighbor atoms are at points 000 and $\frac{1}{2}a \frac{1}{2}a \frac{1}{2}a$. The distance between the point (x, y, z) and the

origin is $(x^2 + y^2 + z^2)^{1/2}$, so the distance between nearest-neighbor atoms is $(a^2/16 + a^2/16 + a^2/16)^{1/2} = \frac{1}{2}\sqrt{3}a = 1.54_5 \text{ \AA}$.

24.26 There is one atom at each lattice point. In the face-centered cubic unit cell in Fig. 24.6, the closest distance between points is the distance between the point at a center of a face and a point at a corner of that face. (This also equals the distance between two points on adjacent faces.) The nearest-neighbor distance is thus one-half the length of the diagonal of a unit-cell face, namely, $\frac{1}{2}\sqrt{2}a = \frac{1}{2}\sqrt{2}(5.311 \text{ \AA}) = 3.755 \text{ \AA}$.

24.27 (a) From Fig. 24.9b, the (100) planes are spaced by $a = 4.70 \text{ \AA}$; Eq. (24.13) gives $\sin \theta = n\lambda/2d_{hkl} = n(1.54 \text{ \AA})/2(4.70 \text{ \AA}) = 0.1638n = 0.1638, 0.3276, 0.4914, \dots$. We get $\theta = 9.4^\circ, 19.1^\circ, 29.4^\circ, 40.9^\circ, 55.0^\circ$, and 79.4° . (b) Planes s and u in Fig. 24.9a are (110) planes. We see that the distance between these planes is half the length of the diagonal of the bottom face of the cubic unit cell, namely, $d_{110} = \frac{1}{2}\sqrt{2}a = a/\sqrt{2}$. [This also follows from the formula $d_{hkl} = a/(h^2 + k^2 + l^2)^{1/2}$ in Sec. 24.9.] So $\sin \theta = n(1.54 \text{ \AA})/2(3.32_3 \text{ \AA}) = 0.2317n$ and $\theta = 13.4^\circ, 27.6^\circ, 44.0^\circ$, and 67.9° .

24.28 (a) The $\sin^2 \theta$ values are 0.1069, 0.1424, 0.2849, 0.3916, 0.4273, 0.5696, and 0.6767. The ratios of these $\sin^2 \theta$ values are 1 : 1.33 : 2.67 : 3.66 : 4.00 : 5.33 : 6.33.

The lattice is therefore face-centered (F). (b) From Sec. 24.9, these are the 111, 200, 220, 311, 222, 400, and 331 reflections. (c) $a = \lambda(h^2 + k^2 + l^2)^{1/2}/2 \sin \theta = (1.542 \text{ \AA})(1^2 + 1^2 + 1^2)^{1/2}/2 \sin 19.08^\circ = 4.085 \text{ \AA}$. Similarly, the other angles give 4.086, 4.086, 4.086, 4.086, 4.086, and 4.085 \AA.

24.29 The band extends from 392 \AA to 422 \AA, which (using $\nu = c/\lambda$) is from $7.65 \times 10^{15} \text{ Hz}$ to $7.10 \times 10^{15} \text{ Hz}$. So the band width is $\Delta E = h \Delta \nu = (6.626 \times 10^{-34} \text{ J s}) \times (0.55 \times 10^{15} \text{ s}^{-1})(1 \text{ eV}/1.60 \times 10^{-19} \text{ J}) = 2.3 \text{ eV}$.

24.30 (a) Equations (24.19) and (22.38) give $U = kT^2(\partial \ln Z/\partial T)_{V,N} = kT^2[U_0/kT^2 - 3N(-\Theta_E/T^2)e^{-\Theta_E/T}/(1 - e^{-\Theta_E/T})] = U_0 + 3Nk\Theta_E/(e^{\Theta_E/T} - 1)$. (b) $C_V = (\partial U/\partial T)_V = 3Nk(\Theta_E/T)^2 e^{\Theta_E/T}/(e^{\Theta_E/T} - 1)^2$.

24.31 $A = -kT \ln Z = U_0 + 3NkT \ln(1 - e^{-\Theta_E/T})$.

24.32 $U = U_0 + 3Nk\Theta_E/[\exp(\Theta_E/T) - 1]$ (p. 885).

(a) In the high-T limit, Θ_E/T goes to 0 and we can use the e^x Taylor series to write $\exp(\Theta_E/T) - 1 \approx (1 + \Theta_E/T + \dots) - 1 = \Theta_E/T$. Then $U \rightarrow U_0 + 3NkT$. (b) In the low-T limit, $\exp(\Theta_E/T)$ is very large and the -1 in the denominator can be neglected to give $U \rightarrow U_0 + 3Nk\Theta_E/e^{\Theta_E/T}$, which becomes U_0 at $T = 0$.

24.33 (a) $S = U/T + k \ln Z = U_0/T + 3Nk(\Theta_E/T)(e^{\Theta_E/T} - 1) - U_0/T - 3Nk \ln(1 - e^{-\Theta_E/T}) = 3Nk(\Theta_E/T)/(e^{\Theta_E/T} - 1) - 3Nk \ln(1 - e^{-\Theta_E/T})$. (b) For Al, $N/n = N_A$, $Nk/n = R$, $\bar{S} = 3(1.987 \text{ cal/mol-K})(240 \text{ K}/298 \text{ K})/(e^{240/298} - 1) - 3(1.987 \text{ cal/mol-K}) \ln(1 - e^{-240/298}) = 7.41 \text{ cal/mol-K}$. For diamond, replacement of 240 by 1220 gives $\bar{S} = 0.514 \text{ cal/mol-K}$. Agreement with experiment is fair.

24.34 (a) $\Theta_E/T = (240 \text{ K})/(50 \text{ K}) = 4.8$. Dividing Eq. (24.20) by n and using $Nk/n = N_A k = R$, we have $\bar{C}_V = 3(1.987 \text{ cal/mol-K})(4.8)^2 e^{4.8}/(e^{4.8} - 1)^2 = 1.15 \text{ cal/mol-K}$. (b) $\Theta_E/T = (240 \text{ K})/(100 \text{ K}) = 2.40$, and we get $\bar{C}_V = 3.77 \text{ cal/mol-K}$. (c) $\Theta_E/T = 1.00$ and $\bar{C}_V = 5.49 \text{ cal/mol-K}$. (d) $\Theta_E/T = 0.600$ and $\bar{C}_V = 5.79 \text{ cal/mol-K}$.

24.35 (a) Using the equation in Problem 15.14, we have $U = kT^2(\partial \ln Z/\partial T)_{V,N} = kT^2\{U_0/kT^2 - (9N/\nu_m^3) \int_0^{\nu_m} [e^{-h\nu/kT}(-h\nu/kT^2)/(1 - e^{-h\nu/kT})] \nu^2 d\nu\} = U_0 + (9Nh/\nu_m^3) \int_0^{\nu_m} [\nu^3/(e^{h\nu/kT} - 1)] d\nu$. (b) $C_V = (\partial U/\partial T)_{V,N} = (9Nh/\nu_m^3) \int_0^{\nu_m} [(h\nu^4/kT^2)e^{h\nu/kT}/(e^{h\nu/kT} - 1)^2] d\nu$. Let $x = h\nu/kT$. Then $d\nu = (kT/h) dx$ and $C_V = (9Nh^2/kT^2 \nu_m^3) \times \int_0^{h\nu_m/kT} [(kTx/h)^4 e^x/(e^x - 1)^2](kT/h) dx = 9Nk(T/\Theta_D)^3 \times \int_0^{\Theta_D/T} [x^4 e^x/(e^x - 1)^2] dx$, where $\Theta_D = h\nu_m/k$.

24.36 One mole of a metallic element has N_A molecules, and the Einstein and Debye theories show that the limit-

ing high-temperature \bar{C}_V for a solid metallic element is $3N_A k = 3R$. The Debye temperature for most metals is not high, so \bar{C}_V of most metals is reasonably close to $3R$ for temperatures near room temperature. Hence, $\bar{C}_V \approx \bar{C}_P \approx 3R = 6 \text{ cal/mol-K}$. For a metallic element, $\bar{C}_P = c_P(A_r \text{ g/mol})$, where c_P is the specific heat (capacity) and A_r is the (dimensionless) atomic weight. Hence, $c_P A_r = \bar{C}_P \text{ mol/g} \approx 6 \text{ cal/(g K)}$.

24.37 (a) T is quite low; Eq. (24.27) gives $(\Theta_D)^3 = T^3 (12\pi^4 N_A k / 5\bar{C}_V) = (10 \text{ K})^3 12\pi^4 (6.022 \times 10^{23} / \text{mol}) \times (1.381 \times 10^{-23} \text{ J/K}) / 5(0.96 \times 4.184 \text{ J/mol-K}) = 4.84 \times 10^5 \text{ K}^3$ and $\Theta_D = 78.5 \text{ K}$. (b) Equation (24.27) shows that C_V is proportional to T^3 at low temperatures, so at 12 K we have $\bar{C}_V = (12/10)^3 (0.96 \text{ cal/mol-K}) = 1.66 \text{ cal/mol-K}$.

24.38 (a) $T/\Theta_D = 298 \text{ K} / 320 \text{ K} = 0.931$. Figure 24.27 gives $C_V/3Nk = 0.94$ at $T/\Theta_D = 0.93$. NaCl has $2N_A$ particles per mole and $Nk/\gamma = 2N_A k = 2R$, so $\bar{C}_{V, \text{Debye}} = 3(2R)(0.94) = 47 \text{ J/mol-K}$. \bar{C}_V and \bar{C}_P don't differ greatly for solids at room temperature (Sec. 4.5) and the Appendix \bar{C}_P value is 50.5 J/mol-K . (b) $T/\Theta_D = 298/2230 = 0.134$. Figure 24.27 gives $C_V/3Nk = 0.17$ at $T/\Theta_D = 0.134$, so $\bar{C}_V = 3R(0.17) = 4.2 \text{ J/mol-K}$ compared to the experimental $\bar{C}_P = 6.1 \text{ J/mol-K}$.

24.39 (a) Adding Eq. (24.28) to (24.27), we have at low T for a metal: $\bar{C}_V = (12\pi^4 N_A k / 5)(T/\Theta_D)^3 + bT$ and $\bar{C}_V/T =$

$b + (12\pi^4 R/5\Theta_D^3)T^2$. A plot of \bar{C}_V/T vs. T^2 should be linear with intercept b and slope $12\pi^4 R/5\Theta_D^3$. (b) The data are:

$10^3(\bar{C}_V/T)/(\text{cal/mol-K}^2)$	0.188	0.313	0.523	0.757
T^2/K^2	1.82	4.00	9.00	16.00

The straight-line fit is fairly good; the intercept is $1.4 \times 10^{-4} \text{ cal mol}^{-1} \text{ K}^{-2} = b$; the slope is $3.95 \times 10^{-5} \text{ cal/mol-K}^4$. So $\Theta_D^3 = 12\pi^4(1.987 \text{ cal/mol-K})/5(3.95 \times 10^{-5} \text{ cal/mol-K}^4) = 1.176 \times 10^7 \text{ K}^3$ and $\Theta_D = 227 \text{ K}$.

$$24.40 \text{ (a) } S_{\text{solid}} - S_{\text{solid},0} = S_{\text{solid}} = \int_0^T (C_P/T') dT' \approx \int_0^T (C_V/T') dT' = (12\pi^4 Nk/5\Theta_D^3) \int_0^T T'^2 dT' = 4\pi^4 NkT^3/5\Theta_D^3.$$

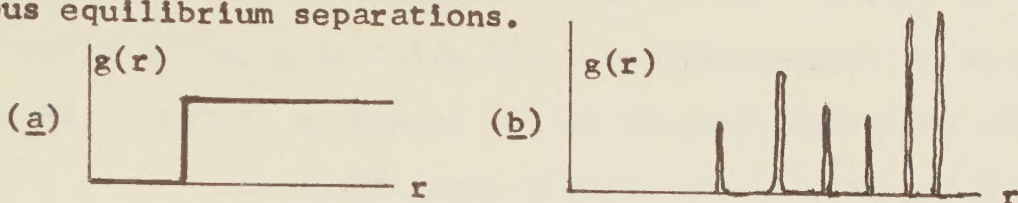
$$\text{(b) } S_{\text{gas}} - S_{\text{solid}} = S_{\text{tr}} + S_{\text{el}} - S_{\text{solid}} = nR \ln g_{\text{el},0} + 2.5nR + nR \ln [(2\pi m)^{3/2} (kT)^{5/2} / h^3 P] - 4\pi^4 NkT^3/5\Theta_D^3 =$$

$$\Delta H_{\text{sub}}/T. \text{ Solving this equation for } P, \text{ we get } P = g_{\text{el},0} \times (2\pi m)^{3/2} (kT_e)^{5/2} h^{-3} \exp[-4\pi^4 NkT^3/5nR\Theta_D^3] \exp(-\Delta H_{\text{sub}}/nRT).$$

At very low T ($T \ll \Theta_D$), the first exponential is accurately approximated as 1, and $P = g_{\text{el},0} (2\pi m)^{3/2} (kT_e)^{5/2} \times h^{-3} e^{-\Delta H_{\text{sub}}/nRT}$, which has the form $AT^{5/2} e^{-c/T}$, since ΔH_{sub} varies only slowly with T . As $T \rightarrow 0$, both $T^{5/2}$ and $e^{-c/T}$ go to 0, so $P \rightarrow 0$.

24.41 (a) For a gas of hard spheres of diameter d , there is zero probability for a pair of molecules to be closer than d , and (since there are no intermolecular forces for distances greater than d) there is equal probability for all distances greater than d to occur. (b) For a solid,

the atoms, molecules, or ions vibrate about fixed equilibrium locations and $g(r)$ shows narrow peaks at the various equilibrium separations.



24.42 U of an ideal gas is independent of pressure, so

$$\bar{U}_{\text{liq}} - \bar{U}_{\text{gas}} = -\Delta U_{\text{vap},298}^{\circ} = -(\Delta H_{298}^{\circ} - P^{\circ}\Delta V^{\circ}) \approx -\Delta H_{298}^{\circ} + P^{\circ}\bar{V}_{\text{gas}}^{\circ} = -\Delta H_{298}^{\circ} + RT = -44012 \text{ J/mol} + RT = -41.53 \text{ kJ/mol}$$

S of an ideal gas depends on P . The 25°C molar volume of liquid water (density 0.99704 g/cm^3) is 18.07 cm^3 .

We use the following 25°C path for one mole:

$$\text{liq}(P^{\circ}, 18.07 \text{ cm}^3) \xrightarrow{1} \text{Ideal gas}(P^{\circ}) \xrightarrow{2} \text{Ideal gas}(18.07 \text{ cm}^3).$$

The Appendix and Eq. (3.29) give $S_{\text{liq}} - S_{\text{gas}} = -(\Delta S_1 + \Delta S_2) = -118.92 \text{ J/mol-K} - R \ln [(18.07 \text{ cm}^3)P^{\circ}/RT] = -(118.92 - 60.06) \text{ J/mol-K} = -58.86 \text{ J/mol-K} = -14.07 \text{ cal/mol-K}.$

24.43 (a) Special theory of relativity, Brownian motion theory, distance travelled by diffusing molecules, photon explanation of photoelectric effect, quantum theory of C_V of solids, Bose-Einstein statistics. (b) Probability interpretation of wave function, work on matrix mechanics form of quantum mechanics, calculation of E_c of ionic solids, Born-Oppenheimer approximation. (c) Debye-Hückel theory, Debye theory of C_V of solids, Debye-Langevin equation, Debye equation for ionic diffusion-controlled reactions, work on electrical conductivity of solutions.

24.44 (a) One gram of solid Ar has a volume of $(1.00 \text{ g})/$

$(1.59 \text{ g/cm}^3) = 0.629 \text{ cm}^3$. The hard-sphere atoms occupy
 $(100 - 26)\% = 74\%$ of this volume, which is 0.46_5 cm^3 . One
 gram of liquid occupies $(1.00 \text{ g})/(1.42 \text{ g/cm}^3) = 0.704 \text{ cm}^3$.
 The empty-space volume in the liquid is $(0.704 - 0.46_5) \text{ cm}^3$
 $= 0.23_9 \text{ cm}^3$, so the percent empty space is
 $(0.23_9/0.704)100\% = 34\%$. (b) The volume of 1 g of the gas
 is $V \approx (1\text{g}/39.9 \text{ g mol}^{-1})RT/P = 179 \text{ cm}^3$. The percent of
 filled space in the gas is $(0.46_5/179)100\% = 0.26\%$ and
 the empty space is 99.74%.

24.45 (a) T. (b) T. (c) T. (d) T.

EXAMINATION COPY



McGraw-Hill



Book Company

7-037475-9

Not For Sale