


STUDENT'S SOLUTION MANUAL

to accompany

PHYSICAL CHEMISTRY



Joseph H. Noggle



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NOGGLE

PHYSICAL CHEMISTRY

THIRD EDITION

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
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CHAPTER 1 *Properties of Matter*

SECTION 1.1

1.1

To obtain molar volume, we divide the molecular weight by the density. This is easier to see if you just consider the units of density and molar volume.

$$\rho = 37.7 \cdot \frac{\text{g}}{\text{liter}}$$

Calculating molecular weight:

$$\text{MW} = 32.066 \cdot \frac{\text{g}}{\text{mole}} + 2 \cdot 15.9994 \cdot \frac{\text{g}}{\text{mole}} \quad \text{MW} = 64.065 \cdot \frac{\text{g}}{\text{mole}}$$

Calculating molar volume:

$$V = \frac{\text{MW}}{\rho} \quad V = 1.699 \cdot \frac{\text{liter}}{\text{mole}}$$

1.3

Given information:

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T = 313.15 \cdot \text{K} \quad V = 250 \cdot \text{cm}^3 \quad V = 2.5 \cdot 10^{-4} \cdot \text{m}^3$$

For both RK equation and ideal gas, we must first calculate the molar volume:

$$n = \frac{58.0 \cdot \text{g}}{2 \cdot 12.011 \cdot \frac{\text{g}}{\text{mole}} + 6 \cdot 1.00794 \cdot \frac{\text{g}}{\text{mole}}}$$

$$n = 1.929 \cdot \text{mole}$$

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$$V_m = \frac{V}{n} \quad V_m = 1.296 \cdot 10^{-4} \cdot \frac{\text{m}^3}{\text{mole}}$$

For the ideal gas law result:

$$P = \frac{R \cdot T}{V_m} \quad P = 2.009 \cdot 10^7 \cdot \text{Pa} \quad \text{MPa} \quad 10^6 \cdot \text{Pa}$$

$$P = 20.09 \cdot \text{MPa}$$

For the RK equation, we get the parameters from Table 1.1.

$$a = 9.882 \cdot \frac{\text{Pa} \cdot \text{m}^6}{\text{mole}^2 \cdot \text{K}^{0.5}} \quad b = 56.84 \cdot 10^{-6} \cdot \frac{\text{m}^3}{\text{mole}}$$

$$P = \frac{R \cdot T}{V_m - b} - \frac{a}{T \cdot V_m \cdot (V_m + b)}$$

$$P = 1.267 \cdot 10^7 \cdot \text{Pa}$$

$$P = 12.67 \cdot \text{MPa}$$

The result from the RK equation is almost half that obtained using the ideal gas law.

1.5

We first convert the given density to molar volume, and then plug this volume into the RK equation to obtain a pressure. The constants a and b for neon can be obtained from Table 1.1.

Given information:

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T = 298.15 \cdot \text{K} \quad \rho = 10.0 \cdot \frac{\text{g}}{\text{liter}} \quad \text{MW} = 20.179 \cdot \frac{\text{g}}{\text{mole}}$$

$$a = 0.1488 \cdot \frac{\text{Pa} \cdot \text{m}^6}{\text{mole}^2 \cdot \text{K}^{0.5}} \quad b = 12.22 \cdot 10^{-6} \cdot \frac{\text{m}^3}{\text{mole}}$$

Calculating molar volume from density, converting liters to cubic meters:

$$V_m = \frac{\text{MW}}{\rho}$$

$$V_m = 0.002 \cdot \frac{\text{m}^3}{\text{mole}}$$

Calculation of pressure:

$$P = \frac{R \cdot T}{V_m - b} - \frac{a}{T \cdot V_m \cdot (V_m + b)}$$

$$P = 1.234 \cdot 10^6 \cdot \text{Pa} \quad \text{MPa} = 10^6 \cdot \text{Pa}$$

$$P = 1.23 \cdot \text{MPa}$$

1.7

The easiest way to do this is to find the molar volume and convert this to a density. Given information:

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T = 400 \cdot \text{K} \quad MW = 3 \cdot 12.011 \cdot \frac{\text{g}}{\text{mole}} + 6 \cdot 1.00794 \cdot \frac{\text{g}}{\text{mole}} \quad MW = 42.081 \cdot \frac{\text{g}}{\text{mole}}$$

$$P = 10 \cdot \text{atm} \cdot \frac{101325 \cdot \text{Pa}}{1 \cdot \text{atm}} \quad P = 1.013 \cdot 10^6 \cdot \text{Pa} \quad a = 0.8391 \cdot \frac{\text{Pa} \cdot \text{m}^6}{\text{mole}} \quad b = 82.01 \cdot 10^{-6} \cdot \frac{\text{m}^3}{\text{mole}}$$

For the ideal gas case:

$$V_m = \frac{R \cdot T}{P} \quad V_m = 0.003282 \cdot \frac{\text{m}^3}{\text{mole}} \quad \rho = \frac{MW}{V_m} \quad \rho = 12.8 \cdot \frac{\text{g}}{\text{liter}}$$

For the van der Waals equation, we rearrange it into a cubic equation in volume (eq. 1.6), and then solve for volume:

$$V_m = \text{root} \left(P \cdot V_m^3 + (R \cdot T - b \cdot P) \cdot V_m^2 - a \cdot V_m - a \cdot b, V_m \right) \quad V_m = 0.003105 \cdot \frac{\text{m}^3}{\text{mole}}$$

$$\rho = \frac{MW}{V_m} \quad \rho = 13.6 \cdot \frac{\text{g}}{\text{liter}}$$

Given information:

$$R = 8.31451 \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T = 300 \cdot \text{K}$$

$$P = 60 \cdot \text{atm} \cdot \frac{101325 \cdot \text{Pa}}{1 \cdot \text{atm}} \quad P = 6.08 \cdot 10^6 \cdot \text{Pa} \quad a = 0.1364 \cdot \frac{\text{Pa} \cdot \text{m}^6}{\text{mole}} \quad b = 38.58 \cdot 10^{-6} \cdot \frac{\text{m}^3}{\text{mole}}$$

We solve the ideal gas case to use as an initial guess to solve the van der Waals equation:

$$V_m = \frac{R \cdot T}{P} \quad V_m = 4.102892 \cdot 10^{-4} \cdot \frac{\text{m}^3}{\text{mole}}$$

We rearrange the van der Waals equation into a cubic equation in volume (eq. 1.6), and then solve for volume:

$$V_m = \text{root } P \cdot V_m^3 - (R \cdot T + b \cdot P) \cdot V_m^2 - a \cdot V_m - a \cdot b \cdot V_m \quad V_m = 398 \cdot \frac{\text{cm}^3}{\text{mole}}$$

SECTION 1.2

1.11

The necessary equations come straight from Table 1.2. Given information:

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T = 125 \cdot \text{K}$$

For the van der Waals equation:

$$a = 0.2283 \cdot \frac{\text{Pa} \cdot \text{m}^6}{\text{mole}} \quad b = 42.69 \cdot 10^{-6} \cdot \frac{\text{m}^3}{\text{mole}}$$

$$B = b - \frac{a}{R \cdot T} \quad B = -177 \cdot \frac{\text{cm}^3}{\text{mole}}$$

For the RK equation:

$$a = 3.194 \cdot \frac{\text{Pa} \cdot \text{m}^6}{\text{mole} \cdot \text{K}^{0.5}} \quad b = 29.59 \cdot 10^{-6} \cdot \frac{\text{m}^3}{\text{mole}}$$

$$B = b - \frac{a}{R \cdot T^{1.5}} \quad B = -245 \cdot \frac{\text{cm}^3}{\text{mole}}$$

For the Berthelot equation:

$$T_c = 190.6 \cdot \text{K} \quad P_c = 4.641 \cdot 10^6 \cdot \text{Pa}$$

$$B = \frac{9 \cdot R \cdot T_c}{128 \cdot P_c} \left(1 - \frac{6 \cdot T_c^2}{T^2} \right) \quad B = -311 \cdot \frac{\text{cm}^3}{\text{mole}}$$

As was noted in the text, the van der Waals equation gives the least accurate result, and the RK and Berthelot expressions are both fairly accurate.

1.13

At the Boyle temperature, the second virial coefficient equals zero. We use the equations in Table 1.2, set B equal to zero, and solve for temperature.

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

For the van der Waals equation:

$$a = 0.1342 \cdot \frac{\text{Pa} \cdot \text{m}^6}{\text{mole}}$$

$$b = 31.67 \cdot 10^{-6} \cdot \frac{\text{m}^3}{\text{mole}}$$

$$B = b - \frac{a}{R \cdot T_B} = 0$$

$$T_B = \frac{a}{b \cdot R}$$

$$T_B = 510 \cdot \text{K}$$

For the Berthelot equation:

$$T_c = 151 \cdot \text{K}$$

$$P_c = 4.955 \cdot 10^6 \cdot \text{Pa}$$

$$B = \frac{9 \cdot R \cdot T_c}{128 \cdot P_c} \left(1 - \frac{6 \cdot T_c^2}{T^2} \right) = 0$$

$$T_B = \sqrt{6} \cdot T_c$$

$$T_B = 370 \cdot \text{K}$$

For the RK equation:

$$a = 1.671 \cdot \frac{\text{Pa} \cdot \text{m}^6}{\text{mole} \cdot \text{K}^{0.5}}$$

$$b = 21.95 \cdot 10^{-6} \cdot \frac{\text{m}^3}{\text{mole}}$$

$$B = b - \frac{a}{R \cdot T_B^{1.5}} = 0$$

$$T_B = \left(\frac{a}{b \cdot R} \right)^{\frac{2}{3}}$$

$$T_B = 438 \cdot \text{K}$$

1.15

At the Boyle temperature, the second virial coefficient equals zero. We set the expression for the Boyle temperature equal to zero and solve for temperature. As noted in Table 1.3, the Beattie-Bridgeman constants given are for volume in liters and pressure in atmospheres, so we must use a different value for R . From Table 1.2:

$$R = 0.08206 \quad B(T) = B_0 - \frac{A_0}{R \cdot T} - \frac{c}{T^3} = 0$$

$$A_0 = 0.1975 \quad B_0 = 0.02096 \quad c = 0.050 \cdot 10^{-4}$$

We can calculate B at several temperatures to get some idea of where the Boyle temperature is:

$$T = 400, 300, \dots, 100$$

T	$B_0 - \frac{A_0}{R \cdot T} - \frac{c}{T^3}$
400	0.015
300	0.013
200	0.009
100	-0.004

The root lies somewhere between 100 K and 200 K.

We use 100 K as our first guess for the Boyle temperature.

$$T_B = 100 \cdot K$$

$$T_B = \text{root} \left(B_0 - \frac{A_0}{R \cdot T_B} - \frac{c}{T_B^3}, T_B \right)$$

$$T_B = 117 \cdot K$$

1.17

This is similar to example 1.6 in the text. The virial series can be written as:

$$z = 1 + Bc + Cc^2 + \dots$$

where $c = 1/V$. From the data given, we must first calculate the concentration:

$$T := 295 \text{ K} \quad R := 8.31451 \frac{\text{joule}}{\text{mole K}} \quad V := \frac{RT}{P} \quad c := \frac{1}{V}$$

Now, we can fit the data using a nonlinear regression program. Doing this, we obtain:

$$B = -143 \text{ cm}^3/\text{mole}$$

$$C = 5.7 \cdot 10^3 \text{ cm}^6/\text{mole}^2$$

1.19

$$i = 0..6 \quad R = 8.31451 \frac{\text{joule}}{\text{mole K}} \quad T = 700 \cdot \text{K} \quad \text{MPa} = 1000000 \cdot \text{Pa}$$

The Virial Series typically takes the form $z = 1 + B(T) \cdot c^2 + C(T) \cdot c^3 + \dots$, so therefore we need to relate concentration, c , to the compressibility factor, z . Recalling that $z = P \cdot V_m / (R \cdot T)$ and $c = 1/V_m$, $c = P / (z \cdot R \cdot T)$.

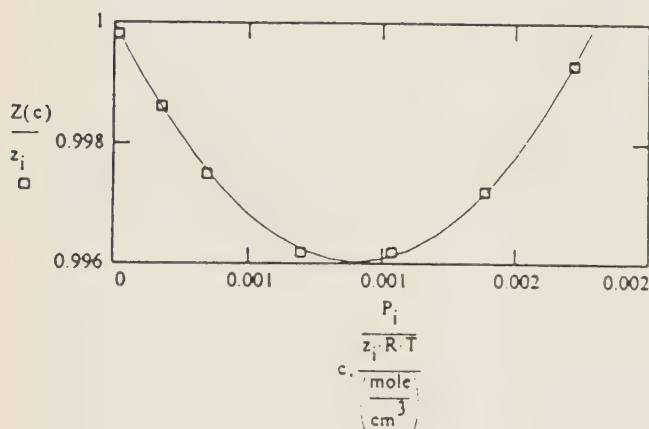
$P_i =$	$z_i =$	$\frac{P_i}{z_i \cdot R \cdot T}$ $\left(\frac{\text{mole}}{\text{cm}^3} \right)$
0.1 MPa	.9998	
1.0 MPa	.9986	
2.0 MPa	.9973	$1.719 \cdot 10^{-5}$
4.0 MPa	.9962	$1.721 \cdot 10^{-4}$
6.0 MPa	.9962	$3.445 \cdot 10^{-4}$
8.0 MPa	.9972	$6.899 \cdot 10^{-4}$
10.0 MPa	.9993	$1.035 \cdot 10^{-3}$
		$1.378 \cdot 10^{-3}$
		$1.719 \cdot 10^{-3}$

A least squares fit of the compressibility factor, z , versus concentration, c , to the form:

$$z = 1 + B \cdot c + C \cdot c^2 \quad \text{yields } B = -8.817 \text{ cm}^3/\text{mol} \quad \text{and } C = 4.9 \cdot 10^3 \text{ cm}^6/\text{mol}^2$$

$$c = 0, .0001 \dots .002$$

$$Z(c) = 1 - 8.817 \cdot c - 4.9 \cdot 10^3 \cdot c^2$$



This plot shows compressibility factor versus concentration. The parabolic shape shows very clearly the importance of the third virial coefficient in this case.

1.21

The derivation is very similar to example 1.8 from the text. First, start with the RK equation. Multiply through by the molar volume and divide by RT to obtain the compressibility, z , on one side of the equation.

$$P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T} V_m (V_m + b)}$$

$$z = \frac{PV}{RT} = \frac{V_m}{V_m - b} - \frac{a}{RT^{3/2} (V_m + b)}$$

Divide the first term by molar volume on the top and bottom:

$$z = \frac{1}{1 - \frac{b}{V_m}} - \frac{a}{RT^{3/2}(V_m + b)}$$

Expand the first term using a power series ($x = b/V_m$):

$$\frac{1}{1 - x} = 1 + x + x^2 + x^3 + \dots$$

$$z = 1 + \frac{b}{V_m} + \frac{b^2}{V_m^2} + \frac{b^3}{V_m^3} + \dots - \frac{a}{RT^{3/2}(V_m + b)}$$

Divide the second term by $V_m RT^{3/2}$ on the top and bottom, and expand again in a power series ($x = -b/V_m$):

$$z = 1 + \frac{b}{V_m} + \frac{b^2}{V_m^2} + \frac{b^3}{V_m^3} + \dots - \frac{a/V_m RT^{3/2}}{1 + \frac{b}{V_m}}$$

$$z = 1 + \frac{b}{V_m} + \frac{b^2}{V_m^2} + \frac{b^3}{V_m^3} + \dots - \frac{a}{V_m RT^{3/2}} \left(1 - \frac{b}{V_m} + \frac{b^2}{V_m^2} - \dots \right)$$

$$z = 1 + \frac{b}{V_m} + \frac{b^2}{V_m^2} + \frac{b^3}{V_m^3} + \dots - \frac{a}{V_m RT^{3/2}} + \frac{ab}{V_m^2 RT^{3/2}} - \frac{ab^2}{V_m^3 RT^{3/2}} + \dots$$

Collect like powers of V_m , and compare to the virial equation:

$$z = 1 + \frac{1}{V_m} \left(b - \frac{a}{RT^{3/2}} \right) + \frac{1}{V_m^2} \left(b^2 + \frac{ab}{RT^{3/2}} \right) + \frac{1}{V_m^3} \left(b^3 - \frac{ab^2}{RT^{3/2}} \right) - \dots$$

$$z = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \frac{D(T)}{V_m^3} + \dots$$

Therefore:

$$B(T) = b - \frac{a}{RT^{3/2}} \quad C(T) = b^2 + \frac{ab}{RT^{3/2}}$$

1.23

We use equation 1.11 and the expressions for the virial coefficients derived in problem 1.22:

$$\gamma = \frac{C - B^2}{RT} \qquad B(T) = b - \frac{a}{RT^2} \qquad C(T) = b^2$$

$$\gamma = \frac{C - B^2}{RT} = \frac{1}{RT} \left(b^2 - \left(b - \frac{a}{RT^2} \right)^2 \right)$$

$$\gamma = \frac{1}{RT} \left(b^2 - \left(b^2 - \frac{2ab}{RT^2} + \frac{a^2}{R^2T^4} \right) \right)$$

$$\gamma = \frac{1}{RT} \left(b^2 - b^2 + \frac{2ab}{RT^2} - \frac{a^2}{R^2T^4} \right) = \frac{1}{RT} \left(\frac{2ab}{RT^2} - \frac{a^2}{R^2T^4} \right)$$

$$\gamma = \frac{2ab}{R^2T^3} - \frac{a^2}{R^3T^5}$$

1.25

Table 1.2 gives us $B(T)$ and $C(T)$ for the RK equation in terms of the constants a and b . Equation 1.1 from the text gives the relationship between the coefficients of the truncated virial series, β and γ , and $B(T)$ and $C(T)$. We plug the expressions from Table 1.2 into equations 1.11.

$$B(T) = b - \frac{a}{RT^{3/2}} \qquad C(T) = b^2 + \frac{ab}{RT^{3/2}}$$

$$\beta = B \qquad \beta = b - \frac{a}{RT^{3/2}}$$

$$\gamma = \frac{C - B^2}{RT} \qquad \gamma = \frac{1}{RT} \left(b^2 + \frac{ab}{RT^{3/2}} - \left(b - \frac{a}{RT^{3/2}} \right)^2 \right)$$

$$\gamma = \frac{1}{RT} \left(b^2 + \frac{ab}{RT^{3/2}} - \left(b^2 - \frac{2ab}{RT^{3/2}} + \frac{a^2}{R^2 T^3} \right) \right)$$

$$\gamma = \frac{1}{RT} \left(b^2 + \frac{ab}{RT^{3/2}} - b^2 + \frac{2ab}{RT^{3/2}} - \frac{a^2}{R^2 T^3} \right)$$

$$\gamma = \frac{1}{RT} \left(\frac{3ab}{RT^{3/2}} - \frac{a^2}{R^2 T^3} \right) = \frac{3ab}{R^2 T^{5/2}} - \frac{a^2}{R^3 T^4}$$

We plug the results for β and γ into the original equation to obtain:

$$V_m = \frac{RT}{P} + \left(b - \frac{a}{RT^{3/2}} \right) + \left(\frac{3ab}{R^2 T^{5/2}} - \frac{a^2}{R^3 T^4} \right) P$$

1.27

Table 1.2 gives us the expressions for the virial coefficients in terms of the Beattie-Bridgeman constants. We plug these in, along with R in the correct units, to obtain equations for the virial coefficients. The Beattie-Bridgeman constants for hydrogen can be found on Table 1.3.

$$A_0 = 0.1975 \quad B_0 = 0.0296 \quad c = 500$$

$$a = -0.00506 \quad b = -0.04359 \quad R = 0.082057$$

$$B = B_0 - \frac{A_0}{R \cdot T} - \frac{c}{T^3}$$

$$C = \frac{A_0 \cdot a}{R \cdot T} - B_0 \cdot b - \frac{B_0 \cdot c}{T^3}$$

$$B = 2.96 \cdot 10^{-2} - \frac{2.407}{T} - \frac{500}{T^3}$$

$$C = \frac{1.22 \cdot 10^{-2}}{T} + 1.29 \cdot 10^{-3} - \frac{14.8}{T^3}$$

Now, to obtain the equation for the molar volume as a function of pressure, we start with the virial series in pressure, equation 1.10. We divide this by pressure to obtain molar volume on one side of the equation by itself.

$$P \cdot V_m = R \cdot T + \beta \cdot P + \gamma \cdot P^2 + \dots$$

$$V_m = \frac{R \cdot T}{P} + \beta - \gamma \cdot P$$

We use equations 1.11 to convert the virial coefficients we have derived into the coefficients for this equation, and plug in 250 for the temperature:

$$T = 250$$

$$RT = (0.082057) \cdot (250)$$

$$RT = 20.51425$$

$$\beta = B$$

$$\gamma = \frac{C - B^2}{R \cdot T}$$

$$\beta = 2.96 \cdot 10^{-2} - \frac{2.407}{T} - \frac{500}{T^3}$$

$$\gamma = 12.1866 \cdot \left[\frac{1.22 \cdot 10^{-2}}{T} - 1.29 \cdot 10^{-3} - \frac{14.8}{T^3} - 2.96 \cdot 10^{-2} - \frac{2.407}{T} - \frac{500}{T^3} \right]$$

$$\beta = 1.994 \cdot 10^{-2}$$

$$\gamma = 4.583 \cdot 10^{-5}$$

This gives us the expression we need to calculate the molar volume at 100 atm.

$$P = 100 \cdot \text{atm}$$

$$V_m = \frac{20.514 \cdot \text{liter} \cdot \text{atm}}{P} + 1.994 \cdot 10^{-2} \cdot \text{liter} + 4.583 \cdot 10^{-5} \cdot \frac{\text{liter}}{\text{atm}} \cdot P$$

$$V_m = 0.2297 \cdot \frac{\text{liter}}{\text{mole}}$$

SECTION 1.3

1.29

As was discussed in the text, we should avoid using the relationship $b = V_c/3$, since the critical volume is usually not known very accurately. The expressions for P_c and T_c , derived in the previous problem, are:

$$P_c = \sqrt{\frac{aR}{216b^3}} \qquad T_c = \sqrt{\frac{8a}{27bR}}$$

We solve these equations for a and b . There are many different ways to do this. Rearranging the expression for the critical temperature:

$$T_c^2 = \frac{8a}{27bR} \qquad a = \frac{27bRT_c^2}{8}$$

Plugging this into the equation for the critical pressure, we obtain:

$$P_c^2 = \frac{aR}{216b^3} = \left(\frac{27bRT_c^2}{8}\right)\left(\frac{R}{216b^3}\right)$$

$$P_c^2 = \frac{27bR^2T_c^2}{8 \times 216b^3} = \frac{R^2T_c^2}{64b^2}$$

$$b^2 = \frac{R^2T_c^2}{64P_c^2} \qquad b = \frac{RT_c}{8P_c}$$

We plug this result back into the expression for a derived from the critical temperature, and simplify:

$$a = \frac{27bRT_c^2}{8} = \left(\frac{27RT_c^2}{8}\right)\left(\frac{RT_c}{8P_c}\right) = \frac{27R^2T_c^3}{64P_c}$$

$$a = \frac{27R^2T_c^3}{64P_c} \qquad b = \frac{RT_c}{8P_c}$$

1.31

The equations for a and b come from Table 1.4.

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T_c = 318 \cdot \text{K} \quad P_c = 5.88 \cdot 10^6 \cdot \text{Pa}$$

$$a = 0.42748 \cdot \frac{R^2 \cdot T_c^{2.5}}{P_c} \quad a = 9.063 \cdot \frac{\text{Pa} \cdot \text{m}^6}{\text{mole}^2 \cdot \text{K}^{0.5}}$$

$$b = 0.086640 \cdot \frac{R \cdot T_c}{P_c} \quad b = 3.9 \cdot 10^{-5} \cdot \frac{\text{m}^3}{\text{mole}}$$

1.33

Calculating the critical compressibility:

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T_c = 536.4 \cdot \text{K} \quad P_c = 5.5 \cdot 10^6 \cdot \text{Pa} \quad V_c = 240 \cdot \frac{\text{cm}^3}{\text{mole}}$$

$$z_c = \frac{P_c \cdot V_c}{R \cdot T_c} \quad z_c = 0.296$$

RK constants can be calculated from equations in Table 1.4:

$$a = 0.42748 \cdot \frac{R^2 \cdot T_c^{2.5}}{P_c} \quad a = 35.8 \cdot \frac{\text{Pa} \cdot \text{m}^6}{\text{mole}^2 \cdot \text{K}^{0.5}}$$

$$b = 0.086640 \cdot \frac{R \cdot T_c}{P_c} \quad b = 7.03 \cdot 10^{-5} \cdot \frac{\text{m}^3}{\text{mole}}$$

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The value obtained for b can be used to recalculate the critical volume. Because a and b were calculated from P_c and T_c , calculating V_c from b and comparing it to the experimental value provides a measure for how accurate the RK equation is in the critical region. Again, from Table 1.4:

$$V_c = 3.847 \cdot b \qquad V_c = 270 \cdot \frac{\text{cm}^3}{\text{mole}}$$

SECTION 1.4

1.35

The critical constants are given in Table 1.1:

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T_c = 190.6 \cdot \text{K} \quad P_c = 4.955 \cdot 10^6 \cdot \text{Pa}$$

$$T = 229 \cdot \text{K} \quad T_r = \frac{T}{T_c} \quad T_r = 1.2$$

$$P = 14 \cdot 10^6 \cdot \text{Pa} \quad P_r = \frac{P}{P_c} \quad P_r = 2.83$$

From Figure 1.11, the critical compressibility is approximately 0.54. From this, we calculate the molar volume and density:

$$z = 0.54 \quad V_m = \frac{z \cdot R \cdot T}{P} \quad V_m = 7.344 \cdot 10^{-5} \cdot \text{m}^3 \quad MW = 16.043 \cdot 10^{-3} \cdot \frac{\text{kg}}{\text{mole}}$$

$$\rho = \frac{MW}{V_m} \quad \rho = 218 \cdot \frac{\text{kg}}{\text{m}^3}$$

SECTION 1.5

SECTION 1.6

1.37

We use equation 1.20. Given information:

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T = 300 \cdot \text{K} \quad M = 2 \cdot 14.0067 \cdot 10^{-3} \cdot \frac{\text{kg}}{\text{mole}} \quad M = 0.02801 \cdot \frac{\text{kg}}{\text{mole}}$$

$$u = \sqrt{\frac{3 \cdot R \cdot T}{M}} \quad u = 516.8 \cdot \frac{\text{m}}{\text{sec}}$$

1.39

We use equation 1.32 from the text. We are given:

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T = 500 \cdot \text{K} \quad M = 256 \cdot 10^{-3} \cdot \frac{\text{kg}}{\text{mole}} \quad A = 1.235 \cdot 10^{-10} \cdot \text{m}^2$$

$$\Delta W = 1.234 \cdot 10^{-4} \cdot \text{kg} \quad \Delta t = 6 \cdot \text{min}$$

$$\mu = \frac{\Delta W}{A \cdot \Delta t} \quad \mu = 2.776 \cdot 10^3 \cdot \frac{\text{kg}}{\text{m}^2 \cdot \text{sec}}$$

$$P = \mu \cdot \left(\frac{2 \cdot \pi \cdot R \cdot T}{M} \right)^{0.5} \quad P = 8.87 \cdot 10^5 \cdot \text{Pa}$$

$$P = 6.65 \cdot 10^3 \cdot \text{torr}$$

1.41

At this low pressure, argon can be treated as an ideal gas. We use equations 1.15b and 1.31 from the text. Given information:

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad L = 6.022137 \cdot 10^{23} \cdot \frac{1}{\text{mole}} \quad T = 293.15 \cdot \text{K} \quad M = 39.948 \cdot 10^{-3} \cdot \frac{\text{kg}}{\text{mole}}$$

$$P = 0.001 \cdot \text{torr} \quad P = 0.133 \cdot \text{Pa}$$

$$n_{\text{star}} = \frac{P \cdot L}{R \cdot T} \quad n_{\text{star}} = 3.294 \cdot 10^{19} \cdot \text{m}^{-3}$$

$$Z_{\text{wall}} = n_{\text{star}} \cdot \left(\frac{R \cdot T}{2 \cdot \pi \cdot M} \right)^{0.5} \quad Z_{\text{wall}} = 3.246 \cdot 10^{21} \cdot \frac{1}{\text{m}^2 \cdot \text{sec}}$$

Z_{wall} is the number of collisions per area per time. To get the number of collisions, we multiply by the area:

$$\text{num} = Z_{\text{wall}} \cdot 1 \cdot \text{cm}^2 \quad \text{num} = 3.246 \cdot 10^{17} \cdot \frac{1}{\text{sec}}$$

1.43

We rearrange equation 1.32 from the text to solve for μ , and then solve for the ratio of $\Delta W / \Delta t$, here called "ratio." Assume an average molecular weight for air, similar to example 1.16 or problem 1.62.

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T = 293.15 \cdot \text{K} \quad M = 28.9321 \cdot 10^{-3} \cdot \frac{\text{kg}}{\text{mole}} \quad A = 1.3 \cdot \text{cm}^2$$

$$P = 2.5 \cdot 10^{-6} \cdot \text{torr} \quad L = 6.022137 \cdot 10^{23} \cdot \frac{1}{\text{mole}}$$

$$\mu = P \cdot \left(\frac{M}{2 \cdot \pi \cdot R \cdot T} \right)^{0.5} \quad \mu = 4.581 \cdot 10^{-7} \cdot \frac{\text{kg}}{\text{m}^2 \cdot \text{sec}}$$

$$\text{ratio} = \mu \cdot A \quad \text{ratio} = 5.956 \cdot 10^{-11} \cdot \frac{\text{kg}}{\text{sec}}$$

This gives us the flow rate in mass per time. We want a flow rate in molecules per time, so we divide by the molecular weight and multiply by Avogadro's number:

$$\text{flowrate} = \frac{\text{ratio} \cdot L}{M} \quad \text{flowrate} = 1.24 \cdot 10^{15} \cdot \frac{1}{\text{sec}}$$

If this problem seems a little confusing, it helps to realize that there is a lot of information in the problem statement that you don't need. Even if you pick the right equation to use, it still maybe confusing as to what variable to solve for. If you think about the units of the answer that you want - a rate of molecules means molecules/sec - then is it a little easier to see that you need to solve for the ratio $\Delta W/\Delta t$, which has units of mass/sec.

1.45

We use equations 1.20, 1.35, and 1.34, respectively. Given information:

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T = 423.15 \cdot \text{K} \quad M = 4.002602 \cdot 10^{-3} \cdot \frac{\text{kg}}{\text{mole}}$$

For the rms speed:

$$u = \sqrt{\frac{3 \cdot R \cdot T}{M}} \quad u = 1624 \cdot \frac{\text{m}}{\text{sec}}$$

We show four significant figures in the answer due to the broadness of the distribution. This is discussed in detail in example 1.13 in the text.

For the average speed:

$$v = \sqrt{\frac{8 \cdot R \cdot T}{\pi \cdot M}} \quad v = 1496 \cdot \frac{\text{m}}{\text{sec}}$$

For the most probable speed:

$$v_p = \sqrt{\frac{2 \cdot R \cdot T}{M}} \quad v_p = 1326 \cdot \frac{\text{m}}{\text{sec}}$$

Here we have made the substitution that $k/m = R/M$.

1.47

This is similar to example 1.21 from the text. To determine the percent of molecules traveling with a certain range of speeds, we integrate the distribution function. It is easiest to do this integral in terms of dimensionless variables. This integral is given in equation 1.37b, and must be solved numerically. We assume an average molecular weight for air, as in example 1.16.

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad M = 28.9321 \cdot 10^{-3} \cdot \frac{\text{kg}}{\text{mole}} \quad T = 293.15 \cdot \text{K} \quad v_1 = 0 \cdot \frac{\text{mi}}{\text{hr}} \quad v_2 = 55 \cdot \frac{\text{mi}}{\text{hr}}$$

$$i = 1..2 \quad w_i = \frac{v_i}{\sqrt{\frac{2 \cdot R \cdot T}{M}}} \quad w_1 = 0 \quad w_2 = 0.0598992$$

Recall that $k/m = R/M$. Also note that it is usually a good idea to keep lots of significant figures in intermediate results when you are doing an integral numerically to avoid round-off errors. When we get the final result, we keep that to the correct amount of significant figures.

$$P = \frac{4}{\sqrt{\pi}} \cdot \frac{e^{-w_2^2}}{w_1} \cdot w_2^2 \cdot dw \quad P = 0.00016$$

$$P = 0.016 \cdot \%$$

1.49

This is similar to example 1.21 from the text. To determine the percent of molecules traveling with a certain range of speeds, we integrate the distribution function. However, this problem asks for molecules with speeds greater than 1500 m/s - essentially this means in the range of 1500 m/s to infinity. It is possible to integrate numerically out to a large value, since the distribution function drops off. However, it is much easier to remember that you are integrating to find a percent of molecules. If we find the percent of molecules travelling with speeds between 0 and 1500 m/s and subtract this percentage from 100%, we will find the percent of molecules with speeds greater than 1500. We do the integral in terms of dimensionless variables, as shown in equation 1.37b.

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$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T = 750 \cdot \text{K}$$

$$v_1 = 0 \cdot \frac{\text{m}}{\text{sec}} \quad v_2 = 1500 \cdot \frac{\text{m}}{\text{sec}}$$

$$M = 1 \cdot 12.011 \cdot 10^{-3} \cdot \frac{\text{kg}}{\text{mole}} + 4 \cdot 1.00794 \cdot 10^{-3} \cdot \frac{\text{kg}}{\text{mole}}$$

$$M = 1.60428 \cdot 10^{-2} \cdot \frac{\text{kg}}{\text{mole}}$$

$$i = 1..2 \quad w_i = \frac{v_i}{\sqrt{\frac{2 \cdot R \cdot T}{M}}} \quad w_1 = 0$$

$$w_2 = 1.7012449$$

Recall that $k/m = R/M$. Also note that it is usually a good idea to keep lots of significant figures in intermediate results when you are doing an integral numerically to avoid round-off errors. When we get the final result, we keep that to the correct amount of significant figures.

$$P_1 = \frac{4}{\sqrt{\pi}} \cdot \int_{w_1}^{w_2} e^{-w^2} \cdot w^2 \, dw \quad P_1 = 0.87763$$

$$P_1 = 87.8\%$$

This is the percent of molecules travelling with speeds less than 1500 m/s. The rest of the molecules must be travelling with speeds greater than 1500 m/s, so to get the answer we want, we subtract this from 100%.

$$P_2 = 100\% - P_1 \quad P_2 = 12.2\%$$

1.51

This problem is very similar to example 1.19 from the text, except that a different distribution function is used. The average speed is calculated using equation 1.30:

$$\bar{v} = \int_0^{\infty} v f(v) dv$$

Our distribution function is:

$$f(v) dv = \frac{m}{kT} \exp\left(-\frac{mv^2}{2kT}\right) v dv$$

Thus, we have:

$$\bar{v} = \int_0^{\infty} v^2 \frac{m}{kT} \exp\left(-\frac{mv^2}{2kT}\right) dv$$

From an integral table (such as the one found on the inside front cover of your P-Chem book):

$$\int_0^{\infty} x^2 e^{-ax^2} dx = \frac{1}{4a} \sqrt{\frac{\pi}{a}}$$

Using $a = m/2kT$, we obtain the average speed:

$$\bar{v} = \frac{m}{kT} \left(\frac{2kT}{4m}\right) \sqrt{\frac{2kT}{m} \pi} = \frac{1}{2} \sqrt{\frac{2\pi kT}{m}} = \sqrt{\frac{\pi kT}{m}} = \sqrt{\frac{\pi RT}{M}}$$

Recall that $k/m = R/M$.

SECTION 1.7

1.53

To find the distance at which $U(r)$ is a minimum, we take the first derivative of $U(r)$, set it equal to zero, and solve for r :

$$U(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \qquad \frac{dU}{dr} = 4\varepsilon \left[\frac{-12\sigma^{12}}{r^{13}} + \frac{6\sigma^6}{r^7} \right] = 0$$

$$\frac{-12\sigma^{12}}{r^{13}} + \frac{6\sigma^6}{r^7} = 0 \qquad \frac{6\sigma^6}{r^7} = \frac{12\sigma^{12}}{r^{13}} \qquad 1 = \frac{2\sigma^6}{r^6}$$

$$r^6 = 2\sigma^6 \qquad r = 2^{1/6}\sigma$$

To find the value of U at this minimum, we just plug this value of r back into the Lennard-Jones potential:

$$U_{\min} = 4\varepsilon \left[\frac{\sigma^{12}}{(2^{1/6}\sigma)^{12}} - \frac{\sigma^6}{(2^{1/6}\sigma)^6} \right] = 4\varepsilon \left[\frac{\sigma^{12}}{4\sigma^{12}} - \frac{\sigma^6}{2\sigma^6} \right] = 4\varepsilon \left[\frac{1}{4} - \frac{1}{2} \right] = 4\varepsilon \left[\frac{-1}{4} \right] = -\varepsilon$$

$$U_{\min} = -\varepsilon$$

1.55

Equation 1.38 allows us to compute the second virial coefficient, given an expression for the potential. The Sutherland potential, with $n = 6$, is given by:

$$U = \infty \text{ for } 0 < r < \sigma$$

$$U = -\epsilon \left(\frac{\sigma}{r}\right)^6 \text{ for } \sigma < r < \infty$$

We plug this into equation 1.38. Since the Sutherland potential is discontinuous at $r = \sigma$, we split the integral into two integrals:

$$B(T) = 2\pi L \int_0^{\infty} (1 - e^{-U/kT}) r^2 dr \qquad B(T) = 2\pi L \int_0^{\sigma} (1 - e^{-\infty/kT}) r^2 dr + 2\pi L \int_{\sigma}^{\infty} (1 - e^{\epsilon(\sigma/r)^6/kT}) r^2 dr$$

The first of these integrals is equal to zero, since e raised to negative infinity tends toward zero. For the second integral, we make the substitution that $\rho = r/\sigma$, and plug in the definition of b_0 :

$$B(T) = 2\pi L \sigma^3 \int_1^{\infty} (1 - e^{\frac{\epsilon}{kT} \rho^{-6}}) \rho^2 d\rho \qquad b_0 = \frac{2\pi L \sigma^3}{3}$$

$$B(T) = 3b_0 \int_1^{\infty} (1 - e^{\frac{\epsilon}{kT} \rho^{-6}}) \rho^2 d\rho$$

Now, expand the exponential in a power series.

$$B(T) = 3b_0 \int_1^{\infty} \left(1 - \left(1 + \frac{\epsilon}{kT} \frac{1}{\rho^6} + \left(\frac{\epsilon}{kT}\right)^2 \frac{1}{2\rho^{12}} + \left(\frac{\epsilon}{kT}\right)^3 \frac{1}{6\rho^{18}} + \left(\frac{\epsilon}{kT}\right)^4 \frac{1}{24\rho^{24}} + \left(\frac{\epsilon}{kT}\right)^5 \frac{1}{120\rho^{30}} + \left(\frac{\epsilon}{kT}\right)^6 \frac{1}{720\rho^{36}} + \dots \right) \right) \rho^2 d\rho$$

Let $x = \epsilon/kT$. Cancel the leading ones, multiply through by ρ^2 , and integrate:

$$B(T) = 3b_0 \int_1^{\infty} \left(1 - \left(1 + \frac{x}{\rho^6} + \frac{x^2}{2\rho^{12}} + \frac{x^3}{6\rho^{18}} + \frac{x^4}{24\rho^{24}} + \frac{x^5}{120\rho^{30}} + \frac{x^6}{720\rho^{36}} + \dots \right) \right) \rho^2 d\rho$$

$$B(T) = 3b_0 \int_1^{\infty} \left(-\frac{x}{\rho^4} - \frac{x^2}{2\rho^{10}} - \frac{x^3}{6\rho^{16}} - \frac{x^4}{24\rho^{22}} - \frac{x^5}{120\rho^{28}} - \frac{x^6}{720\rho^{34}} - \dots \right) d\rho$$

$$B(T) = 3b_0 \left[-\frac{x}{3\rho^3} - \frac{x^2}{18\rho^9} - \frac{x^3}{90\rho^{15}} - \frac{x^4}{504\rho^{21}} - \frac{x^5}{3240\rho^{27}} - \frac{x^6}{23760\rho^{33}} - \dots \right]_1^{\infty}$$

The terms at infinity disappear nicely to give us:

$$B(T) = b_0 \left[-x - \frac{x^2}{6} - \frac{x^3}{30} - \frac{x^4}{168} - \frac{x^5}{1080} - \frac{x^6}{7920} - \dots \right]$$

1.57

This is discussed in section 1.7 of the text, and particularly in the caption for Figure 1.20. The Lennard-Jones potential works reasonably well for closed-shell, neutral, nonpolar, fairly symmetric molecules. Thus, it would not work well for open shell molecules, such as the methyl radical, any ionic species, such as a hydroxide ion, and polar species, such as HCl, and any long molecule, such as octane.

1.59

The Lennard-Jones and square-well potential constants are given in Table 1.7. For the Lennard-Jones potential, we will use Figure 1.21 to determine B^* and C^* , and then calculate B and C . (B^* is defined in terms of an integral, and in theory we could just perform the integration to get B^* . However, this integral is difficult to do numerically, and if you try this you may have problems getting it to converge. Just use Figure 1.21).

$$\epsilon_k = 243 \cdot K \quad b_0 = 77.97 \cdot \frac{\text{cm}^3}{\text{mole}} \quad T = 295 \cdot K \quad T_{\text{star}} = \frac{T}{\epsilon_k} \quad T_{\text{star}} = 1.214$$

For $T^* = 1.214$, B^* can be read off of Figure 1.21(a) as approximately -1.58.

$$B_{\text{star}} = -1.58 \quad B = b_0 \cdot B_{\text{star}} \quad B = -123 \cdot \frac{\text{cm}^3}{\text{mole}}$$

C^* for this reduced temperature is approximately 0.61.

$$C^* = 0.61 \quad C = b_0^2 \cdot C^* \quad C = 3.7 \cdot 10^3 \cdot \frac{\text{cm}^3}{\text{mole}}$$

For the square-well potential, the integration can be carried out to yield an expression for B, which is given by equation 1.44.

$$\epsilon_k = 224 \cdot \text{K} \quad b_0 = 55.72 \cdot \frac{\text{cm}^3}{\text{mole}} \quad R = 1.652 \quad B = b_0 \left[1 - (R^3 - 1) \cdot \left(e^{\frac{\epsilon_k}{T}} - 1 \right) \right]$$

$$B = -167 \cdot \frac{\text{cm}^3}{\text{mole}}$$

SECTION 1.8

1.61

We use the definition of partial pressure, equation 1.45:

$$\text{MPa} = 10^6 \cdot \text{Pa} \quad P = 8.45 \cdot \text{MPa} \quad x_i = 0.2095 \quad P_i = x_i \cdot P$$

$$P_i = 1.77 \cdot \text{MPa}$$

1.63

We solve the RK equation just as we did before, but now we use equation 1.47 to calculate a and b for the mixture of gases. Given information:

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T = 500 \cdot \text{K} \quad n_{\text{tot}} = 3 \cdot \text{mole} + 2 \cdot \text{mole} + 1 \cdot \text{mole} \quad n_{\text{tot}} = 6 \cdot \text{mole}$$

$$V = 2.4 \cdot \text{liter} \quad V_m = \frac{V}{n_{\text{tot}}} \quad V_m = 4 \cdot 10^{-4} \cdot \frac{\text{m}^3}{\text{mole}}$$

We will let ammonia be species 1, nitrogen be species 2, and hydrogen be species 3. The RK constants for the individual species are obtained from Table 1.1.

$$i = 1..3 \quad n_1 = 3 \cdot \text{mole} \quad n_2 = 2 \cdot \text{mole} \quad n_3 = 1 \cdot \text{mole}$$

$$a_1 = 8.650 \cdot \frac{\text{Pa} \cdot \text{m}^6}{\text{mole}^2 \cdot \text{K}^{0.5}} \quad a_2 = 1.551 \cdot \frac{\text{Pa} \cdot \text{m}^6}{\text{mole}^2 \cdot \text{K}^{0.5}} \quad a_3 = 0.1447 \cdot \frac{\text{Pa} \cdot \text{m}^6}{\text{mole}^2 \cdot \text{K}^{0.5}}$$

$$b_1 = 25.85 \cdot 10^{-6} \cdot \frac{\text{m}^3}{\text{mole}} \quad b_2 = 26.74 \cdot 10^{-6} \cdot \frac{\text{m}^3}{\text{mole}} \quad b_3 = 18.44 \cdot 10^{-6} \cdot \frac{\text{m}^3}{\text{mole}}$$

Calculating mole fractions and RK constants:

$$x = \frac{n}{n_{\text{tot}}} \quad a_{\text{mix}} = \left(\sum_i x_i \cdot \sqrt{a_i} \right)^2 \quad b_{\text{mix}} = \sum_i x_i \cdot b_i$$

$$a_{\text{mix}} = 3.799 \cdot \frac{\text{Pa} \cdot \text{m}^6}{\text{mole}^2 \cdot \text{K}^{0.5}} \quad b_{\text{mix}} = 2.491 \cdot 10^{-5} \cdot \frac{\text{m}^3}{\text{mole}}$$

$$P = \frac{R \cdot T}{V_m - b_{\text{mix}}} - \frac{a_{\text{mix}}}{\sqrt{T} \cdot V_m \cdot (V_m + b_{\text{mix}})} \quad P = 1.008 \cdot 10^7 \cdot \text{Pa} \quad \text{MPa} = 10^6 \cdot \text{Pa}$$

$$P = 10.08 \cdot \text{MPa}$$

SECTION 1.9

1.65

Equation 1.49 defines the coefficient of thermal expansion; however, this definition is in terms of the total volume, while the equation we are given is for the specific volume. We use the total mass, m , to convert from total volume to specific volume:

$$V = mv \qquad \left(\frac{\partial V}{\partial T}\right)_P = m \left(\frac{\partial v}{\partial T}\right)_P \qquad \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{mv} \left[m \left(\frac{\partial v}{\partial T}\right)_P \right] = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_P$$

In this case, the factor of mass cancels out, and so it does not affect how we do the derivation. However, it is always good to check. Taking the derivative of specific volume:

$$v = \exp\left(-6.0781 + 1.01257 \ln T + \frac{280.663}{T}\right)$$

$$\left(\frac{\partial v}{\partial T}\right)_P = \left(\frac{1.01257}{T} - \frac{280.663}{T^2}\right) \times \left[\exp\left(-6.0781 + 1.01257 \ln T + \frac{280.663}{T}\right)\right]$$

$$\alpha = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_P$$

$$\alpha = \frac{\left(\frac{1.01257}{T} - \frac{280.663}{T^2}\right) \times \left[\exp\left(-6.0781 + 1.01257 \ln T + \frac{280.663}{T}\right)\right]}{\exp\left(-6.0781 + 1.01257 \ln T + \frac{280.663}{T}\right)}$$

$$\alpha = \frac{1.01257}{T} - \frac{280.663}{T^2}$$

1.67

We use equation 1.50, the definition of the isothermal compressibility:

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

$$V = \frac{RT}{P} - B(T) \qquad \left(\frac{\partial V}{\partial P} \right)_T = -\frac{RT}{P^2}$$

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{\frac{RT}{P} - B} \left(-\frac{RT}{P^2} \right) = \frac{RT}{P^2 \left(\frac{RT}{P} - B \right)} = \frac{RT}{PRT - P^2B}$$

$$\kappa_T = \frac{RT}{PRT - P^2B}$$

1.69

We start with equation 1.50, the definition of the isothermal compressibility.

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

However, since the van der Waals equation is explicit in pressure, not in volume, we use the following property of partial derivatives, which are reviewed in Appendix II of the text:

$$\left(\frac{\partial V}{\partial P} \right)_T = \frac{1}{\left(\frac{\partial P}{\partial V} \right)_T}$$

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$\left(\frac{\partial P}{\partial V_m}\right)_T = \frac{-RT}{(V_m - b)^2} + \frac{2a}{V_m^3} = \frac{-RTV_m^3 + 2a(V_m - b)^2}{V_m^3(V_m - b)^2}$$

$$\left(\frac{\partial V_m}{\partial P}\right)_T = \frac{V_m^3(V_m - b)^2}{-RTV_m^3 + 2a(V_m - b)^2} = \frac{V_m^3(V_m - b)^2}{-RTV_m^3 + 2a(V_m^2 - 2bV_m + b^2)} = \frac{V_m^3(V_m - b)^2}{-RTV_m^3 + 2aV_m^2 - 4abV_m + 2ab^2}$$

$$\kappa_T = -\frac{1}{V_m} \left(\frac{\partial V_m}{\partial P}\right)_T = \frac{V_m^2(V_m - b)^2}{RTV_m^3 - 2aV_m^2 + 4abV_m - 2ab^2}$$

$$\kappa_T = \frac{V_m^2(V_m - b)^2}{RTV_m^3 - 2aV_m^2 + 4abV_m - 2ab^2}$$

1.71

This problem is similar to example 1.27 from the text. We use equation 1.51. The isothermal compressibility of benzene and its molar volume at one atm are given in Table 1.7.

$$V_0 = 89 \cdot \text{cm}^3 \quad \kappa_T = 63.5 \cdot 10^{-6} \cdot \frac{1}{\text{atm}} \quad P = 1000 \cdot \text{atm} \quad P_0 = 1 \cdot \text{atm}$$

$$V = V_0 \cdot [1 - \kappa_T (P - P_0)]$$

$$V = 83 \cdot \text{cm}^3$$

1.73

This problem is similar to example 1.28 from the text. We use equation 1.53, rearranged and written in difference form instead of as a derivative. The coefficients of thermal expansion and compressibility for CCl_4 are given in Table 1.7.

$$\alpha = 1.236 \cdot 10^{-3} \cdot \frac{1}{\text{K}} \quad \kappa_T = 91.0 \cdot 10^{-6} \cdot \frac{1}{\text{atm}} \quad \Delta T = 1 \cdot \text{K}$$

$$\Delta P = \left(\frac{\alpha}{\kappa_T} \right) \cdot \Delta T \quad \Delta P = 13.6 \cdot \text{atm}$$

If you were a little confused about which equation to use, it helps to remember just what the meaning of a partial derivative is. $(dP/dT)_V$ indicates a change in pressure with respect to temperature at a constant volume, which is exactly what this problem asks for.

CHAPTER 2 *The First Law of Thermodynamics*

SECTION 2.3

2.1

He is a monoatomic gas, so we use $C_{vm} = 3/2 R$:

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad C_{vm} = \frac{3}{2} \cdot R \quad C_{vm} = 12.47 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad C_{vm}(\text{obs}) = 12.55 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

For this simple monatomic, equipartition theory gives a good result. Oxygen is a diatomic, so we must take into account rotation and vibration.

$$C_{vm} = \frac{7}{2} \cdot R \quad C_{vm} = 29.1 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad C_{vm}(\text{obs}) = 20.81 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

The calculated value is incorrect, but is not that far off. The remaining molecules are polyatomics, so we use equation 2.7. CO₂ is linear, so we have:

$$N = 3 \quad C_{vm} = \frac{5}{2} \cdot R + (3 \cdot N - 5) \cdot R \quad C_{vm} = 54.04 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad C_{vm}(\text{obs}) = 28.09 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

Ammonia is nonlinear, so we have:

$$N = 4 \quad C_{vm} = 3 \cdot R + (3 \cdot N - 6) \cdot R \quad C_{vm} = 74.83 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad C_{vm}(\text{obs}) = 28.47 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

For ethylene we again use the linear formula:

$$N = 4 \quad C_{vm} = \frac{5}{2} \cdot R + (3 \cdot N - 5) \cdot R \quad C_{vm} = 78.99 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad C_{vm}(\text{obs}) = 31.16 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

Ethane is nonlinear:

$$N = 8 \quad C_{vm} = 3 \cdot R + (3 \cdot N - 6) \cdot R \quad C_{vm} = 174.6 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad C_{vm}(\text{obs}) = 39.46 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

None of the heat capacities for the polyatomics came close to that predicted by equipartition theory, and this is not surprising. As was mentioned in the text, equipartition theory usually does not give good results for polyatomics.

SECTION 2.4

2.3

We use equation 2.15, and assume methane to be an ideal gas at these temperatures. With this assumption, the second term in equation 2.15 is equal to zero, and simplifies to equation 2.16. We are told to assume a constant heat capacity, which means that we can pull the heat capacity out of the integral for internal energy.

$$n = 1 \cdot \text{mole} \quad C_{vm} = 30.86 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad C_v = n \cdot C_{vm} \quad T_1 = 300 \cdot \text{K} \quad T_2 = 400 \cdot \text{K}$$

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad \text{kJ} = 10^3 \cdot \text{joule}$$

(a) At constant pressure:

$$\Delta U = \int_{T_1}^{T_2} C_v dT \quad \Delta U = 3.086 \cdot 10^3 \cdot \text{joule} \quad \Delta U = 3.086 \cdot \text{kJ}$$

$$w = - \int_{V_1}^{V_2} P dV = -P \cdot (V_2 - V_1) = -n \cdot R \cdot (T_2 - T_1)$$

Since the pressure is constant, we can pull it out of the integral for work. We then use the ideal gas law to convert the pressure and volume terms into a change in temperature, which we know.

$$w = -n \cdot R \cdot (T_2 - T_1) \quad w = -0.831 \cdot \text{kJ}$$

$$q = \Delta U - w \quad q = 3.917 \cdot \text{kJ}$$

(b) At constant volume, the change in internal energy will still be the same. However, since dV equals zero, and the only type of work that can be done is PV work, the work done will be zero. Thus, q will be equal to the change in internal energy.

$$\Delta U = 3.086 \cdot \text{kJ}$$

$$w = 0 \cdot \text{kJ} \quad q = \Delta U - w$$

$$q = 3.086 \cdot \text{kJ}$$

2.5

We use equation 2.13:

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$$

The virial series is easily rearranged to obtain an equation explicit in pressure:

$$z = \frac{PV_m}{RT} = 1 + \frac{B(T)}{V_m} \qquad PV_m = RT + \frac{RT B(T)}{V_m} \qquad P = \frac{RT}{V_m} + \frac{RT B(T)}{V_m^2}$$

Keep in mind that B is a function of temperature when you take the derivative:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V_m} + \frac{BR}{V_m^2} + \frac{RT}{V_m^2} \left(\frac{dB}{dT}\right)$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P = T \left[\frac{R}{V_m} + \frac{BR}{V_m^2} + \frac{RT}{V_m^2} \left(\frac{dB}{dT}\right) \right] - P = \frac{RT}{V_m} + \frac{BRT}{V_m^2} + \frac{RT^2}{V_m^2} \left(\frac{dB}{dT}\right) - \frac{RT}{V_m} - \frac{BRT}{V_m^2}$$

Terms cancel to give us:

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{RT^2}{V_m^2} \left(\frac{dB}{dT}\right)$$

2.7

This problem is similar to example 2.4. Using equation 2.14:

$$P = 1 \cdot \text{atm} \qquad T = 273.15 \cdot \text{K} \qquad \alpha = -0.0547 \cdot 10^{-3} \cdot \frac{1}{\text{K}} \qquad \kappa_T = 47 \cdot 10^{-6} \cdot \frac{1}{\text{atm}}$$

$$\text{intpress} = \frac{T \cdot \alpha}{\kappa_T} - P \qquad \text{intpress} = -319 \cdot \text{atm}$$

2.9

Assuming methane obeys the RK equation, we use the result derived in problem 2.8 and the RK constants given in Table 1.1:

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T = 100 \cdot \text{K} \quad V_m = 0.0351 \cdot \text{liter} \quad \text{MPa} = 10^6 \cdot \text{Pa}$$

$$a = 3.194 \cdot \frac{\text{Pa} \cdot \text{m}^6}{\text{mole}^2 \cdot \text{K}^{0.5}} \quad b = 29.59 \cdot 10^{-6} \cdot \frac{\text{m}^3}{\text{mole}}$$

$$\text{intpress} = \frac{3 \cdot a}{2 \cdot \sqrt{T} \cdot V_m \cdot (V_m + b)} \quad \text{intpress} = 211 \cdot \text{MPa}$$

SECTION 2.5

2.11

Our starting point is equation 2.22. Since the process takes places at constant pressure, the dP term is zero, and the equation simplifies to equation 2.23. Table 2.2 gives us an expression for the dependence of C_{pm} on temperature, which we can integrate.

$$T_1 = 300\cdot K \quad T_2 = 700\cdot K \quad \text{mass} = 1\cdot\text{kg} \quad \text{MW} = 2\cdot(12.011 + 1.00794)\cdot 10^{-3}\cdot\frac{\text{kg}}{\text{mole}}$$

$$\text{MW} = 0.026\cdot\frac{\text{kg}}{\text{mole}} \quad n = \frac{\text{mass}}{\text{MW}} \quad n = 38.406\cdot\text{mole} \quad kJ = 10^3\cdot\text{joule}$$

$$c_1 = 47.18\cdot\frac{\text{joule}}{\text{mole}\cdot K} \quad c_2 = 25.91\cdot 10^{-3}\cdot\frac{\text{joule}}{\text{mole}\cdot K^2} \quad c_3 = -4.23\cdot 10^{-6}\cdot\frac{\text{joule}}{\text{mole}\cdot K^3} \quad c_4 = -9.37\cdot 10^{-5}\cdot\frac{\text{joule}\cdot K}{\text{mole}}$$

$$\Delta H = \int_{T_1}^{T_2} n\left[c_1 + c_2\cdot T + c_3\cdot T^2 + \frac{c_4}{T^2}\right] dT \quad \Delta H = 838.151\cdot kJ$$

2.13

Our starting point is equation 2.22. Since the process takes places at constant pressure, the dP term is zero, and the equation simplifies to equation 2.23. Table 2.2 gives us an expression for the dependence of C_{pm} on temperature, which we can integrate. Don't forget to convert temperatures to Kelvins.

$$T_1 = 298.15\cdot K \quad T_2 = 600.652\cdot K \quad \text{mass} = 1\cdot\text{kg} \quad \text{MW} = 207.2\cdot 10^{-3}\cdot\frac{\text{kg}}{\text{mole}}$$

$$n = \frac{\text{mass}}{\text{MW}} \quad n = 4.826\cdot\text{mole} \quad kJ = 10^3\cdot\text{joule}$$

$$c_1 = 22.13\cdot\frac{\text{joule}}{\text{mole}\cdot K} \quad c_2 = 11.72\cdot 10^{-3}\cdot\frac{\text{joule}}{\text{mole}\cdot K^2} \quad c_4 = 0.96\cdot 10^{-5}\cdot\frac{\text{joule}\cdot K}{\text{mole}}$$

$$\Delta H = \int_{T_1}^{T_2} n\left[c_1 + c_2\cdot T + \frac{c_4}{T^2}\right] dT \quad \Delta H = 40.78\cdot kJ$$

2.15

Our starting point is equation 2.22. Since the process takes places at constant pressure, the dP term is zero, and the equation simplifies to equation 2.23. Table 2.2 gives us an expression for the dependence of C_{pm} on temperature, which we can integrate. Don't forget to convert temperatures to Kelvins.

$$T_1 = 298.15 \cdot K \quad T_2 = 933.52 \cdot K \quad \text{mass} = 1 \cdot \text{kg} \quad \text{MW} = 26.98154 \cdot 10^{-3} \cdot \frac{\text{kg}}{\text{mole}}$$

$$n = \frac{\text{mass}}{\text{MW}} \quad n = 37.062 \cdot \text{mole} \quad \text{kJ} = 10^3 \cdot \text{joule}$$

$$c_1 = 20.67 \cdot \frac{\text{joule}}{\text{mole} \cdot K} \quad c_2 = 12.38 \cdot 10^{-3} \cdot \frac{\text{joule}}{\text{mole} \cdot K^2} \quad c_4 = 0 \cdot \frac{\text{joule} \cdot K}{\text{mole}}$$

$$\Delta H = \int_{T_1}^{T_2} n \cdot \left(c_1 + c_2 \cdot T + \frac{c_4}{T^2} \right) dT \quad \Delta H = 666.3 \cdot \text{kJ}$$

2.17

Our starting point is equation 2.22. Since the process takes places at constant pressure, the dP term is zero, and the equation simplifies to equation 2.23. Table 2.3 gives us an expression for the dependence of C_{pm} on temperature, which we can integrate. Don't forget to convert temperatures to Kelvins.

$$T_1 = 330.15 \cdot K \quad T_2 = 673.15 \cdot K \quad n = 3.52 \cdot \text{mole} \quad \text{kJ} = 10^3 \cdot \text{joule}$$

$$a = 8.468 \cdot \frac{\text{joule}}{\text{mole} \cdot K} \quad b = 269.45 \cdot 10^{-3} \cdot \frac{\text{joule}}{\text{mole} \cdot K^2} \quad c = -143.45 \cdot 10^{-6} \cdot \frac{\text{joule}}{\text{mole} \cdot K^3} \quad d = 29.63 \cdot 10^{-9} \cdot \frac{\text{joule}}{\text{mole} \cdot K^4}$$

$$\Delta H = \int_{T_1}^{T_2} n \cdot (a + b \cdot T + c \cdot T^2 + d \cdot T^3) dT \quad \Delta H = 133.18 \cdot \text{kJ}$$

2.19

We use equation 2.21:

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_P$$

$$V_m = \frac{RT}{P} + B(T) \qquad \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{dB}{dT}$$

Don't forget that B is a function of T.

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_P = \frac{RT}{P} + B - T \left(\frac{R}{P} + \frac{dB}{dT}\right) = \frac{RT}{P} + B - \frac{RT}{P} - T \frac{dB}{dT}$$

Terms cancel to give us:

$$\left(\frac{\partial H}{\partial P}\right)_T = B - T \frac{dB}{dT}$$

2.21

The only thing we can do with the data we are given is approximate the partial derivative as a ratio of differences.

$$\text{kJ} = 10^3 \cdot \text{joule} \qquad \text{MPa} = 10^6 \cdot \text{Pa}$$

$$P_1 = 0.1 \cdot \text{MPa} \qquad P_2 = 1.0 \cdot \text{MPa} \qquad H_1 = 1391.7 \cdot \frac{\text{kJ}}{\text{kg}} \qquad H_2 = 1375.7 \cdot \frac{\text{kJ}}{\text{kg}}$$

$$\Delta P = P_1 - P_2 \qquad \Delta H = H_1 - H_2$$

$$\text{derivative} = \frac{\Delta H}{\Delta P} \qquad \text{derivative} = -17.78 \cdot \frac{\text{cm}^3}{\text{gm}}$$

To convert this to a molar basis:

$$\text{MW} = 30.0696400 \cdot \frac{\text{gm}}{\text{mole}} \qquad \text{derivmol} = \text{MW} \cdot \text{derivative} \qquad \text{derivmol} = -535 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{MPa}}$$

2.23

To determine the final temperature, we must do an energy balance around the system, the system being the two gases we are mixing. Since no heat can escape, what this amounts to is saying that the enthalpy of the gases before they are mixed must equal the enthalpy of the gases after they are mixed. However, we cannot calculate absolute enthalpies, only differences in enthalpies. What we will do is pick a reference state of 0 K, and calculate the enthalpies of the initial and final states relative to these reference states. Let species 1 be methane and species 2 be ethylene.

$$m_1 = 1 \cdot \text{gm} \quad m_2 = 1 \cdot \text{gm} \quad MW_1 = 16.04276 \cdot \frac{\text{gm}}{\text{mole}} \quad MW_2 = 28.05376 \cdot \frac{\text{gm}}{\text{mole}}$$

$$n_1 = \frac{m_1}{MW_1} \quad n_2 = \frac{m_2}{MW_2}$$

To calculate the enthalpy change, we start with equation 2.22. For a change at constant pressure, this reduces to equation 2.23. We are told to assume constant heat capacities. For methane, we use the heat capacity at 15 C, since this is the temperature closest to 300 K that Table 2.1 lists. The enthalpy change before mixing is given by:

$$T_{\text{ref}} = 0 \cdot \text{K} \quad T_{1\text{initial}} = 300 \cdot \text{K} \quad T_{2\text{initial}} = 600 \cdot \text{K}$$

$$C_{p1} = 35.46 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad C_{p2} = 42.17 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\Delta H_{\text{initial}} = n_1 \int_{T_{\text{ref}}}^{T_{1\text{initial}}} C_{p1} dT + n_2 \int_{T_{\text{ref}}}^{T_{2\text{initial}}} C_{p2} dT \quad \Delta H_{\text{initial}} = 1.565 \cdot 10^3 \cdot \text{joule}$$

To find the final temperature, we integrate symbolically the expression for the change in enthalpy after mixing (no great feat with constant heat capacities), set it equal to the change in enthalpy before mixing, and solve for the final temperature. Since the system will have reached equilibrium, the two gases will have the same final temperature.

$$\Delta H_{\text{final}} = n_1 \int_{T_{\text{ref}}}^{T_{\text{final}}} C_{p1} dT + n_2 \int_{T_{\text{ref}}}^{T_{\text{final}}} C_{p2} dT$$

$$\Delta H_{\text{final}} = n_1 (C_{p1} \cdot T_{\text{final}} - C_{p1} \cdot T_{\text{ref}}) + n_2 (C_{p2} \cdot T_{\text{final}} - C_{p2} \cdot T_{\text{ref}})$$

$$\Delta H_{\text{final}} = (n_1 \cdot C_{p1} \cdot T_{\text{final}} - n_1 \cdot C_{p1} \cdot T_{\text{ref}} + n_2 \cdot C_{p2} \cdot T_{\text{final}}) - n_2 \cdot C_{p2} \cdot T_{\text{ref}}$$

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$$\Delta H_{\text{final}} = \Delta H_{\text{initial}}$$

$$T_{\text{final}} = \frac{(\Delta H_{\text{initial}} - n_1 \cdot C_{p1} \cdot T_{\text{ref}} + n_2 \cdot C_{p2} \cdot T_{\text{ref}})}{(-n_1 \cdot C_{p1} - C_{p2} \cdot n_2)} \quad T_{\text{final}} = 421 \cdot \text{K}$$

SECTION 2.6

2.25

We start with equation 2.25:

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

Taking the derivative of volume with respect to temperature:

$$V = \frac{RT}{P} + B(T) \qquad \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{dB}{dT} \qquad \frac{\partial}{\partial T} \left(\frac{\partial V}{\partial T}\right)_P = 0 + \frac{d^2B}{dT^2}$$

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P = -T \frac{d^2B}{dT^2}$$

2.27

Starting with equation 2.25:

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

Taking the derivative of volume with respect to temperature:

$$V = \frac{RT}{P} + B(T) \qquad \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{dB}{dT} \qquad \frac{\partial}{\partial T} \left(\frac{\partial V}{\partial T}\right)_P = 0 + \frac{d^2B}{dT^2}$$

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P = -T \frac{d^2B}{dT^2}$$

We use the RK form of the second virial coefficient from Table 1.2 and take the derivative with respect to temperature:

$$B = b - \frac{a}{RT^{3/2}} \quad \frac{dB}{dT} = -\frac{3}{2} \left(\frac{a}{RT^{5/2}} \right) = -\frac{3a}{2RT^{5/2}} \quad \frac{d^2B}{dT^2} = \frac{5}{2} \left(\frac{3a}{2RT^{7/2}} \right) = \frac{15a}{4RT^{7/2}}$$

$$\left(\frac{\partial C_p}{\partial P} \right)_T = -T \left(\frac{15a}{4RT^{7/2}} \right) = -\frac{15a}{4RT^{5/2}}$$

To calculate the difference between the zero-pressure heat capacity and the heat capacity at 1 bar, we write this derivative as a finite difference, and plug in values for a and b from Table 1.1:

$$\frac{\Delta C_p}{\Delta P} = \frac{15a}{4RT^{5/2}} = \frac{15 \left(1.551 \frac{\text{Pa m}^6}{\text{mole}^2 \text{K}^{1/2}} \right)}{4 \left(8.31451 \frac{\text{joule}}{\text{mole K}} \right) (298.15 \text{ K})^{5/2}} = 4.557 \times 10^{-7} \frac{\text{joule}}{\text{mole Pa K}}$$

$$\Delta C_p = \left(4.557 \times 10^{-7} \frac{\text{joule}}{\text{mole Pa K}} \right) \Delta P = \left(4.557 \times 10^{-7} \frac{\text{joule}}{\text{mole Pa K}} \right) \left(\frac{10^5 \text{ Pa}}{1 \text{ bar}} \right) (1 \text{ bar})$$

$$\Delta C_p = 0.046 \frac{\text{joule}}{\text{mole K}}$$

2.29

The result from the previous problem is:

$$\left(\frac{\partial C_v}{\partial V} \right)_T = T \left(\frac{\partial^2 P}{\partial T^2} \right)_V$$

Since the van der Waals equation is explicit in pressure, taking the derivative is straightforward:

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad \left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V_m - b} \quad \left(\frac{\partial^2 P}{\partial T^2} \right)_V = 0$$

$$\left(\frac{\partial C_v}{\partial V} \right)_T = T \left(\frac{\partial^2 P}{\partial T^2} \right)_V = T \times 0 = 0$$

The derivative of C_v with respect to volume is zero, so C_v of a van der Waals gas is not a function of volume.

SECTION 2.7

2.31

Equation 2.27 gives us an expression for $C_{pm} - C_{vm}$:

$$C_{pm} - C_{vm} = T \left(\frac{\partial V_m}{\partial T} \right)_P \left(\frac{\partial P}{\partial T} \right)_{V_m}$$

The virial series is explicit in volume, and one of the derivatives we have to take requires an expression which is explicit in pressure. The virial series can be solved for pressure, but we can also use some properties of partial derivatives to transform the derivative into one which is a little easier to compute. The second approach is shown here, since it is a useful trick to know in case an equation cannot be solved explicitly for both pressure and volume, which is often the case. Properties of partial derivatives are reviewed in Appendix II of the text.

$$\left(\frac{\partial P}{\partial T} \right)_{V_m} = - \left(\frac{\partial P}{\partial V_m} \right)_T \left(\frac{\partial V_m}{\partial T} \right)_P = - \frac{\left(\frac{\partial V_m}{\partial T} \right)_P}{\left(\frac{\partial V_m}{\partial P} \right)_T}$$

$$V_m = \frac{RT}{P} + B \qquad \left(\frac{\partial V_m}{\partial T} \right)_P = \frac{R}{P} + \frac{dB}{dT} = \frac{R + B'}{P} \qquad \left(\frac{\partial V_m}{\partial P} \right)_T = - \frac{RT}{P^2}$$

$$\left(\frac{\partial P}{\partial T} \right)_{V_m} = - \frac{\left(\frac{\partial V_m}{\partial T} \right)_P}{\left(\frac{\partial V_m}{\partial P} \right)_T} = - \left(\frac{R + B'P}{P} \right) \left(- \frac{P^2}{RT} \right) = P \left(\frac{R + B'P}{RT} \right)$$

$$C_{pm} - C_{vm} = T \left(\frac{R + B'P}{P} \right) \times P \left(\frac{R + B'P}{RT} \right) = PT \left(\frac{(R + B'P)^2}{PRT} \right) = \frac{(R + B'P)^2}{R}$$

$$C_{pm} - C_{vm} = \frac{(R + B'P)^2}{R}$$

2.33

We use equation 2.28 and calculate C_{vm} at 20 °C, since this is the temperature at which the other data are given:

$$T = 293 \cdot K \quad V_m = 14.8 \cdot \text{cm}^3 \quad \alpha = 0.18 \cdot 10^{-3} \cdot \frac{1}{K} \quad \kappa_T = 3.9 \cdot 10^{-6} \cdot \frac{1}{\text{atm}} \quad C_{pm} = 27.8 \cdot \frac{\text{joule}}{\text{mole} \cdot K}$$

$$C_{vm} = C_{pm} - \frac{T \cdot V_m \cdot \alpha^2}{\kappa_T} \quad C_{vm} = 24.1 \cdot \frac{\text{joule}}{\text{mole} \cdot K}$$

The observed value is 23.4 joule/mole K.

2.35

Equation 2.27 gives us an expression for $C_{pm} - C_{vm}$:

$$C_{pm} - C_{vm} = T \left(\frac{\partial V_m}{\partial T} \right)_P \left(\frac{\partial P}{\partial T} \right)_{V_m}$$

The van der Waals equation is explicit in pressure, so we must use the cyclic rule for partial derivatives to evaluate one of the derivatives. Properties of partial derivatives are reviewed in Appendix II of the text.

$$\left(\frac{\partial V_m}{\partial T} \right)_P = - \left(\frac{\partial V_m}{\partial T} \right)_P \left(\frac{\partial P}{\partial T} \right)_{V_m} = - \frac{\left(\frac{\partial P}{\partial T} \right)_{V_m}}{\left(\frac{\partial P}{\partial V_m} \right)_T}$$

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad \left(\frac{\partial P}{\partial T} \right)_{V_m} = \frac{R}{V_m - b} \quad \left(\frac{\partial P}{\partial V_m} \right)_T = - \frac{RT}{(V_m - b)^2} + \frac{2a}{V_m^3} = \frac{-RTV_m^3 + 2a(V_m - b)^2}{V_m^3(V_m - b)^2}$$

$$\left(\frac{\partial V_m}{\partial T} \right)_P = - \frac{\left(\frac{\partial P}{\partial T} \right)_{V_m}}{\left(\frac{\partial P}{\partial V_m} \right)_T} = - \left(\frac{R}{V_m - b} \right) \left(\frac{V_m^3(V_m - b)^2}{-RTV_m^3 + 2a(V_m - b)^2} \right) = \frac{RV_m^3(V_m - b)}{RTV_m^3 - 2a(V_m^2 + 2bV_m + b^2)}$$

$$\left(\frac{\partial V_m}{\partial T}\right)_P = \frac{RV^3(V_m - b)}{RTV^3 - 2aV_m^2 + 4abV_m - 2ab^2}$$

$$C_{pm} - C_{vm} = T \left(\frac{\partial V_m}{\partial T}\right)_P \left(\frac{\partial P}{\partial V_m}\right)_T = T \left(\frac{RV^3(V_m - b)}{RTV^3 - 2aV_m^2 + 4abV_m - 2ab^2}\right) \left(\frac{R}{V_m - b}\right)$$

$$C_{pm} - C_{vm} = \frac{R^2TV^3}{RTV^3 - 2aV_m^2 + 4abV_m - 2ab^2}$$

SECTION 2.8

2.37

The enthalpy imperfection is most easily calculated from eq. 2.34:

$$H_i = U_i + PV_m - RT$$

The internal energy imperfection for a Redlich-Kwong gas was derived in problem 2.36 as:

$$U_{im} = \frac{3a}{2b\sqrt{T}} \ln \left[\frac{V_m}{V_m + b} \right]$$

The PV_m term in eq. 2.34 is easily evaluated for the Redlich-Kwong equation of state:

$$PV_m = \frac{RTV_m}{V_m - b} - \frac{a}{\sqrt{T}(V_m + b)}$$

Therefore, the enthalpy imperfection is:

$$H_i = \frac{3a}{2b\sqrt{T}} \ln \left[\frac{V_m}{V_m + b} \right] + \frac{RTV_m}{V_m - b} - \frac{a}{\sqrt{T}(V_m + b)} - \frac{RT(V_m - b)}{(V_m - b)}$$

$$H_i = \frac{bRT}{V_m - b} - \frac{a}{\sqrt{T}(V_m + b)} + \frac{3a}{2b\sqrt{T}} \ln \left[\frac{V_m}{V_m + b} \right]$$

2.39

The energy imperfection is given by equation 2.31:

$$U_i = \int_{-\infty}^V \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV$$

$$P = \frac{RT}{V_m - b} - \frac{a}{TV_m^2}$$

$$\left(\frac{\partial P}{\partial T} \right)_{V_m} = \frac{R}{V_m - b} + \frac{a}{T^2 V_m^2}$$

$$T \left(\frac{\partial P}{\partial T} \right)_{V_m} - P = \frac{RT}{V_m - b} + \frac{aT}{T^2 V_m^2} - \frac{RT}{V_m - b} + \frac{a}{TV_m^2} = \frac{2a}{TV_m^2}$$

$$U_i = \int_{\infty}^{V_m} \left[T \left(\frac{\partial P}{\partial T} \right)_{V_m} - P \right] dV_m = \int_{\infty}^{V_m} \frac{2a}{TV_m^2} dV_m = \left[-\frac{2a}{TV_m} \right]_{\infty}^{V_m} = -\frac{2a}{TV_m}$$

$$U_i = -\frac{2a}{TV_m}$$

2.41

Use equation 2.35 to calculate the enthalpy change of a real gas. Since the compression is isothermal, dT is equal to zero, so the only contribution to the enthalpy change comes from the enthalpy imperfection. The enthalpy imperfection for a van der Waals gas is derived in example 2.15 in the text.

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad a = 0.5581 \cdot \frac{\text{Pa} \cdot \text{m}^6}{\text{mole}^2} \quad b = 65.14 \cdot 10^{-6} \cdot \frac{\text{m}^3}{\text{mole}} \quad \text{kJ} = 10^3 \cdot \text{joule}$$

$$V_{m1} = 25.6228 \cdot \frac{\text{liter}}{\text{mole}} \quad V_{m2} = 1.11902 \cdot \frac{\text{liter}}{\text{mole}} \quad T = 310 \cdot \text{K}$$

$$H_{i1} = \frac{b \cdot R \cdot T}{V_{m1} - b} - \frac{2 \cdot a}{V_{m1}} \quad H_{i2} = \frac{b \cdot R \cdot T}{V_{m2} - b} - \frac{2 \cdot a}{V_{m2}}$$

$$\Delta H = H_{i2} - H_{i1} \quad \Delta H = -0.801 \cdot \frac{\text{kJ}}{\text{mole}}$$

2.43

We use the RK equation to calculate the pressure for each volume given, and from this, the compressibility factor. The equations for the energy and enthalpy imperfections are given in problems 2.36 and 2.37.

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad a = 1.551 \cdot \frac{\text{Pa} \cdot \text{m}^6}{\text{mole}^2 \cdot \sqrt{\text{K}}} \quad b = 26.74 \cdot 10^{-6} \cdot \frac{\text{m}^3}{\text{mole}} \quad T = 300 \cdot \text{K}$$

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$$j = 0..3 \quad V_{m_0} = 1 \cdot \text{liter} \quad V_{m_1} = 10 \cdot \text{liter} \quad V_{m_2} = 100 \cdot \text{liter} \quad V_{m_3} = 1000 \cdot \text{liter} \quad \text{bar} = 10^5 \cdot \text{Pa}$$

$$P_j = \frac{R \cdot T}{V_{m_j} - b} - \frac{a}{\sqrt{T} \cdot V_{m_j} \cdot (V_{m_j} + b)} \quad z_j = \frac{P_j \cdot V_{m_j}}{R \cdot T}$$

$$U_{i,j} = \frac{-3 \cdot a}{2 \cdot b \cdot \sqrt{T}} \cdot \ln \left(\frac{V_{m_j} + b}{V_{m_j}} \right) \quad H_{i,j} = \frac{b \cdot R \cdot T}{V_{m_j} - b} - \frac{a}{\sqrt{T} \cdot (V_{m_j} + b)} + \frac{3 \cdot a}{2 \cdot b \cdot \sqrt{T}} \cdot \ln \left(\frac{V_{m_j}}{V_{m_j} + b} \right)$$

$$V_m = \begin{bmatrix} 1 \\ 10 \\ 100 \\ 1000 \end{bmatrix} \cdot \text{liter} \quad P = \begin{bmatrix} 24.757 \\ 2.492 \\ 0.249 \\ 0.025 \end{bmatrix} \cdot \text{bar} \quad z = \begin{bmatrix} 0.99251 \\ 0.999101 \\ 0.999909 \\ 0.999991 \end{bmatrix}$$

$$V_m = \begin{bmatrix} 1 \\ 10 \\ 100 \\ 1000 \end{bmatrix} \cdot \text{liter} \quad H_i = \begin{bmatrix} -151.239 \\ -15.657 \\ -1.571 \\ -0.157 \end{bmatrix} \cdot \text{joule} \quad U_i = \begin{bmatrix} -132.556 \\ -13.414 \\ -1.343 \\ -0.134 \end{bmatrix} \cdot \text{joule}$$

SECTION 2.9

2.45

Isothermal, reversible expansions are discussed in the first part of section 2.9 of the text. If we assume the methane is an ideal gas at 400 K, then we can calculate the work of a reversible isothermal change using equation 2.36:

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T = 400 \cdot \text{K} \quad m = 1 \cdot \text{kg} \quad MW = 16.04276 \cdot \frac{\text{gm}}{\text{mole}} \quad n = \frac{m}{MW}$$

$$P_1 = 1 \cdot \text{atm} \quad V_1 = \frac{R \cdot T}{P_1} \quad \text{kJ} = 10^3 \cdot \text{joule}$$

$$P_2 = 10 \cdot \text{atm} \quad V_2 = \frac{R \cdot T}{P_2}$$

$$w = -n \cdot R \cdot T \cdot \ln\left(\frac{V_2}{V_1}\right) \quad w = 477 \cdot \text{kJ}$$

2.47

Isothermal, reversible expansions are discussed in the first part of section 2.9 of the text. Since we are concerned with a reversible expansion, we can substitute the pressure given by the van der Waals equation for P_{ex} .

$$w = - \int_{V_1}^{V_2} P_{\text{ex}} dV \quad P_{\text{ex}} = P \quad P = \frac{n \cdot R \cdot T}{V - n \cdot b} - \frac{n^2 \cdot a}{V^2}$$

$$w = - \int_{V_1}^{V_2} \left(\frac{n \cdot R \cdot T}{V - n \cdot b} - \frac{n^2 \cdot a}{V^2} \right) dV$$

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$$w = -n \cdot \frac{(\ln(V_2 - n \cdot b) \cdot R \cdot T \cdot V_2 + n \cdot a)}{V_2} - n \cdot \frac{(\ln(V_1 - n \cdot b) \cdot R \cdot T \cdot V_1 + n \cdot a)}{V_1}$$

$$w = -n \cdot \ln(V_2 - n \cdot b) \cdot R \cdot T - \frac{n^2}{V_2} \cdot a + n \cdot \ln(V_1 - n \cdot b) \cdot R \cdot T - \frac{n^2}{V_1} \cdot a$$

$$w = -n \cdot R \cdot T \cdot \ln\left(\frac{V_2 - n \cdot b}{V_1 - n \cdot b}\right) - n^2 \cdot a \cdot \left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

Evaluating this for the reversible, isothermal expansion stated in the problem:

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T = 303.15 \cdot \text{K} \quad n = 6.00 \cdot \text{mole} \quad a = 0.6849 \cdot \frac{\text{Pa} \cdot \text{m}^6}{\text{mole}^2} \quad b = 56.76 \cdot 10^{-6} \cdot \frac{\text{m}^3}{\text{mole}}$$

$$V_1 = 10 \cdot \text{liter} \quad V_2 = 150 \cdot \text{liter} \quad \text{kJ} = 10^3 \cdot \text{joule}$$

$$w = -n \cdot R \cdot T \cdot \ln\left(\frac{V_2 - n \cdot b}{V_1 - n \cdot b}\right) - n^2 \cdot a \cdot \left(\frac{1}{V_2} - \frac{1}{V_1}\right) \quad w = -39.14 \cdot \text{kJ}$$

For the ideal gas case, we use equation 2.36:

$$w = -n \cdot R \cdot T \cdot \ln\left(\frac{V_2}{V_1}\right) \quad w = -41 \cdot \text{kJ}$$

2.49

We plug the conditions given into the result of problem 2.48:

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T = 300 \cdot \text{K} \quad n = 1 \cdot \text{mole} \quad a = 7.895 \cdot \frac{\text{Pa} \cdot \text{m}^6}{\text{mole}^2 \cdot \sqrt{\text{K}}} \quad b = 35.43 \cdot 10^{-6} \cdot \frac{\text{m}^3}{\text{mole}}$$

$$V_1 = 24 \cdot \text{liter} \quad V_2 = 1.22 \cdot \text{liter}$$

$$w = -n \cdot R \cdot T \cdot \ln\left(\frac{V_2 - n \cdot b}{V_1 - n \cdot b}\right) - \frac{n^2 \cdot a}{b \cdot \sqrt{T}} \cdot \ln\left[\frac{(V_2 + n \cdot b) \cdot V_1}{(V_1 + n \cdot b) \cdot V_2}\right] \quad w = 7152 \cdot \frac{\text{joule}}{\text{mole}}$$

For the ideal gas case, we use equation 2.36:

$$w = -n \cdot R \cdot T \cdot \ln\left(\frac{V_2}{V_1}\right) \quad w = 7431 \cdot \frac{\text{joule}}{\text{mole}}$$

2.51

This problem is similar to example 2.17 from the text. We use equation 2.38 and $C_{vm} = 3/2 R$, since we have an ideal monatomic gas::

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T_1 = 1200 \cdot \text{K} \quad V_1 = 1 \cdot \text{liter} \quad V_2 = 22 \cdot \text{liter} \quad C_{vm} = \frac{3}{2} \cdot R$$

$$C_{vm} \cdot \ln\left(\frac{T_2}{T_1}\right) = -R \cdot \ln\left(\frac{V_2}{V_1}\right) \quad T_2 = \exp\left(-R \cdot \frac{\ln\left(\frac{V_2}{V_1}\right)}{C_{vm}}\right) \cdot T_1 \quad T_2 = 153 \cdot \text{K}$$

2.53

Remember that assuming ideal gas does NOT mean that $C_{vm} = 3/2 R$; this is only true for ideal, monatomic gases, and ammonia is polyatomic. The ideal gas approximation allows us to use equation 2.39a to evaluate the final temperature. As a first approximation to the final temperature, we assume a constant heat capacity and integrate equation 2.39a to obtain equation 2.39b. The heat capacity of ammonia can be found on Table 2.1.

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T_1 = 293.15 \cdot \text{K} \quad \text{MPa} = 10^6 \cdot \text{Pa} \quad P_1 = 0.10 \cdot \text{MPa} \quad P_2 = 2.0 \cdot \text{MPa}$$

$$C = K$$

$$C_{pm} = 37.29 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$C_{pm} \cdot \ln\left(\frac{T_2}{T_1}\right) = R \cdot \ln\left(\frac{P_2}{P_1}\right) \quad T_2 = \exp\left[R \cdot \frac{\ln\left(\frac{P_2}{P_1}\right)}{C_{pm}}\right] \cdot T_1 \quad T_2 = 572 \cdot \text{K}$$

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However, since ammonia is a polyatomic gas, it would be more accurate to use the temperature-dependent heat capacities given on Table 2.1. We go back to equation 2.39a and integrate it with a temperature-dependent heat capacity. This will give us an equation for the final temperature.

$$c_1 = 29.75 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad c_2 = 25.10 \cdot 10^{-3} \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}^2} \quad c_4 = -1.55 \cdot 10^5 \cdot \frac{\text{joule} \cdot \text{K}}{\text{mole}}$$

$$\int_{T_1}^{T_2} \frac{c_1 + c_2 \cdot T + \frac{c_4}{T^2}}{T} dT = R \cdot \ln \left(\frac{P_2}{P_1} \right)$$

$$\frac{1}{2} \cdot \frac{(-c_4 + 2 \cdot c_1 \cdot \ln(T_2) \cdot T_2^2 + 2 \cdot c_2 \cdot T_2^3)}{T_2^2} - \frac{1}{2} \cdot \frac{(-c_4 + 2 \cdot c_1 \cdot \ln(T_1) \cdot T_1^2 + 2 \cdot c_2 \cdot T_1^3)}{T_1^2} = R \cdot \ln \left(\frac{P_2}{P_1} \right)$$

The final temperature must be solved for numerically. We use the result obtained assuming a constant heat capacity as our first guess.

$$T_2 = \text{root} \left[\frac{1}{2} \cdot \frac{(-c_4 + 2 \cdot c_1 \cdot \ln(T_2) \cdot T_2^2 + 2 \cdot c_2 \cdot T_2^3)}{T_2^2} - \frac{1}{2} \cdot \frac{(-c_4 + 2 \cdot c_1 \cdot \ln(T_1) \cdot T_1^2 + 2 \cdot c_2 \cdot T_1^3)}{T_1^2} \dots, T_2 \right. \\ \left. + R \cdot \ln \left(\frac{P_2}{P_1} \right) \right]$$

$$T_2 = 555 \cdot \text{K}$$

$$T_2 = T_2 - 273.15 \cdot \text{K}$$

$$T_2 = 282 \cdot \text{C}$$

2.55

We will assume ideal gas, which allows us to use equation 2.39a to evaluate the final temperature. We also assume that air is an ideal mixture, so that the heat capacity of the mixture is just a weighted average of the heat capacity of oxygen and nitrogen. Assume the air is 21% oxygen and 79% nitrogen. As a first approximation to the final temperature, we assume a constant heat capacity and integrate equation 2.39a to obtain equation 2.39b. Heat capacities can be found on Table 2.1.

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T_1 = 295.15 \cdot \text{K} \quad P_1 = 14.7 \cdot \text{psi} \quad P_2 = 65 \cdot \text{psi} + 14.7 \cdot \text{psi} \quad C = K$$

$$C_{\text{pm}} = 0.79 \cdot 29.04 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} + 0.21 \cdot 29.16 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$C_{\text{pm}} \cdot \ln\left(\frac{T_2}{T_1}\right) = R \cdot \ln\left(\frac{P_2}{P_1}\right) \quad T_2 = \exp\left[R \cdot \frac{\ln\left(\frac{P_2}{P_1}\right)}{(C_{\text{pm}})}\right] \cdot T_1 \quad T_2 = 479 \cdot \text{K}$$

However, it would be more accurate to use the temperature-dependent heat capacities given on Table 2.1. We go back to equation 2.39a and integrate it with a temperature-dependent heat capacity. This will give us an equation for the final temperature.

$$c_1 = 25.79 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad c_2 = 8.09 \cdot 10^{-3} \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}^2} \quad c_3 = -1.46 \cdot 10^{-6} \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}^3} \quad c_4 = 0.88 \cdot 10^{-5} \cdot \frac{\text{joule} \cdot \text{K}}{\text{mole}}$$

$$c_5 = 29.30 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad c_6 = 6.14 \cdot 10^{-3} \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}^2} \quad c_7 = 0.88 \cdot 10^{-6} \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}^3} \quad c_8 = -1.59 \cdot 10^{-5} \cdot \frac{\text{joule} \cdot \text{K}}{\text{mole}}$$

$$\int_{T_1}^{T_2} \frac{0.79 \cdot \left(c_1 + c_2 \cdot T + c_3 \cdot T^2 + \frac{c_4}{T^2}\right) + 0.21 \cdot \left(c_5 + c_6 \cdot T + c_7 \cdot T^2 + \frac{c_8}{T^2}\right)}{T} dT = R \cdot \ln\left(\frac{P_2}{P_1}\right)$$

$$\begin{aligned}
 &.395 \cdot T_2^2 \cdot c_3 - \frac{.105}{T_2^2} \cdot c_8 + .21 \cdot T_2 \cdot c_6 - \frac{.395}{T_2^2} \cdot c_4 - .79 \cdot c_1 \cdot \ln(T_2) + .21 \cdot \ln(T_2) \cdot c_5 \dots \quad R \cdot \ln\left(\frac{P_2}{P_1}\right) \\
 &+ .79 \cdot T_2 \cdot c_2 - .105 \cdot T_2^2 \cdot c_7 + \frac{.395}{T_1^2} \cdot c_4 - .79 \cdot c_1 \cdot \ln(T_1) - .395 \cdot T_1^2 \cdot c_3 - .21 \cdot \ln(T_1) \cdot c_5 \dots \\
 &+ .79 \cdot T_1 \cdot c_2 - .105 \cdot T_1^2 \cdot c_7 - .21 \cdot T_1 \cdot c_6 + \frac{.105}{T_1^2} \cdot c_8
 \end{aligned}$$

$$\begin{aligned}
 T_2 = \text{root} \left[\begin{aligned} &.395 \cdot T_2^2 \cdot c_3 - \frac{.105}{T_2^2} \cdot c_8 + .21 \cdot T_2 \cdot c_6 - \frac{.395}{T_2^2} \cdot c_4 + .79 \cdot c_1 \cdot \ln(T_2) + .21 \cdot \ln(T_2) \cdot c_5 \dots \\ &+ .79 \cdot T_2 \cdot c_2 + .105 \cdot T_2^2 \cdot c_7 + \frac{.395}{T_1^2} \cdot c_4 - .79 \cdot c_1 \cdot \ln(T_1) - .395 \cdot T_1^2 \cdot c_3 - .21 \cdot \ln(T_1) \cdot c_5 \dots \\ &+ .79 \cdot T_1 \cdot c_2 - .105 \cdot T_1^2 \cdot c_7 - .21 \cdot T_1 \cdot c_6 + \frac{.105}{T_1^2} \cdot c_8 - R \cdot \ln\left(\frac{P_2}{P_1}\right) \end{aligned} , T_2 \right]
 \end{aligned}$$

$$T_2 = 475 \cdot K \quad T_2 = T_2 - 273.15 \cdot K \quad T_2 = 202 \cdot C$$

2.57

We use equation 2.43:

$$T_1 = 295.15 \cdot K \quad V_1 = 9 \quad V_2 = 1 \quad \gamma = 1.4 \quad C = K$$

$$T_2 = T_1 \cdot \left(\frac{V_1}{V_2} \right)^{\gamma-1} \quad T_2 = 711 \cdot K$$

$$T_2 = T_2 - 273.15 \cdot K$$

$$T_2 = 438 \cdot C$$

2.59

This problem is similar to example 2.20 from the text.

(a) Ideal gas: If an ideal gas expands into a vacuum, it does no work. Therefore, its internal energy and hence temperature do not change. The final temperature is 15 °C.

$$T_2 = 288.15 \cdot \text{K}$$

(b) van der Waals gas: We write the expression for the change of internal energy, and find the final temperature at which this change is zero. We use the result for the energy imperfection derived in example 2.14 of the text:

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T_1 = 288.15 \cdot \text{K} \quad V_{m1} = 4.0 \cdot \text{liter} \quad V_{m2} = 20.0 \cdot \text{liter}$$

$$a = 0.1364 \cdot \frac{\text{Pa} \cdot \text{m}^6}{\text{mole}^2} \quad C_{vm} = 29.04 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$C_{vm} \cdot T_2 - C_{vm} \cdot T_1 + \frac{-a}{V_{m2}} - \frac{-a}{V_{m1}} = 0$$

$$T_2 = \frac{-\left(-C_{vm} \cdot T_1 - \frac{a}{V_{m2}} + \frac{a}{V_{m1}}\right)}{C_{vm}} \quad T_2 = 287 \cdot \text{K}$$

(c) RK gas: This is similar to part (b), except we use the expression derived in problem 2.36 for the energy imperfection of an RK gas. To find the final temperature, we must solve the resulting equation numerically.

$$a = 1.551 \cdot \frac{\text{Pa} \cdot \text{m}^6}{\text{mole}^2 \cdot \sqrt{\text{K}}} \quad b = 26.74 \cdot 10^{-6} \cdot \frac{\text{m}^3}{\text{mole}}$$

$$T_2 = \text{root} \left(C_{vm} \cdot T_2 - C_{vm} \cdot T_1 + \frac{-3 \cdot a}{2 \cdot b \cdot \sqrt{T_2}} \cdot \ln \left(\frac{V_{m2} + b}{V_{m2}} \right) - \frac{-3 \cdot a}{2 \cdot b \cdot \sqrt{T_1}} \cdot \ln \left(\frac{V_{m1} + b}{V_{m1}} \right), T_2 \right)$$

$$T_2 = 288 \cdot \text{K}$$

2.61

To do this problem, we must carefully define the system we are working with. A gas is being compressed reversibly and giving off heat to its surroundings, the water bath. The compression of the gas is not adiabatic; however, the water bath and the gas together are adiabatic. To calculate the amount of heat given off to the surroundings by the gas, we define the system as the gas and treat it as an isothermal compression:

$$R = 8.31451 \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T = 300 \cdot \text{K} \quad P_1 = 1 \cdot \text{atm} \quad P_2 = 10 \cdot \text{atm} \quad n = 5 \cdot \text{mole}$$

$$w = -n \cdot R \cdot T \cdot \ln\left(\frac{V_2}{V_1}\right) = -n \cdot R \cdot T \cdot \ln\left[\frac{n \cdot R \cdot \frac{T}{P_2}}{n \cdot R \cdot \frac{T}{P_1}}\right] = -n \cdot R \cdot T \cdot \ln\left(\frac{P_1}{P_2}\right) \quad w = -n \cdot R \cdot T \cdot \ln\left(\frac{P_1}{P_2}\right)$$

$$q = w \quad q = 2.872 \cdot 10^4 \cdot \text{joule}$$

Now, we consider the water bath and the gas together to be the system. Since the system is adiabatic, all of the energy released into the system goes into heating up its contents. The temperature change is simply the heat released divided by the heat capacity of the system.

$$C_p = 9000 \frac{\text{joule}}{\text{K}} \quad \Delta T = \frac{q}{C_p} \quad \Delta T = 3.2 \cdot \text{K}$$

$$T_2 = T + \Delta T \quad T_2 = 303 \cdot \text{K}$$

2.63

This problem is similar to example 2.22 from the text. We start with the result of example 2.21, which gives us the relationship between the second virial coefficient and the Joule-Thomson coefficient.

$$\mu = \frac{T \cdot B_{\text{prime}} - B}{C_{pm}}$$

We plug in the expressions for B and dB/dT. The expression for B for a Berthelot gas can be found on Table 1.2

$$B = \frac{9 \cdot R \cdot T_c}{128 \cdot P_c} \left[1 - \left(\frac{6 \cdot T_c^2}{T^2} \right) \right] \quad B_{\text{prime}} = \frac{27}{32} \cdot R \cdot \frac{T_c^3}{(P_c \cdot T^3)}$$

$$\mu = \frac{\left[\frac{27}{(32 \cdot T_c^2)} \cdot R \cdot \frac{T_c^3}{P_c} - \frac{9}{128} \cdot R \cdot \frac{T_c}{P_c} \cdot \left(1 - 6 \cdot \frac{T_c^2}{T^2} \right) \right]}{C_{pm}}$$

At the Joule-Thomson inversion temperature, the JT coefficient is equal to zero. We set the expression equal to zero and solve for temperature.

$$0 = \frac{\left[\frac{27}{(32 \cdot T_i^2)} \cdot R \cdot \frac{T_c^3}{P_c} - \frac{9}{128} \cdot R \cdot \frac{T_c}{P_c} \cdot \left(1 - 6 \cdot \frac{T_c^2}{T_i^2} \right) \right]}{C_{pm}}$$

$$T_c = 154.3 \cdot K \quad T_i = 3 \cdot \sqrt{2} \cdot T_c \quad T_i = 655 \cdot K$$

2.65

This problem is similar to example 2.22 from the text. We start with the result of example 2.21, which gives us the relationship between the second virial coefficient and the Joule-Thomson coefficient.

$$\mu = \frac{T \cdot B_{\text{prime}} - B}{C_{pm}}$$

We plug in the expressions for B and dB/dT. The expression for B for a Berthelot gas can be found on Table 1.2

$$B = b - \frac{a}{R \cdot T^{1.5}} \quad B_{\text{prime}} = 1.5 \cdot \frac{a}{(R \cdot T^{2.5})}$$

$$\mu = \frac{\left[2.5 \cdot \frac{a}{(R \cdot T^{1.5})} - b \right]}{C_{pm}}$$

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At the Joule-Thomson inversion temperature, the JT coefficient is equal to zero. We set the expression equal to zero and solve for temperature.

$$0 = \frac{\left[2.5 \cdot \frac{a}{(R \cdot T_i^{1.5})} - b \right]}{C_{pm}}$$

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$a = 9.882 \cdot \frac{\text{Pa} \cdot \text{m}^6}{\text{mole}^2 \cdot \sqrt{\text{K}}}$$

$$b = 45.15 \cdot 10^{-6} \cdot \frac{\text{m}^3}{\text{mole}}$$

$$T_i = 1.842015749320193303 \cdot \frac{a^{\left(\frac{2}{3}\right)}}{\left[b^{\left(\frac{2}{3}\right)} \cdot R^{\left(\frac{2}{3}\right)} \right]}$$

$$T_i = 1630 \cdot \text{K}$$

CHAPTER 3 *The Second Law of Thermodynamics*

SECTION 3.1

3.1

To calculate the work obtainable by a steam engine, we rearrange equation 3.2. The temperature of the hot reservoir for each case is given, and the temperature of the cold reservoir is the condensing temperature given. For steam at 1 atm:

$$T_1 = 300.15 \cdot K \quad T_2 = 373.15 \cdot K \quad q_2 = 10^6 \cdot \text{joule} \quad \text{kJ} = 10^3 \cdot \text{joule}$$

$$w = -q_2 \cdot \frac{T_2 - T_1}{T_2}$$

$$w = -196 \cdot \text{kJ}$$

For steam at 15.3 atm:

$$T_2 = 473.15 \cdot K$$

$$w = -q_2 \cdot \frac{T_2 - T_1}{T_2}$$

$$w = -366 \cdot \text{kJ}$$

3.3

Equation (3.3) gives us an expression for the work:

$$w = q_1 \cdot \left(\frac{T_2 - T_1}{T_1} \right)$$

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Since power = work/time, we have:

$$P = \frac{q_1}{t} \cdot \left(\frac{T_2 - T_1}{T_1} \right)$$

Using $q_1/t = (500 \text{ J/sec K} \cdot \Delta T)$ gives us:

$$P = 500 \cdot \frac{\text{joule}}{\text{sec} \cdot \text{K}} \cdot \left(\frac{(T_2 - T_1)^2}{T_1} \right)$$

$$(a) \quad T_2 = 303 \cdot \text{K} \quad T_1 = 298 \cdot \text{K} \quad P = 500 \cdot \frac{\text{joule}}{\text{sec} \cdot \text{K}} \cdot \left(\frac{(T_2 - T_1)^2}{T_1} \right) \quad P = 41.946 \cdot \text{watt}$$

$$(b) \quad T_2 = 303 \cdot \text{K} \quad T_1 = 293 \cdot \text{K} \quad P = 500 \cdot \frac{\text{joule}}{\text{sec} \cdot \text{K}} \cdot \left(\frac{(T_2 - T_1)^2}{T_1} \right) \quad P = 170.648 \cdot \text{watt}$$

3.5

For step 1 of the Carnot cycle,

$$q_2 = R \cdot T_2 \cdot \ln \left(\frac{V_2}{V_1} \right) \quad \Delta S_1 = \frac{q_2}{T_2} = R \cdot \ln \left(\frac{V_2}{V_1} \right)$$

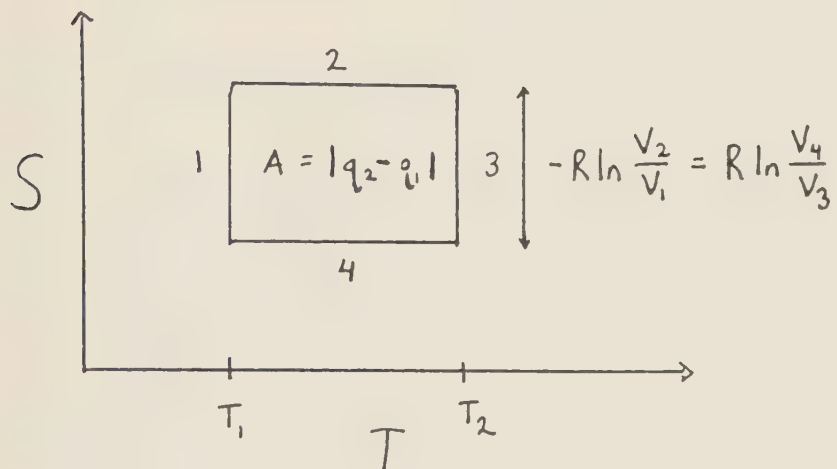
For step 2 of the cycle,

$$w = \Delta U \quad \text{so} \quad dq = 0 \quad \Delta S_2 = 0$$

Similarly, for steps 3 and 4 of the cycle,

$$\Delta S_3 = R \cdot \ln \left(\frac{V_3}{V_4} \right) \quad \Delta S_4 = 0$$

The plot is shown below. For a PV plot, the area enclosed is the work. For a TS plot, the area enclosed is the net heat, since $dq = TdS$.



SECTION 3.3

3.7

The same equations apply for isothermal expansions and isothermal compressions. We use equation 3.14b:

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad MW = 16.043 \cdot \frac{\text{gm}}{\text{mole}} \quad \text{mass} = 1 \cdot \text{kg} \quad \text{MPa} = 10^6 \cdot \text{Pa} \quad \text{kJ} = 10^3 \cdot \text{joule}$$

$$P_1 = 0.1 \cdot \text{MPa} \quad P_2 = 1.0 \cdot \text{MPa} \quad n = \frac{\text{mass}}{MW} \quad n = 62.33 \cdot \text{mole}$$

$$\Delta S = -n \cdot R \cdot \ln \left(\frac{P_2}{P_1} \right) \quad \Delta S = -1.19 \cdot 10^3 \cdot \frac{\text{joule}}{\text{K}} \quad \Delta S = -1.193 \cdot \frac{\text{kJ}}{\text{K}}$$

3.9

We assume that the heat capacity is constant, so that equations 3.13 can be used. From Table 2.1:

$$C_{pm} = 20.93 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad C_{vm} = 12.59 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T_1 = 298.15 \cdot \text{K} \quad T_2 = 373.15 \cdot \text{K}$$

For changes at constant volume:

$$\Delta S = C_{vm} \cdot \ln \left(\frac{T_2}{T_1} \right) \quad \Delta S = 2.825 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

This is only the entropy change for one mole (note the units). We must multiply by the total number of moles:

$$\text{mass} = 1 \cdot \text{kg} \quad \text{MW} = 40.33 \cdot \frac{\text{gm}}{\text{mole}} \quad n = \frac{\text{mass}}{\text{MW}}$$

$$\Delta S_{\text{total}} = n \cdot \Delta S \quad \Delta S_{\text{total}} = 70.05 \cdot \frac{\text{joule}}{\text{K}}$$

For the entropy change at constant pressure:

$$\Delta S = C_{pm} \cdot \ln\left(\frac{T_2}{T_1}\right) \quad \Delta S = 4.696 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\Delta S_{\text{total}} = n \cdot \Delta S \quad \Delta S_{\text{total}} = 116.45 \cdot \frac{\text{joule}}{\text{K}}$$

3.11

We use eq. (3.9) and the heat capacity from Table 2.2. Assume $C_v = C_p - R$.

$$T_1 = 310 \cdot \text{K} \quad T_2 = 867 \cdot \text{K} \quad R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$C_{vm}(T) = 29.75 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} + 25.10 \cdot 10^{-3} \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}^2} \cdot T + 1.55 \cdot 10^{-5} \cdot \frac{\text{joule} \cdot \text{K}}{\text{mole}} \cdot \frac{1}{T^2} \cdot R$$

$$\Delta S = \int_{T_1}^{T_2} \frac{C_{vm}(T)}{T} dT \quad \Delta S = 35.323 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

3.13

We integrate eq. (3.11a) numerically:

$$i = 0..4 \quad C_{pm_i} = \quad T_i =$$

$$n = 0..3$$

8.53 · $\frac{\text{joule}}{\text{mole} \cdot \text{K}}$	298 · K
14.63 · $\frac{\text{joule}}{\text{mole} \cdot \text{K}}$	500 · K
21.54 · $\frac{\text{joule}}{\text{mole} \cdot \text{K}}$	1000 · K
23.84 · $\frac{\text{joule}}{\text{mole} \cdot \text{K}}$	1500 · K
24.54 · $\frac{\text{joule}}{\text{mole} \cdot \text{K}}$	2000 · K

$$\Delta S = \sum_n \frac{1}{2} \cdot \frac{C_{pm_n}}{T_n} - \frac{C_{pm_{n+1}}}{T_{n+1}} \cdot T_{n+1} - T_n$$

$$\Delta S = 34.945 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

3.15

(a) Since the gas is ideal and monatomic, we know that $C_{vm} = 3/2R$ and $C_{pm} = 5/2R$. We use equations 3.14b and 2.36 to calculate the entropy change and the work. Because enthalpy and internal energy are only functions of temperature for an ideal gas, they are zero for an isothermal process:

$$R = 8.31451 \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad C_{vm} = \frac{3}{2} \cdot R \quad \text{bar} = 10^5 \cdot \text{Pa} \quad P_1 = 1 \cdot \text{bar} \quad P_2 = 10 \cdot \text{bar}$$

$$n = 1 \cdot \text{mole} \quad T = 400 \cdot \text{K} \quad V_1 = \frac{n \cdot R \cdot T}{P_1} \quad V_2 = \frac{n \cdot R \cdot T}{P_2}$$

$$\Delta S = -n \cdot R \cdot \ln\left(\frac{P_2}{P_1}\right) \quad \Delta S = -19.14 \cdot \frac{\text{joule}}{\text{K}}$$

$$\Delta U = 0 \cdot \text{joule}$$

$$\Delta H = 0 \cdot \text{joule}$$

$$w = - \int_{V_1}^{V_2} \frac{n \cdot R \cdot T}{V} dV \quad w = 7658 \cdot \text{joule}$$

$$q = \Delta U - w \quad q = -7658 \cdot \text{joule}$$

(b) Before calculating the change in internal energy or enthalpy, we must find the final temperature. This is most easily done using equation 2.39b:

$$T_1 = 400 \cdot \text{K} \quad C_{pm} = \frac{5}{2} \cdot R$$

$$T_2 = T_1 \cdot e^{\frac{R}{C_{pm}} \cdot \ln\left(\frac{P_2}{P_1}\right)} \quad T_2 = 1005 \cdot \text{K}$$

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Equations 2.16 and 2.23 can now be used to find changes in internal energy and enthalpy:

$$\Delta U = n \cdot \int_{T_1}^{T_2} C_{vm} dT \quad \Delta U = 7542 \cdot \text{joule}$$

$$\Delta H = n \cdot \int_{T_1}^{T_2} C_{pm} dT \quad \Delta H = 12571 \cdot \text{joule}$$

Since the process is adiabatic, $q = 0$, and we can thus find w :

$$q = 0 \cdot \text{joule}$$

$$w = \Delta U - q$$

$$w = 7542 \cdot \text{joule}$$

Finally, as was discussed in Example 3.7, for an adiabatic, reversible expansion, the change in entropy is zero. This may become more apparent if the reader reviews Section 2.7, which deals with adiabatic expansions.

$$\Delta S = 0 \cdot \frac{\text{joule}}{\text{K}}$$

(c) The heat capacities are constant, so we use equation 3.13 to calculate the entropy. Again, equation 2.16 can be used to calculate the change in internal energy.

$$T_2 = 273 \cdot \text{K}$$

$$\Delta S = n \cdot C_{vm} \cdot \ln\left(\frac{T_2}{T_1}\right) \quad \Delta S = -4.76 \cdot \frac{\text{joule}}{\text{K}}$$

$$\Delta U = \int_{T_1}^{T_2} n \cdot C_{vm} dT \quad \Delta U = -1584 \cdot \text{joule}$$

Since the process occurs at constant volume, the work done is zero (see the definition of work, eq. 2.9). The change in internal energy is equal to the heat plus the work, so once we know work, we can find q:

$$w = 0 \cdot \text{joule}$$

$$q = \Delta U - w$$

$$q = -1584 \cdot \text{joule}$$

Finally, the change in enthalpy is determined using the definition of enthalpy and the ideal gas law:

$$\Delta PV = n \cdot R \cdot (T_2 - T_1)$$

$$\Delta H = \Delta U + \Delta PV$$

$$\Delta H = -2640 \cdot \text{joule}$$

(b) We use equations 3.13, 2.16, and 2.9 (we could also use 2.23 to calculate the enthalpy change, the result will be the same):

$$C_{pm} = \frac{5}{2} \cdot R$$

$$\Delta S = n \cdot C_{pm} \cdot \ln\left(\frac{T_2}{T_1}\right)$$

$$\Delta S = -7.94 \cdot \frac{\text{joule}}{\text{K}}$$

$$\Delta U = \int_{T_1}^{T_2} n \cdot C_{vm} dT$$

$$\Delta U = -1584 \cdot \text{joule}$$

$$w = - \int_{V_1}^{V_2} P_{ex} dV$$

for ideal gases, this reduces to $w = -n \cdot R \cdot (T_2 - T_1)$

$$w = 1056 \cdot \text{joule}$$

$$q = \Delta U - w$$

$$q = -2640 \cdot \text{joule}$$

$$\Delta H = \Delta U + \Delta PV$$

$$\Delta H = -2640 \cdot \text{joule}$$

3.17

This is similar to example 3.2. A heat balance on the system gives us:

$$\Delta H_1 + \Delta H_2 = 0$$

$$C_{p1} \cdot (T_{\text{final}} - T_1) = C_{p2} \cdot (T_2 - T_{\text{final}})$$

$$T_1 = 273 \cdot \text{K} \quad T_2 = 373 \cdot \text{K} \quad C_{p1} = 34.5 \cdot \frac{\text{joule}}{\text{K}} \quad C_{p2} = 17.5 \cdot \frac{\text{joule}}{\text{K}}$$

$$T_{\text{final}} = \frac{(C_{p1} \cdot T_1 + C_{p2} \cdot T_2)}{(C_{p1} + C_{p2})} \quad T_{\text{final}} = 306.7 \cdot \text{K}$$

The entropy change for the system is:

$$\Delta S_{\text{system}} = \Delta S_1 + \Delta S_2$$

$$\Delta S_{\text{system}} = C_{p1} \cdot \ln\left(\frac{T_{\text{final}}}{T_1}\right) + C_{p2} \cdot \ln\left(\frac{T_{\text{final}}}{T_2}\right)$$

$$\Delta S_{\text{system}} = 0.583 \cdot \frac{\text{joule}}{\text{K}}$$

3.19

Since U, H, and S are all state variables, we can break up the change into two steps: a constant pressure heating and an isothermal change in pressure. For an ideal gas, the internal energy and enthalpy depend only on temperature. For the entropy change, we combine eq. (3.11) and (3.14b).

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T_1 = 500 \cdot \text{K} \quad T_2 = 300 \cdot \text{K} \quad \text{bar} = 10^5 \cdot \text{Pa}$$

$$C_{vm} = \frac{3}{2} \cdot R \quad C_{pm} = C_{vm} + R \quad P_1 = 1 \cdot \text{bar} \quad P_2 = 3 \cdot \text{bar}$$

$$\begin{aligned}\Delta U &= C_{vm} \cdot (T_2 - T_1) & \Delta U &= -2494 \cdot \frac{\text{joule}}{\text{mole}} \\ \Delta H &= C_{pm} \cdot (T_2 - T_1) & \Delta H &= -4157 \cdot \frac{\text{joule}}{\text{mole}} \\ \Delta S &= C_{pm} \cdot \ln\left(\frac{T_2}{T_1}\right) - R \cdot \ln\left(\frac{P_2}{P_1}\right) & \Delta S &= -19.75 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}\end{aligned}$$

3.21

Step (a): Adiabatic expansion. Since this process is reversible and adiabatic, $q = 0$ and the entropy change is 0. We can find the final temperature by rearranging eq. 2.38.

$$\begin{aligned}T_1 &= 400 \cdot \text{K} & \text{bar} &= 10^5 \cdot \text{Pa} & P_1 &= 1 \cdot \text{bar} & R &= 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} & C_{pm} &= \frac{5}{2} \cdot R \\ V_1 &= \frac{R \cdot T_1}{P_1} & V_1 &= 33.258 \cdot \text{liter} & V_2 &= 2 \cdot V_1 & C_{vm} &= \frac{3}{2} \cdot R\end{aligned}$$

$$C_{vm} \cdot \ln\left(\frac{T_2}{T_1}\right) - R \cdot \ln\left(\frac{V_2}{V_1}\right) = 0 \quad T_2 = \exp\left(-R \cdot \frac{\ln\left(\frac{V_2}{V_1}\right)}{C_{vm}}\right) \cdot T_1 \quad T_2 = 251.98 \cdot \text{K}$$

$$\begin{aligned}\Delta U_a &= C_{vm} \cdot (T_2 - T_1) & \Delta U_a &= -1846 \cdot \frac{\text{joule}}{\text{mole}} \\ \Delta H_a &= C_{pm} \cdot (T_2 - T_1) & \Delta H_a &= -3077 \cdot \frac{\text{joule}}{\text{mole}} \\ \Delta S_a &= 0 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} & q_a &= 0 \cdot \frac{\text{joule}}{\text{mole}} & w_a &= \Delta U_a - q_a & w_a &= -1846 \cdot \frac{\text{joule}}{\text{mole}}\end{aligned}$$

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Step (b). Constant volume heating. Since this is a constant volume process, no PV work is done.

$$\begin{aligned}
 T_1 &= 251.98 \cdot \text{K} & T_2 &= 400 \cdot \text{K} & P_2 &= \frac{R \cdot T_2}{V_2} & P_2 &= 0.5 \cdot \text{bar} \\
 \Delta U_b &= C_{vm} \cdot (T_2 - T_1) & \Delta U_b &= 1846 \cdot \frac{\text{joule}}{\text{mole}} \\
 \Delta H_b &= C_{pm} \cdot (T_2 - T_1) & \Delta H_b &= 3077 \cdot \frac{\text{joule}}{\text{mole}} \\
 \Delta S_b &= C_{vm} \cdot \ln\left(\frac{T_2}{T_1}\right) & \Delta S_b &= 5.763 \cdot \frac{\text{joule}}{\text{mole}} \\
 w_b &= 0 \cdot \frac{\text{joule}}{\text{mole}} & q_b &= \Delta U_b - w_b & q_b &= 1846 \cdot \frac{\text{joule}}{\text{mole}}
 \end{aligned}$$

Step (c): Isothermal expansion. Since the process is isothermal, and U and H for an ideal gas only depend on temperature, the change in internal energy and enthalpy is zero.

$$\begin{aligned}
 P_1 &= 0.5 \cdot \text{bar} & P_2 &= 1 \cdot \text{bar} \\
 \Delta U_c &= 0 \cdot \frac{\text{joule}}{\text{mole}} & \Delta H_c &= 0 \cdot \frac{\text{joule}}{\text{mole}} & V_1 &= \frac{R \cdot T_2}{P_1} & V_2 &= \frac{R \cdot T_2}{P_2} \\
 \Delta S_c &= -R \cdot \ln\left(\frac{P_2}{P_1}\right) & \Delta S_c &= -5.763 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \\
 w_c &= -R \cdot T_2 \cdot \ln\left(\frac{V_2}{V_1}\right) & w_c &= 2305 \cdot \frac{\text{joule}}{\text{mole}} & q_c &= \Delta U_c - w_c & q_c &= -2305 \cdot \frac{\text{joule}}{\text{mole}}
 \end{aligned}$$

For the overall process, we simply add the steps together. Note that for the state variables, the overall

$$\begin{aligned}
 \Delta U &= \Delta U_a + \Delta U_b + \Delta U_c & \Delta U &= 0 \cdot \frac{\text{joule}}{\text{mole}} & \text{change is zero, since the overall final and initial states are the same.} \\
 \Delta H &= \Delta H_a + \Delta H_b + \Delta H_c & \Delta H &= 0 \cdot \frac{\text{joule}}{\text{mole}} & q &= q_a + q_b + q_c & q &= -459 \cdot \frac{\text{joule}}{\text{mole}} \\
 \Delta S &= \Delta S_a + \Delta S_b + \Delta S_c & \Delta S &= 0 \cdot \frac{\text{joule}}{\text{mole}} & w &= w_a + w_b + w_c & w &= 459 \cdot \frac{\text{joule}}{\text{mole}}
 \end{aligned}$$

3.23

We calculate the number of moles of each species, and then use eq. 3.15:

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T = 356 \cdot \text{K} \quad P = 1 \cdot \text{atm} \quad V_1 = 3.5 \cdot \text{liter} \quad V_2 = 5.6 \cdot \text{liter}$$

$$n_1 = \frac{P \cdot V_1}{R \cdot T} \quad n_2 = \frac{P \cdot V_2}{R \cdot T} \quad n_1 = 0.12 \cdot \text{mole} \quad n_2 = 0.192 \cdot \text{mole}$$

$$X_1 = \frac{n_1}{n_1 + n_2} \quad X_2 = \frac{n_2}{n_1 + n_2} \quad X_1 = 0.385 \quad X_2 = 0.615$$

$$\Delta S = -R \cdot (n_1 \cdot \ln(X_1) + n_2 \cdot \ln(X_2)) \quad \Delta S = 1.73 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

3.25

(a) This is straightforward:

$$\Delta H_{\text{fus}} = 7070 \cdot \frac{\text{joule}}{\text{mole}} \quad T_{\text{fus}} = 505.05 \cdot \text{K} \quad \Delta S = \frac{\Delta H_{\text{fus}}}{T_{\text{fus}}} \quad \Delta S = 14 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

(b) This is similar to example 3.9 in the text.

$$C_{p \text{ solid}} = 28.1 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad C_{p \text{ liq}} = 30.2 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$T = T_{\text{fus}} - 55 \cdot \text{K} \quad T = 450.05 \cdot \text{K}$$

$$\Delta S = C_{p \text{ liq}} \cdot \ln\left(\frac{T_{\text{fus}}}{T}\right) - \frac{\Delta H_{\text{fus}}}{T_{\text{fus}}} + C_{p \text{ solid}} \cdot \ln\left(\frac{T}{T_{\text{fus}}}\right) \quad \Delta S = -13.8 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

SECTION 3.5

3.27

There is a pattern to deriving Maxwell equations which is a little clearer after looking at a few derivations. This derivation is similar to example 3.11 in the text. We start with the equation of state for U , since T and P multiply the partial derivatives in this equation, and these are the variables which appear in the top of the partial derivatives in the final solution:

$$dU = TdS - PdV$$

Next, we write the total derivative for U in terms of S and V , since these are the variables which are in the bottom of the partial derivatives in the final solution:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

Comparing these two equations, we can see that:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

Taking partial derivatives, we obtain:

$$\left(\frac{\partial}{\partial V}\right)_S \left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S \qquad \left(\frac{\partial}{\partial S}\right)_V \left(\frac{\partial U}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

By the properties of partial derivatives, the left hand sides of these equations are equal, so we have the Maxwell relation:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

3.29

"Readily measured quantities" just means obtain this partial derivative in terms of T, P, and V, which are quantities you can measure. We can begin by writing the total derivative for H in terms of S and P:

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$

We compare this with the equation of state for enthalpy:

$$dH = TdS + VdP$$

Based on this comparison, we can see that:

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$

Comparing these two equations, we can see that:

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

3.31

This is similar to example 3.12. We begin with the total derivative for H, written in terms of S and P:

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$

We can compare this with the equation of state for enthalpy:

$$dH = TdS + VdP$$

Comparing these two equations, we can see that:

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

We use the chain rule on the partial derivative to obtain:

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

By definition, the partial derivative in the numerator is the constant pressure heat capacity, so we have:

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

$$T \left(\frac{\partial S}{\partial T} \right)_P = C_p$$

3.33

First, we write the partial derivative in terms of P , V , and T by using the second Maxwell relation in Table 3.1:

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$$

We can simply take the derivative of the van der Waals equation with respect to temperature, treating V as a constant:

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V_m - b}$$

3.35

First we write μ and C_p in terms of their definitions, found on Table 3.1:

$$-\mu C_p = -\left(\frac{\partial T}{\partial P}\right)_H \left(\frac{\partial H}{\partial T}\right)_P$$

We can rewrite the partial derivatives using the triple product rule to obtain the solution:

$$-\left(\frac{\partial T}{\partial P}\right)_H \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial H}{\partial P}\right)_T$$

$$-\mu C_p = \left(\frac{\partial H}{\partial P}\right)_T$$

3.37

We begin with the definitions of α and C_p found on Table 3.1, and get the expression in terms of state variables. In the derivation below, the derivatives are all partial derivatives:

$$\frac{\alpha V T}{C_p} = \frac{\frac{1}{V} \cdot \left(\frac{dV}{dT}\right)_P \cdot V \cdot \left(\frac{dV}{dT}\right)_P}{\left(\frac{C_p}{T}\right) \cdot \left(\frac{dS}{dT}\right)_P}$$

We can flip the derivative in the denominator:

$$\frac{\left(\frac{dV}{dT}\right)_P}{\left(\frac{dS}{dT}\right)_P} = \left(\frac{dV}{dT}\right)_P \cdot \left(\frac{dT}{dS}\right)_P$$

Next, we use the chain rule:

$$\left(\frac{dV}{dT}\right)_P \cdot \left(\frac{dT}{dS}\right)_P = \left(\frac{dV}{dS}\right)_P$$

And a Maxwell relation:

$$\left(\frac{dV}{dS}\right)_P = \left(\frac{dT}{dP}\right)_S$$

Thus:

$$\frac{\alpha V T}{C_p} = \left(\frac{dT}{dP}\right)_S$$

To calculate this quantity for CCl₄, we use the data given on Table 1.8:

$$\alpha = 1.236 \cdot 10^{-3} \cdot \frac{1}{K} \quad V = 97 \cdot \frac{\text{cm}^3}{\text{mole}} \quad T = 293.15 \cdot K \quad C_p = 132 \cdot \frac{\text{joule}}{\text{mole} \cdot K}$$

$$\text{answer} = \frac{\alpha \cdot V \cdot T}{C_p} \quad \text{answer} = 0.027 \cdot \frac{K}{\text{atm}}$$

3.39

This can be a frustrating derivation, because it can lead to a lot of dead-ends. We begin with the derived relationships for C_p and C_v , found in Table 3.1:

$$\frac{C_p}{C_v} = \frac{T \left(\frac{\partial S}{\partial T} \right)_P}{T \left(\frac{\partial S}{\partial T} \right)_V} = \left(\frac{\partial S}{\partial T} \right)_P \left(\frac{\partial T}{\partial S} \right)_V$$

We use the triple product rule on both derivatives to obtain:

$$\frac{C_p}{C_v} = \left(\frac{\partial S}{\partial P} \right)_T \left(\frac{\partial P}{\partial T} \right)_S \left(\frac{\partial T}{\partial V} \right)_S \left(\frac{\partial V}{\partial S} \right)_T$$

We replace each of the partial derivatives with the Maxwell relations:

$$\frac{C_p}{C_v} = \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial S}{\partial V} \right)_P \left(\frac{\partial P}{\partial S} \right)_V \left(\frac{\partial T}{\partial P} \right)_V$$

Now, use the triple product rule twice, on the first two partial derivatives, and rearrange:

$$\frac{C_p}{C_v} = \left(\frac{\partial V}{\partial P} \right)_T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial S}{\partial P} \right)_V \left(\frac{\partial P}{\partial V} \right)_S \left(\frac{\partial V}{\partial S} \right)_V \left(\frac{\partial T}{\partial P} \right)_V$$

$$\frac{C_p}{C_v} = \frac{\left(\frac{\partial V}{\partial P} \right)_T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial S}{\partial P} \right)_V \left(\frac{\partial P}{\partial V} \right)_V \left(\frac{\partial T}{\partial P} \right)_V}{\left(\frac{\partial P}{\partial V} \right)_S} = \frac{\left(\frac{\partial V}{\partial P} \right)_T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial S}{\partial P} \right)_V \left(\frac{\partial P}{\partial V} \right)_V \left(\frac{\partial T}{\partial P} \right)_V}{\left(\frac{\partial P}{\partial V} \right)_S}$$

Cancel out some of the partial derivatives, and multiply top and bottom by $-1/V$:

$$\frac{C_p}{C_v} = \frac{-\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T}{-\frac{1}{V} \left(\frac{\partial P}{\partial V} \right)_S}$$

Finally, we use the definitions of κ_S and κ_T to obtain the solution:

$$\frac{C_p}{C_v} = \frac{\kappa_T}{\kappa_S}$$

3.41

We use eq. (3.25), and rearrange to solve for the adiabatic compressibility.

$$V_m = 89.8 \cdot \frac{\text{cm}^3}{\text{mole}}$$

$$C_{pm} = 134 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\alpha = 1.24 \cdot 10^{-3} \cdot \frac{1}{\text{K}}$$

$$c = 1295 \cdot \frac{\text{m}}{\text{sec}}$$

$$M = 78.1136 \cdot \frac{\text{gm}}{\text{mole}}$$

$$T = 298.15 \cdot \text{K}$$

$$\rho = \frac{M}{V_m}$$

$$\rho = 0.87 \cdot \frac{\text{gm}}{\text{cm}^3}$$

$$c = \frac{1}{\sqrt{\rho \cdot \kappa_S}}$$

$$\kappa_S = \frac{1}{\rho \cdot c^2}$$

$$\kappa_S = 6.855 \cdot 10^{-10} \cdot \frac{1}{\text{Pa}}$$

Now, we use eq. (3.27) to find the isothermal compressibility:

$$\kappa_T = \kappa_S + \frac{T \cdot V_m \cdot \alpha^2}{C_{pm}} \quad \kappa_T = 9.927 \cdot 10^{-10} \cdot \frac{1}{\text{Pa}}$$

Finally, we use eq. (3.26) to compute C_v :

$$\gamma = \frac{\kappa_T}{\kappa_S} \quad C_{vm} = \frac{C_{pm}}{\gamma} \quad C_{vm} = 92.5 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

SECTION 3.6

3.43

The Debye T^3 relation is given by eq. (3.29):

$$C_{pm} = aT^3$$

From Table 3.1, one of the basic equations for entropy is:

$$dS = \frac{C_P}{T} dT + \left(\frac{\partial V}{\partial T} \right)_P dP$$

The second term on the right-hand side is zero, since we are dealing with a solid. Thus, we have:

$$\Delta S = \int_0^T \frac{C_P}{T} dT$$

$$\Delta S = \int_0^T aT^2 dT$$

$$\Delta S = \frac{aT^3}{3} = \frac{C_{pm}}{3}$$

3.45

This is similar to example 3.21. We will integrate eq. (3.28) numerically. We can calculate the entropy at 13 K using the Debye law, eq. (3.30).

$$i = 0..22 \quad n = 0..21$$

T_i	C_{p_i}
13·K	2.866
14·K	3.474
15·K	4.167
20·K	8.368
25·K	13.159
30·K	17.991
35·K	22.531
40·K	26.527
50·K	32.991
60·K	37.928
70·K	41.735
80·K	44.978
90·K	47.823
100·K	50.417
120·K	55.689
140·K	61.505
160·K	67.906
180·K	75.396
200·K	83.722
220·K	93.387
240·K	104.098
260·K	116.148
278.69·K	128.7

$$C_{pm_i} = C_{p_i} \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$S_0 = \frac{C_{pm_0}}{3}$$

$$\Delta S = S_0 + \sum_n \frac{C_{pm_n} - C_{pm_{n-1}}}{2} \cdot \ln \frac{T_{n+1}}{T_n}$$

$$\Delta S = 129.085 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

SECTION 3.7

3.47

In example 3.23, the formulas for the entropy imperfection of a gas obeying the virial series is derived:

$$S_i = - \left(B' P - \frac{\gamma P^2}{2} \right)$$

We ignore the γ term. The RK form of the second virial coefficient is given on Table 1.2:

$$B(T) = b - \frac{a}{RT^{3/2}}$$

The derivative with respect to temperature is:

$$B' = \frac{3a}{2RT^{5/2}}$$

Thus, the energy imperfection is given by:

$$S_i = - \frac{3aP}{2RT^{5/2}}$$

The constant a for acetylene in the RK equation can be found on Table 1.1. The standard entropy is given on Table 3.2.

$$\text{bar} := 10^5 \text{ Pa}$$

$$P := 1 \text{ bar}$$

$$T := 298.15 \text{ K}$$

$$R := 8.31451 \frac{\text{joule}}{\text{mole K}}$$

$$a := 7.895 \frac{\text{Pa m}^6 \text{ K}^{1/2}}{\text{mole}^2}$$

$$S^\theta = 200.94 \frac{\text{joule}}{\text{mole K}}$$

$$S := S^\theta - \frac{3aP}{2RT^{5/2}}$$

$$S = 200.85 \frac{\text{joule}}{\text{mole K}}$$

3.49

The standard entropy of Ar at 298.15 K is given on Table 3.2. We will assume ideal gas and use eq. (3.31).

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T_1 = 298.15 \cdot \text{K} \quad T_2 = 775 \cdot \text{K} \quad S_{298} = 154.853 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$C_{pm} = 2.5 \cdot R$$

$$S = S_{298} + C_{pm} \ln \frac{T_2}{T_1} \quad S = 174.709 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

3.51

Table 3.2 gives the standard entropy of ethane at 298.15 K. We use eq. (3.31) and the heat capacity given on Table 2.2:

$$T_1 = 298.15 \cdot \text{K} \quad T_2 = 2500 \cdot \text{K} \quad S_{298} = 5.740 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$C_p(T) = 14.22 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} + 0.00922 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}^2} \cdot T + 1.87 \cdot 10^{-6} \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}^3} \cdot T^2 - 7.51 \cdot 10^{-5} \cdot \frac{\text{joule} \cdot \text{K}}{\text{mole}} \cdot \frac{1}{T^2}$$

$$S = S_{298} + \int_{T_1}^{T_2} \frac{C_p(T)}{T} dT \quad S = 46.354 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

3.53

Since the liquid is incompressible, we use eq. (3.39): The properties of benzene can be found on Table 1.8.

$$\text{MPa} = 10^6 \cdot \text{Pa} \quad P_{\text{ref}} = 0.1 \cdot \text{MPa} \quad P = 15 \cdot \text{MPa} \quad \alpha = 1.237 \cdot 10^{-3} \cdot \frac{1}{\text{K}} \quad V = 89 \cdot \text{cm}^3$$

$$\Delta S = -\alpha \cdot V \cdot (P - P_{\text{ref}}) \quad \Delta S = -1.64 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

3.55

We use eq. (3.39):

$$\text{MPa} = 10^6 \cdot \text{Pa} \quad P_{\text{ref}} = 0.1 \cdot \text{MPa} \quad P = 1 \cdot \text{MPa} \quad \alpha = 1.236 \cdot 10^{-3} \cdot \frac{1}{\text{K}} \quad V = 97 \cdot \text{cm}^3$$

$$S_{\text{ref}} = 216.40 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$S = S_{\text{ref}} - \alpha \cdot V \cdot (P - P_{\text{ref}}) \quad S = 216.292 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

3.57

A reversible, adiabatic process is isentropic. We can set the change in entropy, eq. (3.37), equal to zero and solve for T . As a first guess, we set $T_2 = 500$ K, since we know the gas will probably cool upon expansion.

$$R = 8.31451 \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad V_1 = 0.75 \frac{\text{liter}}{\text{mole}} \quad V_2 = 50.6 \frac{\text{liter}}{\text{mole}} \quad T_1 = 1492 \cdot \text{K}$$

$$C_{pm}(T) = 25.79 \frac{\text{joule}}{\text{mole} \cdot \text{K}} + 0.00809 \frac{\text{joule}}{\text{mole} \cdot \text{K}^2} \cdot T + 1.49 \cdot 10^{-6} \frac{\text{joule}}{\text{mole} \cdot \text{K}^3} \cdot T^2 + 0.88 \cdot 10^{-5} \frac{\text{joule} \cdot \text{K}}{\text{mole}} \cdot \frac{1}{T^2}$$

$$T_2 = 500 \cdot \text{K}$$

$$T_2 = \text{root} \left[\int_{T_1}^{T_2} \frac{C_{pm}(T)}{T} dT + R \cdot \ln \left(\frac{T_1 \cdot V_2}{T_2 \cdot V_1} \right), T_2 \right] \quad T_2 = 323.027 \cdot \text{K}$$

We do something similar for the RK gas. The entropy imperfection for an RK gas is given on Table 3.3.

$$a = 1.551 \frac{\text{Pa} \cdot \text{m}^6}{\text{mole}^2 \cdot \text{K}} \quad b = 26.74 \cdot 10^{-6} \frac{\text{m}^3}{\text{mole}}$$

$$S_i(V, T) = \frac{a}{2 \cdot b \cdot T^{1.5}} \cdot \ln \left(\frac{V}{V+b} \right) - R \cdot \ln \left(\frac{V}{V-b} \right)$$

$$T_2 = \text{root} \left[\int_{T_1}^{T_2} \frac{C_{pm}(T)}{T} dT + R \cdot \ln \left(\frac{T_1 \cdot V_2}{T_2 \cdot V_1} \right) + S_i(V_2, T_2) - S_i(V_1, T_1), T_2 \right]$$

$$T_2 = 318.213$$

SECTION 3.8

3.59

Equation (3.42) gives us the definition of work, and we plug eq. (3.45) into this expression to obtain work in terms of stress.

$$w = \int_{l_0}^l f \, dl \qquad \sigma = \frac{f}{A_0} \qquad w = \int_{l_0}^l \sigma A_0 \, dl$$

$$\frac{w}{V} = \int_{l_0}^l \frac{\sigma A_0}{l_0 A_0} \, dl = \int_{l_0}^l \frac{\sigma}{l_0} \, dl$$

Equation (3.46) gives us the relationship between length and strain. We can substitute this into the integral:

$$\epsilon = \frac{l - l_0}{l_0} \qquad d\epsilon = \frac{dl}{l_0} \qquad \epsilon(l_0) = \frac{l_0 - l_0}{l_0} = 0 \qquad \epsilon(l) = \frac{l - l_0}{l_0} = \epsilon$$

$$\frac{w}{V} = \int_0^\epsilon \sigma \, d\epsilon$$

The stress is given by:

$$\sigma = \frac{\rho RT}{zM} \left(\frac{1}{l_0} - \left(\frac{l_0}{l} \right)^2 \right) \qquad \frac{1}{l} = \frac{1}{l_0} - \frac{l_0}{l} + \frac{l_0}{l} \qquad \frac{1}{l_0} = \frac{1 - l_0}{l_0} + 1 = \epsilon + 1$$

$$\sigma = \frac{\rho RT}{zM} \left(\epsilon + 1 - \left(\frac{1}{\epsilon + 1} \right)^2 \right)$$

We can perform the integration to obtain:

$$\frac{w}{V} = \int_0^{\epsilon} \frac{\rho RT}{zM} \left(\epsilon + 1 - \left(\frac{1}{\epsilon + 1} \right)^2 \right) d\epsilon \quad \text{Let } u = \epsilon + 1.$$

$$\frac{w}{V} = \int_1^{\epsilon+1} \frac{\rho RT}{zM} \left(u - \frac{1}{u^2} \right) du = \frac{\rho RT}{zM} \left[\frac{u^2}{2} + \frac{1}{u} \right]_1^{\epsilon+1} = \frac{\rho RT}{zM} \left[\frac{(\epsilon+1)^2}{2} + \frac{1}{\epsilon+1} - \left[\frac{1^2}{2} + \frac{1}{1} \right] \right]$$

$$\frac{w}{V} = \frac{\rho RT}{zM} \left[\frac{(\epsilon+1)^3 + 2 - 3(\epsilon+1)}{2(\epsilon+1)} \right] = \frac{\rho RT}{zM} \left[\frac{\epsilon^3 + 3\epsilon^2 + 3\epsilon + 1 + 1 - 3\epsilon - 3}{2(\epsilon+1)} \right]$$

$$\frac{w}{V} = \frac{\rho RT}{zM} \left[\frac{\epsilon^2(\epsilon+3)}{2(\epsilon+1)} \right]$$

For isoprene, we have:

$$T := 298.15 \text{ K}$$

$$M := 0.068 \text{ kg}$$

$$\rho := 0.970 \text{ g/cm}^3$$

$$l_o := 10 \text{ cm}$$

$$l := 50 \text{ cm}$$

$$A_o := 0.05 \text{ cm}^2$$

$$V := A_o l_o$$

$$R := 8.31451 \frac{\text{joule}}{\text{mole K}}$$

$$\epsilon := \frac{l - l_o}{l_o}$$

The percent cross-linking is 1.25, so 1.25 out of 100 monomer units is cross-linked. Thus, the number of monomer units in a chain is $100/1.25$.

$$\% \text{cross-link} := 1.25$$

$$z := 100/1.25$$

$$z = 80$$

$$w := \frac{\rho V R T}{zM} \left[\frac{\epsilon^2(\epsilon+3)}{2(\epsilon+1)} \right]$$

$$w = 2.47 \text{ joule}$$

The stress is given by:

$$\sigma = \frac{\rho RT}{zM} \left(\frac{1}{l_0} - \left(\frac{l_0}{l} \right)^2 \right) \qquad \frac{1}{l_0} = \frac{1}{l_0} - \frac{l_0}{l_0} + \frac{l_0}{l_0} \qquad \frac{1}{l_0} = \frac{l - l_0}{l_0} + 1 = \varepsilon + 1$$

$$\sigma = \frac{\rho RT}{zM} \left(\varepsilon + 1 - \left(\frac{1}{\varepsilon + 1} \right)^2 \right)$$

We differentiate with respect to the strain to yield:

$$\left(\frac{\partial \sigma}{\partial \varepsilon} \right) = \frac{\rho RT}{zM} \left(1 + \frac{2}{(\varepsilon + 1)^3} \right)$$

To obtain the initial slope, we plug in $l = l_0$. This is equivalent to substituting $\varepsilon = 0$.

$$\left(\frac{\partial \sigma}{\partial \varepsilon} \right)_{l_0} = \frac{\rho RT}{zM} \left(1 + \frac{2}{(0 + 1)^3} \right) \qquad \left(\frac{\partial \sigma}{\partial \varepsilon} \right)_{l_0} = \frac{3\rho RT}{zM}$$

From Table 3.4:

$$T := 298 \text{ K}$$

$$M := 0.086 \text{ kg}$$

$$\rho := 1.320 \text{ g/cm}^3$$

$$R := 8.31451 \frac{\text{joule}}{\text{mole K}}$$

$$\text{initslope} := 1.6 \cdot 10^6 \text{ Pa}$$

$$z := \frac{3\rho RT}{\text{initslope } M}$$

$$z = 71.3$$

The number of monomer units in a chain is 71.3, so the number of molecules cross-linked will be 100/71.3.

$$\% \text{cross-link} := 100/z$$

$$\% \text{cross-link} = 1.40 \%$$

3.63

By analogy with the coefficient of thermal expansion, we define the coefficient of linear expansion to be:

$$\alpha_L = \frac{1}{L} \left(\frac{dL}{dT} \right)_P$$

We will take the coefficient of linear expansion to be 1/3 the coefficient of thermal expansion. Approximating the derivative as a difference gives us:

$$\Delta L = \frac{1}{3} \cdot \alpha \cdot L \cdot \Delta T$$

We use a typical value from Table 3.4 to approximate the change in L .

$$L = 15 \cdot \text{cm} \quad \Delta T = 100 \cdot \text{K} \quad \alpha = 6.6 \cdot 10^{-4} \cdot \frac{1}{\text{K}} \quad \Delta L = \frac{1}{3} \cdot \alpha \cdot L \cdot \Delta T \quad \Delta L = 0.33 \cdot \text{cm}$$

3.65

From eq. (3.48),

$$dU = TdS + fdl$$

The total differential with respect to temperature and elongation is:

$$dU = \left(\frac{\partial U}{\partial T} \right)_l dT + \left(\frac{\partial U}{\partial l} \right)_T dl$$

Comparing these two equations, we obtain

$$TdS + fdl = \left(\frac{\partial U}{\partial T} \right)_l dT + \left(\frac{\partial U}{\partial l} \right)_T dl$$

Since we are concerned with a change that occurs at constant length, the dL terms on both sides of the equation will be zero, leaving us with:

$$TdS = \left(\frac{\partial U}{\partial T}\right)_l dT$$

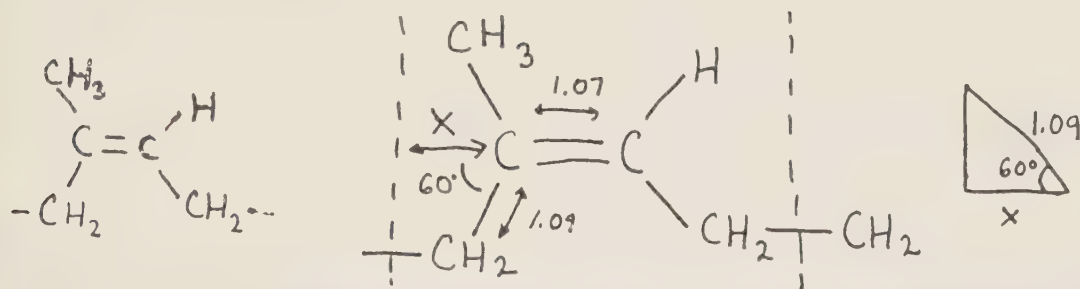
Now we define $\left(\frac{\partial U}{\partial T}\right)_l = C_l$ by analogy with C_v . This gives us:

$$TdS = C_l dT$$

$$\left(\frac{\partial S}{\partial T}\right)_l = \frac{C_l}{T}$$

3.67

(a) An isoprene unit looks like this:



(I don't know how you were supposed to know that. I didn't know it when I took PChem either). From trigonometry, we find that

$$x = 1.09 \cdot 10^{-8} \cdot \text{cm} \cdot \cos\left(\frac{\pi}{3}\right) \quad x = 5.45 \cdot 10^{-9} \cdot \text{cm}$$

which gives us a total length of:

$$l = 1.07 \cdot 10^{-8} \cdot \text{cm} + 2 \cdot x + 1.09 \cdot 10^{-8} \cdot \text{cm} \quad l = 3.25 \cdot 10^{-8} \cdot \text{cm}$$

(b) The mean length is denoted as l_{mean} , and is calculated using the equation given in the problem:

$$N = 80 \quad l_{\text{mean}} = \sqrt{N} \cdot l \quad l_{\text{mean}} = 2.907 \cdot 10^{-7} \cdot \text{cm}$$

(c) First we calculate the volume of the cell:

$$V = l_{\text{mean}}^3 \quad V = 2.456 \cdot 10^{-20} \cdot \text{cm}^3$$

Now, each of the 12 sides of a cell is shared by four other cells (again, refer to the excellent artwork below to make this clearer). Thus, the weight of one cell is 1/4 of the weight of the 12 chains which make up the sides.

$$M = 68 \cdot \frac{\text{gm}}{\text{mole}}$$

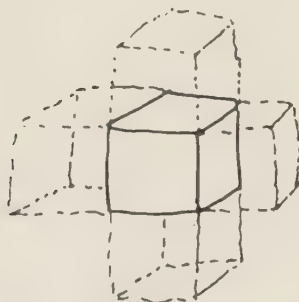
$$L = 6.022 \cdot 10^{23} \cdot \frac{1}{\text{mole}}$$

$$W = \frac{12}{4} \cdot N \cdot \frac{M}{L}$$

$$W = 2.71 \cdot 10^{-20} \cdot \text{gm}$$

$$\rho = \frac{W}{V}$$

$$\rho = 1.103 \cdot \frac{\text{gm}}{\text{cm}^3}$$



CHAPTER 4 *Equilibrium in Pure Substances*

SECTION 4.1

4.1

We can parallel a similar derivation given in section 4.1 of the text. First, we will start with the definition of the Helmholtz free energy,

$$A = U - TS$$

$$\frac{A}{T} = \frac{U}{T} - S$$

Taking the partial derivative of this equation with respect to temperature gives

$$\left(\frac{\partial(A/T)}{\partial T} \right)_V = \frac{1}{T} \left(\frac{\partial U}{\partial T} \right)_V - \frac{U}{T^2} - \left(\frac{\partial S}{\partial T} \right)_V$$

From Table 3.1, the following relations show that the first and third terms on the right add to zero.

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V$$

Therefore, our expression for the temperature dependence of the Helmholtz free energy simplifies to

$$\left(\frac{\partial(A/T)}{\partial T} \right)_V = -\frac{U}{T^2}$$

This can further be simplified by use of the chain rule:

$$\frac{d(A/T)}{dT} = \frac{d(A/T)}{d(1/T)} \frac{d(1/T)}{dT} = -\frac{1}{T^2} \frac{d(A/T)}{d(1/T)}$$

Combining the previous two results gives

$$-\frac{1}{T^2} \left(\frac{\partial(A/T)}{\partial(1/T)} \right)_V = -\frac{U}{T^2}$$

$$\left(\frac{\partial(A/T)}{\partial(1/T)} \right)_V = U$$

4.3

The dependence of the chemical potential on pressure is given by eq. 4.12

$$\left(\frac{\partial \mu}{\partial P} \right)_T = V_m$$

For constant temperature,

$$d\mu = V_m dP$$

Inserting the given equation of state and integrating gives

$$\int_{\mu_1}^{\mu_2} d\mu = \int_{P_1}^{P_2} \left[\frac{RT}{P} + B(T) \right] dP$$

$$\mu_2 - \mu_1 = RT \ln \left(\frac{P_2}{P_1} \right) + B(P_2 - P_1)$$

SECTION 4.2

4.5

The activity is defined by eq. 4.15, where the standard chemical potential is the chemical potential at 1 bar.

$$a \equiv \exp \left[\frac{\mu - \mu^\theta}{RT} \right]$$

The change in the chemical potential with pressure is given by eq. 4.12. We will be able to use this equation to calculate the difference in chemical potential from 1 bar to 100 atm.

$$\left(\frac{\partial \mu}{\partial P} \right)_T = V_m$$

At constant temperature this may be integrated to give,

$$\int_{\mu^\theta}^{\mu} d\mu = V_m \int_{P^\theta}^{100 \text{ atm}} dP$$

$$\mu - \mu^\theta = V_m (100 \text{ atm} - P^\theta)$$

We can now get an expression for the activity of water at 100 atm by inserting the above expression into eq. 4.15, the definition of activity.

$$a = \exp \left[\frac{V_m (100 \text{ atm} - P^\theta)}{RT} \right]$$

With

$$V_m = 18.069 \times 10^{-6} \frac{\text{m}^3}{\text{mol}}, \quad 100 \text{ atm} = 10132500 \text{ Pa}, \quad P^\theta = 10^5 \text{ Pa}, \quad R = 8.31451 \frac{\text{J}}{\text{mol K}}, \quad T = 298.15 \text{ K}$$

$$a = 1.076$$

4.7

The activity is defined by eq. 4.15

$$a = \exp\left(\frac{\mu - \mu^\theta}{RT}\right)$$

The ratio of the activities of two phases, alpha and beta, is thus given by

$$\frac{a_\beta}{a_\alpha} = \exp\left(\frac{\mu_\beta - \mu_\beta^\theta}{RT} - \frac{\mu_\alpha - \mu_\alpha^\theta}{RT}\right)$$

The requirement for equilibrium between the two phases is that the chemical potentials are equal. Therefore the following must be true

$$\mu_\alpha = \mu_\beta$$

Using this to simplify the ratio of activities expression gives

$$\frac{a_\beta}{a_\alpha} = \exp\left(\frac{\mu_\alpha^\theta - \mu_\beta^\theta}{RT}\right)$$

Recall that the chemical potential is just the partial molar Gibbs free energy. In addition, for a pure component, it is also equal to the molar Gibbs free energy. In the problem text, the following relationship was defined.

$$\Delta G^\theta = G_\beta^\theta - G_\alpha^\theta$$

In this equation, the quantities on the right are the standard molar Gibbs free energies for the respective phases. They are equal to the standard chemical potentials for the two phases as well because we are dealing with a pure component. If we were dealing with a multicomponent system we would have to use the partial molar Gibbs free energy for each component, which generally is not equal to the pure component molar Gibbs free energy.

Thus we may write the ratio of activities as

$$\frac{a_\beta}{a_\alpha} = \exp\left(\frac{-\Delta G^\theta}{RT}\right)$$

SECTION 4.3

4.9

If we can assume that the heat of vaporization is constant, we can use eq. 4.22, the integrated form of the Clausius-Clapeyron equation, to find the new boiling point at the reduced pressure.

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta vH}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

This equation gives the equilibrium relation between the temperature and vapor pressure at two points. If we take the normal boiling point of water of 373.15 K (and the corresponding vapor pressure of 1 atmosphere), we can estimate the vapor pressure at any other temperature or the temperature at any other vapor pressure. In this case, the latter will be more useful since we know the pressure but not the boiling temperature at the top of Mount Everest.

$$P_1 = 1 \cdot \text{atm} \quad T_1 = 373.15 \cdot \text{K}$$

$$P_2 = \frac{1}{3} \cdot \text{atm} \quad R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\text{From Table 4.2, we find that } \Delta vH = 40.66 \cdot 10^3 \cdot \frac{\text{joule}}{\text{mole}}$$

$$T_2 = -\Delta vH \cdot \frac{T_1}{\left(\ln\left(\frac{P_2}{P_1}\right) \cdot R \cdot T_1 - \Delta vH\right)}$$

$$T_2 = 344 \cdot \text{K}$$

4.11

The data from Table 4.2 give the normal boiling point of carbon tetrachloride and the heat of vaporization at the normal boiling point.

$$T_1 = 349.9 \cdot \text{K} \quad P_1 = 1 \cdot \text{atm} \quad R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\Delta vH = 30.0 \cdot \frac{\text{kJ}}{\text{mole}} \quad \text{kJ} \equiv 1000 \cdot \text{joule}$$

The Clausius-Clapeyron equation (eq. 4.20) gives the dependence of the vapor pressure-temperature relation on the heat of vaporization. For a constant heat of vaporization, this equation can be integrated to give eq. 4.22. This will allow us to predict the vapor pressure of carbon tetrachloride at any temperature.

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$$\ln \left(\frac{P_2}{P_1} \right) = - \frac{\Delta_v H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$T_2 = 400 \cdot K$$

$$P_2 = \exp \left[\frac{-(\Delta_v H \cdot T_1 - \Delta_v H \cdot T_2)}{R \cdot (T_2 \cdot T_1)} \right] \cdot P_1$$

$$P_2 = 3.64 \cdot \text{atm}$$

4.13

We are given two vapor pressure-temperature pairs. From these data, we can estimate the enthalpy of vaporization using the Clausius-Clapeyron equation (eq. 4.20). The form that is most useful in this case is the integrated form at constant enthalpy of vaporization, eq. 4.22. In that equation, the only unknown is the enthalpy of vaporization itself.

$$\ln \left(\frac{P_2}{P_1} \right) = - \frac{\Delta_v H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Given

$$T_1 = (1284 - 273.15) \cdot K$$

$$T_2 = (1487 - 273.15) \cdot K$$

$$P_1 = 1 \cdot \text{torr}$$

$$P_2 = 10 \cdot \text{torr}$$

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot K}$$

$$\Delta_v H = \frac{- \ln \left(\frac{P_2}{P_1} \right)}{\left(\frac{1}{R \cdot T_2} - \frac{1}{R \cdot T_1} \right)}$$

$$\Delta_v H = 258 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\text{kJ} \equiv 1000 \cdot \text{joule}$$

Now we can use the calculated heat of vaporization and one of the given data points in eq. 4.22 to solve for the temperature for which the vapor pressure is 5 torr.

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta vH}{R} \cdot \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$P_1 = 1 \cdot \text{torr} \quad P_2 = 5 \cdot \text{torr}$$

$$T_1 = (1284 + 273.15) \cdot \text{K}$$

$$T_2 = -\Delta vH \cdot \frac{T_1}{\left(\ln\left(\frac{P_2}{P_1}\right) \cdot R \cdot T_1 - \Delta vH\right)}$$

$$T_2 = 1693.68 \cdot \text{K}$$

$$C = K$$

$$T_2 - 273.15 \cdot \text{K} = 1420.53 \cdot \text{C}$$

4.15

The data from Table 4.2 give the normal boiling point of n-butane and the heat of vaporization at the normal boiling point.

$$T_1 = 272.65 \cdot \text{K} \quad P_1 = 1 \cdot \text{atm} \quad R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\Delta vH = 22.39 \cdot \frac{\text{kJ}}{\text{mole}} \quad \text{kJ} = 1000 \cdot \text{joule}$$

The Clausius-Clapeyron equation (eq. 4.20) gives the dependence of the vapor pressure-temperature relation on the heat of vaporization. For a constant heat of vaporization, this equation can be integrated to give eq. 4.22. This will allow us to predict the vapor pressure of n-butane at any temperature.

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta vH}{R} \cdot \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$T_2 = 300 \cdot \text{K}$$

$$P_2 = \exp\left[\frac{-(\Delta vH \cdot T_1 - \Delta vH \cdot T_2)}{R \cdot (T_2 \cdot T_1)}\right] \cdot P_1$$

$$P_2 = 2.46 \cdot \text{atm}$$

4.17

The Clausius-Clapeyron equation, eq. 4.20, tells us that the slope of $\ln(P)$ versus $1/T$ is equal to $-\Delta_v H/R$.

points = 3 $i = 0 \dots \text{points} - 1$

$T_i =$ $P_i =$

273.15
277.60
283.15

1.268
1.490
1.810

$$x_i = \frac{1}{T_i}$$

$$y_i = \ln(P_i \cdot 101325)$$

We are now ready to perform the regression. Notice that the pressures have been multiplied by a factor that converts atm to the SI unit of pascals. Actually, since we are interested only in the slope of the regression and not the intercept, conversion of pressure units is unnecessary, but it is included here for clarity and rigor.

$m = \text{slope}(x, y)$ $m = -2.753 \cdot 10^3$ m is the slope of the $\ln P$ vs. $1/T$ graph

$r = \text{corr}(x, y)$ $r = -0.9999998$ r is the correlation factor related to the goodness of fit

$b = \text{intercept}(x, y)$ $b = 21.841$ b is the intercept of the $\ln P$ vs $1/T$ graph

The standard deviation of the slope may be calculated using eq. A1.25 of the Appendix.

$$\sigma_m = \frac{m}{r} \cdot \sqrt{\frac{1 - r^2}{\text{points} - 2}}$$

$$\sigma_m = 1.783$$

$$R = 8.31451$$

$$\Delta_v H = -m \cdot R \cdot \frac{\text{joule}}{\text{mole}}$$

$$\Delta_v H = 22.887 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\text{kJ} = 1000 \cdot \text{joule}$$

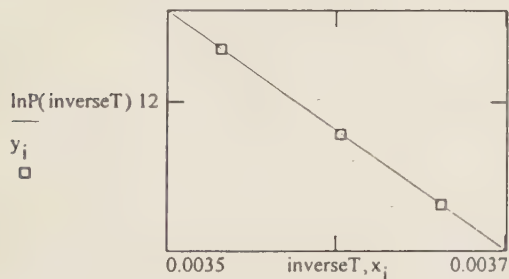
$$\sigma_{\Delta_v H} = \sigma_m \cdot R \cdot \frac{\text{joule}}{\text{mole}}$$

$$\sigma_{\Delta_v H} = 0.015 \cdot \frac{\text{kJ}}{\text{mole}}$$

It may be helpful to see a plot of the data and regressed fit on a $\ln P$ vs $1/T$ graph.

$$\ln P(x) = m \cdot x + b$$

$$\text{inverseT} = 0.0035, 0.00351 \dots 0.00370$$



This graph shows the fit of the $\ln P$ vs $1/T$ data. The slope of this line is $-\Delta_v H/R$ according to the Clausius-Clapeyron equation.

Summary

$$\Delta_v H = 22.887 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\sigma \Delta_v H = 0.015 \cdot \frac{\text{kJ}}{\text{mole}}$$

4.19

The Clausius-Clapeyron equation, eq. 4.20, tells us that the slope of $\ln(P)$ vs $1/T$ is equal to $-\Delta_v H/R$.

points 8 i 0..points 1

T_i	P_i
187.45	5
195.35	10
204.25	20
214.05	40
220.35	60
228.95	100
241.95	200
256.85	400

$$x_i = \frac{1}{T_i} \quad y_i = \ln P_i - 133.332$$

We are now ready to perform the regression. Notice that the pressures have been multiplied by a factor that converts torr to the SI unit of pascals. Actually, since we are interested only in the slope of the regression and not the intercept, conversion of pressure units is unnecessary, but it is included here for clarity and rigor.

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$m = \text{slope}(x, y) = 3.04 \cdot 10^3$ m is the slope of the $\ln P$ vs. $1/T$ graph

$r = \text{corr}(x, y) = -0.999847$ r is the correlation factor related to the goodness of fit

$b = \text{intercept}(x, y) = 22.759$ b is the intercept of the $\ln P$ vs $1/T$ graph

The standard deviation of the slope may be calculated using eq. A1.25 of the Appendix.

$$\sigma_m = \frac{m}{r} \cdot \frac{1}{\sqrt{\text{points} - 2}} \quad \sigma_m = 21.738 \quad R = 8.31451$$

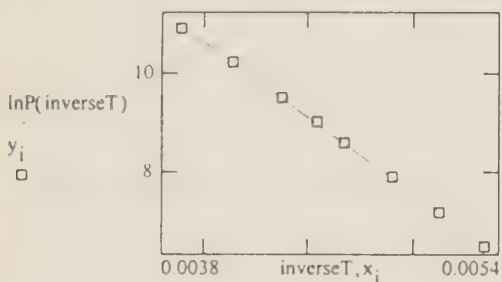
$$\Delta_v H = m \cdot R \cdot \frac{\text{joule}}{\text{mole}} \quad \Delta_v H = 25.28 \cdot \frac{\text{kJ}}{\text{mole}} \quad \text{kJ} = 1000 \cdot \text{joule}$$

$$\sigma_{\Delta_v H} = \sigma_m \cdot R \cdot \frac{\text{joule}}{\text{mole}} \quad \sigma_{\Delta_v H} = 0.18 \cdot \frac{\text{kJ}}{\text{mole}}$$

It may be helpful to see a plot of the data and regressed fit on a $\ln P$ vs $1/T$ graph.

$$\ln P(x) = m \cdot x + b$$

$$\text{inverseT} = 0.0038, 0.0039 \dots 0.0054$$



This graph shows the fit of the $\ln P$ vs $1/T$ data. The slope of this line is $-\Delta_v H/R$ according to the Clausius-Clapeyron equation.

Summary: $\Delta_v H = 25.28 \cdot \frac{\text{kJ}}{\text{mole}} \quad \sigma_{\Delta_v H} = 0.18 \cdot \frac{\text{kJ}}{\text{mole}}$

4.21

$$\ln\left(\frac{P}{\text{torr}}\right) = 25.7735 - \frac{7769.32}{T} - 1.05576 \cdot \ln(T)$$

part a)

$$P(T) = (T)^{1.05576} \cdot \exp\left(25.7735 - \frac{7769.32}{(T)}\right) \cdot \text{torr}$$

$$P(25 - 273.15) = 1.84 \cdot 10^{-3} \cdot \text{torr}$$

part b)

$$T_{\text{guess}} = 500$$

$$T_{\text{boil}} = \text{root}(P(T_{\text{guess}}) - 10^5 \cdot \text{Pa}, T_{\text{guess}}) \cdot \text{K}$$

$$T_{\text{boil}} = 629.11 \cdot \text{K}$$

part c)

From the Clausius-Clapeyron equation, we know that the derivative of $\ln P$ with respect to $1/T$ has a slope of $-\Delta_v H/R$. That derivative is referred to here as $d \ln P$.

$$d \ln P(T) = -7769.32 + 1.05576 \cdot T$$

The original vapor pressure expression is given as $\ln(P/\text{torr})$. The difference between $\ln(P/\text{torr})$ and $\ln(P/\text{Pa})$ is only a constant. When we take the derivative with respect to $1/T$, the constant term vanishes. Thus, for calculating the enthalpy of vaporization, it doesn't matter what pressure units are.

$$\Delta_v H(T) = -R \cdot d \ln P(T) \quad R \approx 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad \text{kJ} \approx 1000 \cdot \text{joule}$$

$$\Delta_v H(273) \cdot \text{K} = 62.2 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta_v H(473) \cdot \text{K} = 60.4 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta_v H(673) \cdot \text{K} = 58.7 \cdot \frac{\text{kJ}}{\text{mole}}$$

4.23

a) The Clausius-Clapeyron equation can be integrated to give an expression for the vapor pressure of N_2 as a function of temperature.

$$\ln(P) \cdot dP = \frac{\Delta_v H}{R \cdot T^2} dT \quad R \approx 8.31451$$

$$\ln(760 \cdot \text{torr}) = \frac{\Delta_v H}{R \cdot T^2} \quad T = 77.33 \cdot \text{K}$$

$$\Delta_v H(T) = 8070 - 32.07 \cdot T$$

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$$\ln \frac{P_2}{760} = \frac{8070}{R \cdot T^2} - \frac{32.07}{R} \cdot T \cdot dT$$

$$P(T) = 760 \cdot \exp \left(\frac{8070}{R \cdot T} - \frac{32.07 \cdot \ln(T)}{R} - \frac{8070}{R \cdot 77.33} + \frac{32.07 \cdot \ln(77.33)}{R} \right)$$

This can also be expressed as follows.

$$\ln \left(\frac{P}{\text{torr}} \right) = 35.9557 - \frac{970.5924}{T} + 3.8571 \cdot \ln(T)$$

b) The boiling temperature at 100 torr is the temperature at which the vapor pressure equals the ambient pressure.

$$T_{\text{guess}} = 150$$

$$T_{\text{boil}} = \text{root}(P(T_{\text{guess}}) - 100, T_{\text{guess}})$$

$$T_{\text{boil}} = 63.20$$

4.25

With heat capacity data, we no longer have to assume a constant heat of vaporization. We can use equation 4.24 to calculate the dependence of $\Delta_v H$ on temperature. With $\Delta_v H(T)$, we can integrate the Clausius-Clapeyron equation to obtain a more accurate description of the temperature dependence of vapor pressure.

$$\text{From Table 4.2: } \Delta_v H = 30.0 \cdot \frac{\text{kJ}}{\text{mole}} \quad T_b = 349.9 \cdot \text{K}$$

$$\text{kJ} = 1000 \cdot \text{joule}$$

$$C_{\text{pgas}} = 83.30 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad C_{\text{pliq}} = 131.74 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\Delta_v H(T) = \Delta_v H + (C_{\text{pgas}} - C_{\text{pliq}}) \cdot (T - 349.9 \cdot \text{K})$$

$$\text{We can now use this in the Clausius Clapeyron equation: } \frac{d(\ln P)}{dT} = \frac{\Delta_v H(T)}{R \cdot T^2}$$

Integrating from $P=1$ atm and $T=349.9$ K to any temperature T and pressure P gives

$$\ln\left(\frac{P}{1 \cdot \text{atm}}\right) = \int_{349.9 \cdot \text{K}}^T \frac{\Delta_v H(T)}{R \cdot T^2} dT$$

$$P(T) = 1 \cdot \text{atm} \cdot \exp\left(\int_{349.9 \cdot \text{K}}^T \frac{\Delta_v H(T)}{R \cdot T^2} dT\right)$$

$$P(400 \cdot \text{K}) = 3.46 \cdot \text{atm}$$

4.27

Part a)

The vapor pressure expression may be rearranged to the following form.

$$P(T) = \text{MPa} \cdot \exp\left(45.8006 - \frac{2681.5}{\left(\frac{T}{\text{K}}\right)} + .012366 \cdot \frac{T}{\text{K}} - 6.8688 \cdot \ln\left(\frac{T}{\text{K}}\right)\right) \quad \text{MPa} \approx 10^6 \cdot \text{Pa}$$

$$T_{\text{guess}} = 150 \cdot \text{K}$$

$$T_{\text{boil}} = \text{root}(P(T_{\text{guess}}) - 101325 \cdot \text{Pa}, T_{\text{guess}})$$

$$T_{\text{boil}} = 184.52 \cdot \text{K}$$

Part b)

The Clausius-Clapeyron equation tells us that the heat of vaporization is proportional to the derivative of $\ln(P)$ with respect to temperature.

$$\frac{d \ln(P)}{dT} = \frac{\Delta_v H}{R \cdot T^2} \quad R \approx 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad \text{kJ} \approx 1000 \cdot \text{joule}$$

We can easily obtain an expression for the left side by taking the derivative of the vapor pressure equation given in the problem text.

$$\ln P(T) = 45.8006 - \frac{2681.5}{T} + 0.012366 \cdot T - 6.8688 \cdot \ln(T)$$

$$\text{deriv}(T) = \left(\frac{2681.5}{T^2} + 0.012366 - \frac{6.8688}{T} \right) \cdot \frac{1}{K}$$

$$\Delta_v H(T) = \text{deriv}(T) \cdot R \cdot (T \cdot K)^2$$

$$\Delta_v H(125) = 16.76 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta_v H(150) = 16.04 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta_v H(175) = 15.45 \cdot \frac{\text{kJ}}{\text{mole}}$$

SECTION 4.4

4.29

The work required can be calculated from equation 4.25. This tells us that the work is equal to the product of the surface tension and the change in surface area.

$$\gamma = 72.0 \cdot 10^{-3} \cdot \frac{\text{newton}}{\text{m}}$$

$$r = 25 \cdot \text{nm}$$

$$\text{nm} = 10^{-9} \cdot \text{m}$$

$$\text{areadroplet} = 4 \cdot \pi \cdot r^2$$

$$\text{volumedroplet} = \frac{4}{3} \cdot \pi \cdot r^3$$

$$N_{\text{droplets}} = \frac{16 \cdot \text{cm}^3}{\text{volumedroplet}}$$

$$\text{totalsurface} = N_{\text{droplets}} \cdot \text{areadroplet}$$

$$\text{totalsurface} = 1920 \cdot \text{m}^2$$

$$\text{work} = \gamma \cdot \text{totalsurface}$$

$$\text{work} = 138 \cdot \text{joule}$$

Strictly, only the surface area change should be included here, but the initial surface area is negligible compared to the final surface area.

4.31

The surface free energy, surface internal energy, and surface entropy are defined by eqs. 4.28, 4.30, and 4.29, respectively. We can approximate these partial derivatives using data from Table 4.3.

$$\gamma_1 = 10.5 \cdot 10^{-3} \cdot \frac{\text{newton}}{\text{m}}$$

$$T_1 = \dots - 203 - 273, \text{ K}$$

$$\gamma_2 = 8.3 \cdot 10^{-3} \cdot \frac{\text{newton}}{\text{m}}$$

$$T_2 = \dots - 193 - 273, \text{ K}$$

$$\gamma_3 = 6.2 \cdot 10^{-3} \cdot \frac{\text{newton}}{\text{m}}$$

$$T_3 = \dots - 183 - 273, \text{ K}$$

Equation 4.28 tells us that the surface free energy is equal to the surface tension. Therefore:

$$A_s = \gamma_2$$

$$A_s = 0.0083 \cdot \frac{\text{newton}}{\text{m}}$$

Equation 4.30 shows that we need to evaluate the partial derivative of surface tension with respect to temperature, here denoted dg/dT .

$$dg/dT = \frac{g_3 - g_1}{T_3 - T_1} \quad dg/dT = -2.15 \cdot 10^{-4} \cdot \frac{\text{newton}}{\text{m} \cdot \text{K}}$$

$$U_s = g_2 - T_2 \cdot dg/dT$$

$$U_s = 0.0255 \cdot \frac{\text{joule}}{\text{m}^2}$$

Equation 4.29 tells us that the surface entropy is equal to the negative of dg/dT .

$$S_s = -dg/dT$$

$$S_s = 2.15 \cdot 10^{-4} \cdot \frac{\text{joule}}{\text{K} \cdot \text{m}^2}$$

4.33

The effect of surface tension on vapor pressure is given by eq. 4.36. This effect occurs because surface tension affects the liquid phase free energy, which in turn affects where the minimum of system free energy occurs, ie. equilibrium.

$$\ln \frac{P}{P_0} = \frac{2 \cdot g \cdot M}{r \cdot r \cdot R \cdot T}$$

$$P = \exp \left(2 \cdot g \cdot \frac{M}{(r \cdot r \cdot R \cdot T)} \right) \cdot P_0$$

$$P = 769 \cdot \text{torr}$$

Data: $P_0 = 760 \cdot \text{torr}$

$$T = (64.7 + 273.15) \cdot \text{K}$$

$$M = 32.04 \cdot \frac{\text{gm}}{\text{mole}}$$

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\rho = 0.7510 \cdot \frac{\text{gm}}{\text{cm}^3}$$

$$r = 50 \cdot 10^{-9} \cdot \text{m}$$

$$g = 20.2 \cdot 10^{-3} \cdot \frac{\text{newton}}{\text{m}}$$

Surface tension data from Table 4.3 at 50 C.

4.35

The effect of surface tension on vapor pressure is given by eq. 4.36. This effect occurs because surface tension affects the liquid phase free energy, which in turn affects where the minimum of system free energy occurs, ie. equilibrium.

$$\ln \frac{P}{P_o} = \frac{2 \cdot \gamma \cdot M}{\rho \cdot r \cdot R \cdot T}$$

$$P = \exp \left(\frac{2 \cdot \gamma \cdot M}{\rho \cdot r \cdot R \cdot T} \right) \cdot P_o$$

$$P = 1.285 \cdot \text{millitorr}$$

$$\text{Data: } P_o = 1.201 \cdot \text{millitorr}$$

$$T = (20 + 273.15) \cdot K$$

$$M = 200.59 \cdot \frac{\text{gm}}{\text{mole}}$$

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot K}$$

$$\text{millitorr} = 10^{-3} \cdot \text{torr}$$

$$\rho = 13.546 \cdot \frac{\text{gm}}{\text{cm}^3}$$

$$r = 85 \cdot 10^{-9} \cdot m$$

$$\gamma = 472 \cdot 10^{-3} \cdot \frac{\text{newton}}{m}$$

Surface tension data from
Table 4.3 at 20 C.

SECTION 4.5

4.37

The enthalpy change of this process consists of 5 steps. Three of the steps are the enthalpy changes of H_2O with temperature corresponding to the solid, liquid, and gas phases. The simplest way to calculate this contribution is to use an average heat capacity for each phase. The enthalpy change then becomes the average heat capacity multiplied by the temperature change. (Remember from chapter 2 that, at constant pressure, the enthalpy change is the integral of C_p with respect to temperature. This is the same as finding the area under the heat capacity lines on Figure 2.3.) Due to the phase changes that occur, the heats of fusion and vaporization must also be added to account for the total enthalpy change.

$$\Delta H_{\text{solid}} = 1.4 \frac{\text{joule}}{\text{K} \cdot \text{gm}} \cdot (273.15 \cdot \text{K} - 73.15 \cdot \text{K})$$

$$\Delta H_{\text{liquid}} = 4.2 \frac{\text{joule}}{\text{K} \cdot \text{gm}} \cdot (373.15 \cdot \text{K} - 273.15 \cdot \text{K})$$

$$\Delta H_{\text{gas}} = 2.0 \frac{\text{joule}}{\text{K} \cdot \text{gm}} \cdot (573.15 \cdot \text{K} - 373.15 \cdot \text{K})$$

$$\Delta H_{\text{fusion}} = 6010 \frac{\text{joule}}{\text{mole}} \cdot \frac{\text{mole}}{18.015 \cdot \text{gm}}$$

$$\Delta H_{\text{vaporization}} = 40660 \frac{\text{joule}}{\text{mole}} \cdot \frac{\text{mole}}{18.015 \cdot \text{gm}}$$

$$\Delta H_{\text{total}} = \Delta H_{\text{solid}} + \Delta H_{\text{liquid}} + \Delta H_{\text{gas}} + \Delta H_{\text{fusion}} + \Delta H_{\text{vaporization}}$$

$$\Delta H_{\text{total}} = 3.7 \cdot 10^3 \frac{\text{joule}}{\text{gm}}$$

4.39

If we may assume that the heat of fusion and molar volumes of liquid and solid lead are constant, we can use the integrated form of the Clapeyron equation (eq. 4.19) given by eq. 4.39.

$$\ln \frac{T_f}{T_{fo}} = \frac{(P - P_o) \cdot \Delta fV}{\Delta fH}$$

Given $\rho_{sol} = 11.23 \cdot \frac{\text{gm}}{\text{cm}^3}$ $\rho_{liq} = 10.51 \cdot \frac{\text{gm}}{\text{cm}^3}$

$$T_{fo} = (327.5 + 273.15) \cdot \text{K}$$

$$P_o = 1 \cdot \text{atm}$$

$$P = 1000 \cdot \text{atm}$$

$$\Delta fH = 5100 \cdot \frac{\text{joule}}{\text{mole}}$$

Heat of fusion from Table 4.2

$$\Delta fV = \frac{1}{\rho_{liq}} - \frac{1}{\rho_{sol}}$$

$$T_f = \exp \left(\frac{\Delta fV \cdot P - \Delta fV \cdot P_o}{\Delta fH} \right) \cdot T_{fo}$$

$$T_f = 615.4 \cdot \text{K} \quad \text{This corresponds to } 342 \text{ degrees Celsius.}$$

$$\Delta T_f = T_f - T_{fo}$$

$$\Delta T_f = 14.8 \cdot \text{K}$$

4.41

Recall that the equilibrium condition is that the chemical potentials are equal. The problem text gives us the difference between the chemical potentials at the standard state ($P=1$ bar) and 25 C. However, as the pressure changes, so do the chemical potentials. Therefore, we must find the pressure at which the chemical potentials become equal at 25 C. The partial derivative of a pure component chemical potential with respect to pressure at constant temperature is the volume, which was derived in chapter 3. Therefore, we can use the volume to predict the variation of the chemical potential with pressure. Since the phases are virtually incompressible, we can use the equilibrium condition of eq. 4.37 to find the pressure at which the two phases are in equilibrium.

$$\mu_o \text{ dia} + Vm_{\text{dia}} \cdot (P - P_o) = \mu_o \text{ gra} + Vm_{\text{gra}} \cdot (P - P_o) \quad \text{Given: } \Delta G_o = 2900 \cdot \frac{\text{joule}}{\text{mole}} \quad P_o = 10^5 \cdot \text{Pa}$$

$$\mu_o \text{ dia} - \mu_o \text{ gra} = \Delta G_o = Vm_{\text{gra}} - Vm_{\text{dia}} \cdot (P - P_o)$$

$$P - P_o = \frac{\Delta G_o}{Vm_{\text{gra}} - Vm_{\text{dia}}}$$

$$P = 1.53 \cdot \text{GPa}$$

$\rho_{\text{dia}} = 3.51 \cdot \frac{\text{gm}}{\text{cm}^3}$ $\rho_{\text{gra}} = 2.26 \cdot \frac{\text{gm}}{\text{cm}^3}$

$MW_C = 12.011 \cdot \frac{\text{gm}}{\text{mole}}$

$Vm_{\text{dia}} = \frac{MW_C}{\rho_{\text{dia}}}$ $Vm_{\text{gra}} = \frac{MW_C}{\rho_{\text{gra}}}$

$\text{GPa} = 10^9 \cdot \text{Pa}$

4.43

Part a)

Since the difference in standard free energy at 25 C is positive for the transition of calcite to aragonite, the calcite form is more stable under those conditions. Recall that the equilibrium form is the one which minimizes free energy.

Part b)

The equilibrium condition is that the chemical potentials are equal. The problem text gives us the difference between the chemical potentials (ΔG_o) at the standard state ($P=1$ bar) and 25 C. However, as the pressure changes, so do the chemical potentials. Therefore, we must find the pressure at which the chemical potentials become equal at 25 C. Since the phases are virtually incompressible, we can use the equilibrium condition of eq. 4.37 to find the pressure at which the two phases are in equilibrium.

Given

$$\mu_{o\text{ ara}} + V_{m\text{ ara}}(P - P_o) = \mu_{o\text{ cal}} + V_{m\text{ cal}}(P - P_o)$$

$$\rho_{\text{cal}} = 2.71 \frac{\text{gm}}{\text{cm}^3} \quad \rho_{\text{ara}} = 2.93 \frac{\text{gm}}{\text{cm}^3}$$

$$MW_{\text{CaCO}_3} = 100.0872 \frac{\text{gm}}{\text{mole}}$$

$$\mu_{o\text{ ara}} - \mu_{o\text{ cal}} = \Delta G_o = (V_{m\text{ cal}} - V_{m\text{ ara}})(P - P_o)$$

$$\text{MPa} = 10^6 \cdot \text{Pa}$$

$$P_o = 10^5 \cdot \text{Pa}$$

$$\Delta G_o = 1040 \frac{\text{joule}}{\text{mole}}$$

$$P - P_o = \frac{\Delta G_o}{(V_{m\text{ cal}} - V_{m\text{ ara}})}$$

$$V_{m\text{ cal}} = \frac{MW_{\text{CaCO}_3}}{\rho_{\text{cal}}} \quad V_{m\text{ ara}} = \frac{MW_{\text{CaCO}_3}}{\rho_{\text{ara}}}$$

$$P = 375 \cdot \text{MPa}$$

Part c)

If we can assume that ΔH_o and ΔS_o are invariant with temperature, we can calculate ΔG_o at 1000 K using $G=H-TS$.

$$\Delta H_o = 0.21 \frac{\text{kJ}}{\text{mole}} \quad \Delta S_o = -4.2 \frac{\text{joule}}{\text{K} \cdot \text{mole}}$$

$$\text{kJ} = 1000 \cdot \text{joule}$$

$$\Delta G_o(T) = \Delta H_o - T \cdot \Delta S_o$$

$$P(T) - P_o = \frac{\Delta G_o(T)}{(V_{m\text{ cal}} - V_{m\text{ ara}})}$$

$$P(1000 \cdot \text{K}) = 1439 \cdot \text{MPa}$$

SECTION 4.6

4.45

The Clausius-Clapeyron equation relates the vapor and sublimation pressures of a substance to the heats of vaporization and sublimation, respectively.

$$\frac{d \cdot \ln P_{\text{vap}}}{d \cdot \frac{1}{T}} = \frac{\Delta_v H}{R} \quad \text{and} \quad \frac{d \cdot \ln P_{\text{sub}}}{d \cdot \frac{1}{T}} = \frac{\Delta_s H}{R} \quad R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad \text{kJ} = 1000 \cdot \text{joule}$$

From Figure 4.2 we can estimate the derivatives in the above equations. The slopes of the figure are related to the needed derivatives. If we multiply the derivatives by $-R$, that will give us $\Delta_v H$ and $\Delta_s H$.

$$\text{slope}_{\text{vap}} = \frac{1.6 - 4.2}{4.6 - 3.3}$$

$$\text{slope}_{\text{sub}} = \frac{1.6 - 1.6}{5.6 - 4.6}$$

$$\text{deriv}_{\text{vap}} = \text{slope}_{\text{vap}} \cdot 1000 \cdot \text{K}$$

$$\text{deriv}_{\text{sub}} = \text{slope}_{\text{sub}} \cdot 1000 \cdot \text{K}$$

$$\Delta_v H = \text{deriv}_{\text{vap}} \cdot (-R)$$

$$\Delta_s H = \text{deriv}_{\text{sub}} \cdot (-R)$$

$$\Delta_v H = 16.6 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta_s H = 26.6 \cdot \frac{\text{kJ}}{\text{mole}}$$

The enthalpy of fusion can be estimated as the difference between the enthalpies of vaporization and sublimation. (See example 4.7 in the text.)

$$\Delta_f H = \Delta_s H - \Delta_v H$$

$$\Delta_f H = 10 \cdot \frac{\text{kJ}}{\text{mole}}$$

4.47

The Clausius-Clapeyron equation relates the vapor and sublimation pressures of a substance to the heats of vaporization and sublimation, respectively.

$$\frac{d \cdot \ln P_{\text{vap}}}{d \cdot \frac{1}{T}} = \frac{\Delta_v H}{R} \quad \text{and} \quad \frac{d \cdot \ln P_{\text{sub}}}{d \cdot \frac{1}{T}} = \frac{\Delta_s H}{R} \quad R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad \text{kJ} = 1000 \cdot \text{joule}$$

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From the given data we can estimate the derivatives in the above equations. They will be referred to as $\text{deriv}_{\text{vap}}$ and $\text{deriv}_{\text{sub}}$. If we multiply the derivatives by $-R$, that will give us $\Delta_{\text{v}}H$ and $\Delta_{\text{s}}H$.

$$i = 0..1$$

$$T_{\text{solid}_i} =$$

$$P_{\text{solid}_i} =$$

$$T_{\text{liquid}_i} =$$

$$P_{\text{liquid}_i} =$$

$$\begin{array}{|c|} \hline 62.7 - 273.15 \\ \hline 51.8 - 273.15 \\ \hline \end{array}$$

$$\begin{array}{|c|} \hline 40 \\ \hline 100 \\ \hline \end{array}$$

$$\begin{array}{|c|} \hline 33 - 273.15 \\ \hline 21 - 273.15 \\ \hline \end{array}$$

$$\begin{array}{|c|} \hline 400 \\ \hline 760 \\ \hline \end{array}$$

$$\ln P_{\text{solid}_i} = \ln(P_{\text{solid}_i})$$

$$\ln P_{\text{liquid}_i} = \ln(P_{\text{liquid}_i})$$

$$\text{inverse}T_{\text{solid}_i} = \frac{1}{T_{\text{solid}_i}}$$

$$\text{inverse}T_{\text{liquid}_i} = \frac{1}{T_{\text{liquid}_i}}$$

$$\text{deriv}_{\text{sub}} = \text{slope}(\text{inverse}T_{\text{solid}}, \ln P_{\text{solid}}) \cdot K$$

$$\text{deriv}_{\text{vap}} = \text{slope}(\text{inverse}T_{\text{liquid}}, \ln P_{\text{liquid}}) \cdot K$$

$$\text{intercept}_{\text{sub}} = \text{intercept}(\text{inverse}T_{\text{solid}}, \ln P_{\text{solid}})$$

$$\text{intercept}_{\text{vap}} = \text{intercept}(\text{inverse}T_{\text{liquid}}, \ln P_{\text{liquid}})$$

$$\Delta_{\text{s}}H = -R \cdot \text{deriv}_{\text{sub}}$$

$$\Delta_{\text{v}}H = -R \cdot \text{deriv}_{\text{vap}}$$

$$\Delta_{\text{s}}H = 32.6 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta_{\text{v}}H = 26.9 \cdot \frac{\text{kJ}}{\text{mole}}$$

The enthalpy of fusion can be estimated as the difference between the enthalpies of vaporization and sublimation. (See example 4.7 in the text.)

$$\Delta_{\text{f}}H = \Delta_{\text{s}}H - \Delta_{\text{v}}H$$

$$\Delta_{\text{f}}H = 5.6 \cdot \frac{\text{kJ}}{\text{mole}}$$

The triple point occurs where the sublimation pressure equals the vapor pressure.

$$\ln P_{\text{sub}}(T) = \text{intercept}_{\text{sub}} + \frac{\text{deriv}_{\text{sub}}}{T}$$

$$\ln P_{\text{vap}}(T) = \text{intercept}_{\text{vap}} + \frac{\text{deriv}_{\text{vap}}}{T}$$

$$T_{\text{guess}} = 300 \cdot K$$

$$T_{\text{c}} = \text{root}(\ln P_{\text{sub}}(T_{\text{guess}}) - \ln P_{\text{vap}}(T_{\text{guess}}), T_{\text{guess}})$$

$$T_{\text{c}} = 240.3 \cdot K$$

$$P_{\text{c}} = \exp(\ln P_{\text{vap}}(T_{\text{c}})) \cdot \text{torr}$$

$$P_{\text{c}} = 402.5 \cdot \text{torr}$$

SECTION 4.7

4.49

For a second order phase transition, the entropy is continuous at the phase transition. Therefore, the entropies of phases a and b must be equal.

$$S_a = S_b$$

In order for the system to remain at equilibrium if the conditions are changed (such as temperature and pressure), the entropy change of each phase must also be equal.

$$dS_a = dS_b$$

We may also write the differential change in entropy using the slope formula for partial derivatives

$$dS = \left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP$$

From Table 3.1, we can easily identify the slopes in the above equation as follows

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

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P = -V\alpha$$

Thus the slope formula becomes

$$dS = \frac{C_P}{T} dT - V\alpha dP$$

Now if we equate the differential entropy changes using the above equation for phases a and b, we get

$$\frac{C_{P,a}}{T} dT - V_a \alpha_a dP = \frac{C_{P,b}}{T} dT - V_b \alpha_b dP$$

Since the volume change at the phase transition is zero, the volumes of phases a and b must be the same. Thus we may drop the volume subscripts. Collecting terms in the above equation gives

$$V(\alpha_a - \alpha_b)dP = \frac{C_{p,a} - C_{p,b}}{T}dT$$

Further rearrangement gives

$$\frac{dP}{dT} = \frac{\Delta C_p}{TV\Delta\alpha}$$

SECTION 4.9

4.51

Gas Constant and Units: R 8.31451 $\text{cm}^3 \cdot 0.01$ MPa $\cdot 10^6$ atm 101325

Constants for Nitrogen: T_c 126 P_c 3.394 MPa

van der Waals constants: $a = \frac{27 \cdot R^2 \cdot T_c^2}{64 \cdot P_c}$ $b = \frac{R \cdot T_c}{8 \cdot P_c}$

T 77.33

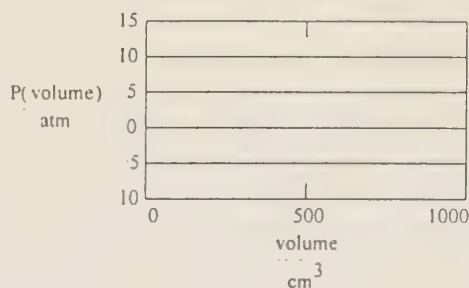
$$P(V_m) = \frac{R \cdot T}{V_m - b} - \frac{a}{V_m^2}$$

This plot can be used to obtain an initial guess for the vapor pressure. The estimate should be chosen in the two phase region where the "areas" bounded by the curve above and below the estimate are about equal.

Vapor Pressure Estimate

$$p_0 = 5 \cdot \text{atm}$$

volume $50 \cdot \text{cm}^3, 51 \cdot \text{cm}^3 \dots 1000 \cdot \text{cm}^3$



The solution can be found by solving eq. 4.40 when $\Delta_v G = 0$. It will be useful to define functions for calculating the liquid volume (V_1), the gas volume (V_2), and the indefinite integral of $P(V_m)dV_m$. Then, it will be possible to iterate to find the vapor pressure.

	Initial Guess	Volume Function
Liquid	$v_b = 1.01 \cdot b$	$V_1(px) = \text{root}(px - P(v_b), v_b)$
Vapor	$v_a = \frac{R \cdot T}{p_0}$	$V_2(px) = \text{root}(px - P(v_a), v_a)$

These initial guesses should converge on the liquid and vapor volumes. Recall that there are three real roots in the critical region. The liquid volume initial guess was chosen to be slightly larger than the van der Waals b constant because this term accounts for the volume occupied by the molecules. Since the liquid phase is compact, this volume is a good initial guess for the liquid volume. (A factor of 1.01 was used so division by 0 is not encountered in the equation solver.) The initial guess for the vapor volume is just the ideal gas volume.

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$$\text{Integral of } P(V_m)dV_m = p_i(V_m) = R \cdot T \cdot \ln(V_m - b) - \frac{a}{V_m}$$

Now we can iterate for the vapor pressure. Eq. 4.40 can be rearranged into the function below when $\Delta_v G = 0$. This iteration uses the pressures and volumes from the previous iteration to calculate a new guess for the pressure.

$$p_k = \frac{p_i(V_2, p_{k-1})}{V_2 - p_{k-1}} - \frac{p_i(V_1, p_{k-1})}{V_1 - p_{k-1}}$$

iterations = 5 k = 1..iterations

5
2.835
3.271
3.311 atm
3.312
3.312

$p_{\text{vap}} = p_{\text{iterations}}$

$p_{\text{vap}} = 3.3 \text{ atm}$

The iteration has converged.

4.53

To calculate the enthalpy of vaporization, we need to estimate the enthalpy imperfections for the liquid and vapor phases.

Given: $V_{\text{liq}} = 0.0490855 \cdot \frac{\text{liter}}{\text{mole}}$ $V_{\text{gas}} = 19.8698 \cdot \frac{\text{liter}}{\text{mole}}$

Gas Constant and Units: $R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$ MPa $10^6 \cdot \text{Pa}$ kJ $1000 \cdot \text{joule}$

Constants for SO_2 : $T_c = 430 \cdot \text{K}$ $P_c = 7.873 \cdot \text{MPa}$

Redlich-Kwong constants: $a = \frac{0.42748 \cdot R^2 \cdot T_c^{5/2}}{P_c}$ $b = \frac{0.086640 \cdot R \cdot T_c}{P_c}$

$T = 247.184 \cdot \text{K}$

$$P \cdot V_m = \frac{R \cdot T}{V_m - b} - \frac{a}{T \cdot V_m \cdot (V_m + b)}$$

From Table 3.3

$$U_i(V_m) = \frac{3 \cdot a}{2 \cdot b} \cdot T \cdot \ln \left(\frac{V_m}{V_m + b} \right) + H_i(V_m) - U_i(V_m) - P \cdot V_m + R \cdot T$$

$$H_i(V_{\text{gas}}) = 110.938 \cdot \frac{\text{joule}}{\text{mole}} \quad H_i(V_{\text{liq}}) = -2.259 \cdot 10^4 \cdot \frac{\text{joule}}{\text{mole}}$$

The enthalpy imperfections represent deviations from the standard state. Since the standard state enthalpies for both the liquid and vapor phases are the same, the enthalpy of vaporization is just the difference between the liquid and gas phase enthalpy imperfections.

$$\Delta_v H = H_i(V_{\text{gas}}) - H_i(V_{\text{liq}})$$

$$\Delta_v H = 22.48 \cdot \frac{\text{kJ}}{\text{mole}}$$

The observed value given in Table 4.2 is 24.92 kJ/mole, so the value calculated here is very close.

4.55

Gas Constant and Units: $R = 8.31451 \quad \text{cm}^3 = 0.01 \quad \text{MPa} \cdot 10^6 \quad \text{atm} \quad 101325$

Constants for Ethane: $T_c = 305.33 \quad P_c = 4.871 \cdot \text{MPa}$

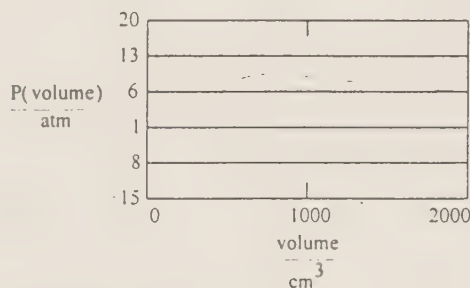
Redlich-Kwong constants: $a = \frac{0.42748 \cdot R^2 \cdot T_c^{5/2}}{P_c} \quad b = \frac{0.086640 \cdot R \cdot T_c}{P_c}$

$T = 184.57$

$$P \cdot V_m = \frac{R \cdot T}{V_m + b} - \frac{a}{T \cdot V_m \cdot (V_m + b)}$$

volume $50 \cdot \text{cm}^3, 51 \cdot \text{cm}^3 \dots 2000 \cdot \text{cm}^3$

This plot can be used to obtain an initial guess for the vapor pressure. The estimate should be chosen in the two phase region where the "areas" bounded by the curve above and below the estimate are about equal.



Vapor Pressure Estimate

$$p_0 = 1 \cdot \text{atm}$$

The solution can be found by solving eq. 4.40 when $\Delta_v G = 0$. It will be useful to define functions for calculating the liquid volume (V_1), the gas volume (V_2), and the indefinite integral of $P(V_m)dV_m$. Then, it will be possible to iterate to find the vapor pressure.

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	Initial Guess	Volume Function
Liquid	$v_b = 1.01 \cdot b$	$V_1(px) = \text{root}(px - P(v_b), v_b)$
Vapor	$v_a = \frac{R \cdot T}{p_0}$	$V_2(px) = \text{root}(px - P(v_a), v_a)$

These initial guesses should converge on the liquid and vapor volumes. Recall that there are three real roots in the critical region. The liquid volume initial guess was chosen to be slightly larger than the Redlich-Kwong b constant because this term accounts for the volume occupied by the molecules. Since the liquid phase is compact, this volume is a good initial guess for the liquid volume. (A factor of 1.01 was used so division by 0 is not encountered in the equation solver.) The initial guess for the vapor volume is just the ideal gas volume.

$$\text{Integral of } P(V_m)dV_m = p_i(V_m) - R \cdot T \cdot \ln(V_m - b) - \frac{a}{T \cdot b} \cdot \ln\left(\frac{V_m - b}{V_m}\right)$$

Now we can iterate for the vapor pressure. Eq. 4.40 can be rearranged into the function below when $\Delta V_G = 0$. This iteration uses the pressures and volumes from the previous iteration to calculate a new guess for the pressure.

$$p_k = \frac{p_i(V_2, p_{k-1}) - p_i(V_1, p_{k-1})}{V_2 - V_1} \quad p = \frac{1}{1.064} \cdot \text{atm}$$

iterations 3 k 1.. iterations

$P_{\text{vap}} = P_{\text{iterations}}$

$P_{\text{vap}} = 1.06 \cdot \text{atm}$

The iteration has converged.

4.57

Gas Constant and Units:	$R = 8.31451$	$\text{cm} = 0.01$	$\text{MPa} = 10^6$	$\text{atm} = 101325$
Constants for Ethane:	$T_c = 305.33$	$P_c = 4.871 \cdot \text{MPa}$		
Redlich-Kwong constants:	$a = \frac{0.42748 \cdot R^2 \cdot T_c^{5/2}}{P_c}$	$b = \frac{0.086640 \cdot R \cdot T_c}{P_c}$		
$T = 184.57$				

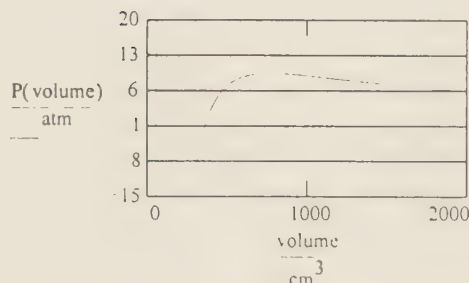
$$P(V_m) = \frac{R \cdot T}{V_m - b} - \frac{a}{T \cdot V_m \cdot (V_m + b)}$$

This plot can be used to obtain an initial guess for the vapor pressure. The estimate should be chosen in the two phase region where the "areas" bounded by the curve above and below the estimate are about equal.

Vapor Pressure Estimate

$$p_0 = 1 \cdot \text{atm}$$

$$\text{volume} = 50 \cdot \text{cm}^3, 51 \cdot \text{cm}^3 \dots 2000 \cdot \text{cm}^3$$



The solution can be found by solving eq. 4.40 when $\Delta_v G = 0$. It will be useful to define functions for calculating the liquid volume (V_1), the gas volume (V_2), and the indefinite integral of $P(V_m)dV_m$. Then, it will be possible to iterate to find the vapor pressure.

	Initial Guess	Volume Function
Liquid	$v_b = 1.01 \cdot b$	$V_1(px) = \text{root}(px - P(v_b), v_b)$
Vapor	$v_a = \frac{R \cdot T}{P_0}$	$V_2(px) = \text{root}(px - P(v_a), v_a)$

These initial guesses should converge on the liquid and vapor volumes. Recall that there are three real roots in the critical region. The liquid volume initial guess was chosen to be slightly larger than the Redlich-Kwong b constant because this term accounts for the volume occupied by the molecules. Since the liquid phase is compact, this volume is a good initial guess for the liquid volume. (A factor of 1.01 was used so division by 0 is not encountered in the equation solver.) The initial guess for the vapor volume is just the ideal gas volume.

$$\text{Integral of } P(V_m)dV_m \quad \pi(V_m) = R \cdot T \cdot \ln(V_m - b) + \frac{a}{T \cdot b} \cdot \ln\left(\frac{V_m + b}{V_m}\right)$$

Now we can iterate for the vapor pressure. Eq. 4.40 can be rearranged into the function below when $\Delta_v G = 0$. This iteration uses the pressures and volumes from the previous iteration to calculate a new guess for the pressure.

$$\text{iterations} = 3 \quad k = 1 \dots \text{iterations}$$

$$p_k = \frac{\pi(V_2(p_{k-1})) - \pi(V_1(p_{k-1}))}{V_2(p_{k-1}) - V_1(p_{k-1})}$$

$$p = \begin{bmatrix} 1.062 \\ 1.064 \\ 1.064 \end{bmatrix} \cdot \text{atm}$$

The iteration has converged.

$$P_{\text{vap}} = P_{\text{iterations}}$$

$$P_{\text{vap}} = 1.06 \cdot \text{atm}$$

CHAPTER 5 *Statistical Thermodynamics*

SECTION 5.1

5.1

By direct expansion, we obtain:

$$\text{ans} = (1 + x)^4 \quad \text{ans} = 1 + 4 \cdot x + 6 \cdot x^2 + 4 \cdot x^3 + x^4$$

Using eq. (5.2) gives:

$$C(N, p) = \frac{N!}{p! \cdot (N - p)!}$$

$$C(4, 0) = 1 \quad C(4, 2) = 6 \quad C(4, 4) = 1$$

$$C(4, 1) = 4 \quad C(4, 3) = 4$$

We get the same results. Computing the sum:

$$\text{sum} = 1 + 4 + 6 + 4 + 1 \quad \text{sum} = 16$$

$$\text{sum} = 2^4 \quad \text{sum} = 16$$

Again, we obtain identical results.

5.3

To find the probability, we use eq. (5.3). N is the total number of flips, and p is the number of heads.

$$P(N, p) = \frac{1}{2^N} \frac{N!}{p! \cdot (N - p)!}$$

$$P(5, 0) = 0.03125 \quad 0 \text{ heads, } 5 \text{ tails}$$

$$P(5, 1) = 0.15625 \quad 1 \text{ head, } 4 \text{ tails}$$

$$P(5, 2) = 0.3125 \quad 2 \text{ heads, } 3 \text{ tails}$$

$$P(5, 3) = 0.3125 \quad 3 \text{ heads, } 2 \text{ tails}$$

$$P(5,4) = 0.15625 \quad 4 \text{ heads, 1 tail}$$

$$P(5,5) = 0.03125 \quad 5 \text{ heads, 0 tails}$$

$$\text{sum} = 0.03125 + 0.15625 + 0.3125 + 0.3125 + 0.15625 + 0.03125$$

$$\text{sum} = 1 \quad \text{Not surprisingly, the sum of the probabilities of all the outcomes is one.}$$

5.5

This is similar to example 5.4. First, we calculate the mean number of molecules using the ideal gas law. Then, we calculate the deviation using the expression given in the problem statement.

$$R = 8.31451 \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad V = 1 \cdot \text{cm}^3 \quad T = 300 \cdot \text{K} \quad L = 6.02 \cdot 10^{23} \frac{1}{\text{mole}} \quad P_{\text{av}} = 0.133 \cdot \text{Pa}$$

$$N_{\text{av}} = \frac{P_{\text{av}} \cdot V \cdot L}{R \cdot T} \quad N_{\text{av}} = 3.21 \cdot 10^{13}$$

$$\Delta N = \frac{2}{N_{\text{av}}} \quad \Delta N = 3.53 \cdot 10^{-7}$$

The fluctuation in pressure will be proportional to this:

$$\Delta P = P_{\text{av}} \cdot \Delta N \quad \Delta P = 4.695 \cdot 10^{-8} \cdot \text{Pa}$$

5.7

In example 5.5, it is derived:

$$\Delta S = C_p \cdot \frac{\Delta T}{T}$$

Eq. (5.7) gives us the probability:

$$P = e^{\frac{\Delta S}{k}}$$

The heat capacity can be found on Table 2.1:

$$C_p = 20.88 \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad k = 1.38066 \cdot 10^{-23} \frac{\text{joule}}{\text{K}} \quad R = 8.31451 \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$V = 2 \cdot \text{cm}^3 \quad P = 1 \cdot \text{Pa} \quad \Delta T = 1 \cdot 10^{-6} \cdot \text{K} \quad T = 10 \cdot \text{K}$$

$$n = \frac{P \cdot V}{R \cdot T} \quad \Delta S = n \cdot C_p \cdot \frac{\Delta T}{T} \quad P = e^{\frac{\Delta S}{k}}$$

$$P = 1.03 \cdot 10^{-158}$$

5.9

This is similar to example 5.8. We use eq. (5.8). There are a total of 9 letters in the word, but since there are four E's, two N's, and two S's, we have:

$$N = 9 \quad N_E = 4 \quad N_N = 2 \quad N_S = 2$$

$$W = \frac{N!}{N_E! \cdot N_N! \cdot N_S!} \quad W = 3780$$

5.11

(a) We use eq. (5.8). If the words are kept separately, then for the word PEEWEE, we have:

$$N = 6 \quad N_E = 4 \quad W = \frac{N!}{N_E!} \quad W = 30$$

For the word REFEREE, we have:

$$N = 7 \quad N_R = 2 \quad N_E = 4 \quad W = \frac{N!}{N_E! \cdot N_R!} \quad W = 105$$

The number of distinct sequences possible if the letters are not mixed is the product of these:

$$W_{\text{unmixed}} = 30 \cdot 105 \quad W_{\text{unmixed}} = 3150$$

(b) When the words are mixed, we obtain:

$$N = 13 \quad N_E = 8 \quad N_R = 2 \quad W_{\text{mixed}} = \frac{N!}{N_E! \cdot N_R!}$$

$$W_{\text{mixed}} = 77220$$

5.13

This is similar to example 5.9. We use eq. (5.10) to calculate the entropy.

$$i = 1..6$$

$$X_1 = 0.0035 \quad \text{mass 78}$$

$$X_2 = 0.0227 \quad \text{mass 80}$$

$$X_3 = 0.1156 \quad \text{mass 82}$$

$$X_4 = 0.1155 \quad \text{mass 83}$$

$$X_5 = 0.569 \quad \text{mass 84}$$

$$X_6 = 0.1737 \quad \text{mass 86}$$

$$\text{sum} \sum_i X_i \quad \text{sum} = 1 \quad \text{Check to see if fractions sum to unity.}$$

Now, we use eq. (5.10) to compute the entropy:

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad \Delta S_{\text{mix}} = R \cdot \sum_i X_i \cdot \ln X_i$$

$$\Delta S_{\text{mix}} = 10.221 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

5.15

There are a total of five species: CH₄, CH₃D, CH₂D₂, CHD₃, and CD₄. The fractions of each of these species is given by:

$i = 1 \dots 5$

$X_1 = 0.15^4$	$X_1 = 0.00050625$	CH ₄
$X_2 = 4 \cdot 0.15^3 \cdot (0.85)$	$X_2 = 0.011475$	CH ₃ D
$X_3 = 6 \cdot 0.15^2 \cdot 0.85^2$	$X_3 = 0.097538$	CH ₂ D ₂
$X_4 = 4 \cdot (0.15) \cdot 0.85^3$	$X_4 = 0.368475$	CHD ₃
$X_5 = 0.85^4$	$X_5 = 0.522006$	CD ₄

Remember, there is more than one way to form some of these species, which is why we multiply by 4 and 6. The coefficients correspond to those of the binomial expansion.

$$\text{sum} \sum_i X_i \quad \text{sum} = 1 \quad \text{Check to see if fractions sum to unity.}$$

Now, we use eq. (5.10) to compute the entropy:

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad \Delta S_{\text{mix}} = R \cdot \sum_i X_i \cdot \ln X_i$$

$$\Delta S_{\text{mix}} = 8.226 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

5.17

The easiest way to do this problem is to work out problems 5.15 and 5.16 and see the pattern developing. If f is the fraction of enriched molecules, and n is the number of available positions, then the fraction of each species, p , is given by:

$$X_p = C(n, p) \cdot e^p \cdot e^{(n-p)}$$

The entropy of mixing is then calculated using

$$S = -R \cdot \sum_p X_p \cdot \ln(X_p)$$

Using the binomial coefficients works because we have only two possibilities for each site: an enriched molecule and a regular molecule. Thus, the problem is analogous to the problem of flipping a coin: there are only two possible outcomes. However, if we had more than two different molecules which could occupy a site, then this approach would not work.

5.19

It may be helpful to reread the subsection entitled "Third Law Anomalies." Since NNO can crystallize in two different orientations, the contribution to the entropy will be:

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\Delta S = R \cdot \ln(2) \quad \Delta S = 5.763 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

Since phosgene can crystallize in three orientations, the contribution to the entropy will be:

$$\Delta S = R \cdot \ln(3) \quad \Delta S = 9.134 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

5.21

(a) From eq. (5.1),

$$S = k \cdot \ln(W)$$

$$S = k \cdot \ln \left(A \cdot L^2 \cdot e^{\frac{L^2}{N \cdot \lambda^2}} \right)$$

$$S = k \cdot \ln A + 2k \cdot \ln L + \frac{k \cdot L^2}{N \cdot \lambda^2}$$

To find the minimum, we set the derivative equal to zero and solve for L:

$$\frac{dS}{dL} = \frac{2 \cdot A \cdot L}{A \cdot L^2} + \frac{2 \cdot L}{N \cdot \lambda^2}$$

$$0 = \frac{2}{L} + \frac{2 \cdot L}{N \cdot \lambda^2} \quad 0 = \frac{1}{L} + \frac{L}{N \cdot \lambda^2} \quad 0 = 1 + \frac{L^2}{N \cdot \lambda^2}$$

$$L^2 = N \cdot \lambda^2$$

$$L = \lambda \cdot \sqrt{N}$$

(b) Let L_0 be the original length. The change in entropy will be:

$$\Delta S = k \cdot \ln \left(\frac{A \cdot (1.1 \cdot L_0)^2}{A \cdot L_0^2} \right) = \frac{(1.1 \cdot L_0)^2}{N \cdot \lambda^2} \ln \left(\frac{1.1 \cdot L_0}{L_0} \right) = \frac{L_0^2}{N \cdot \lambda^2}$$

$$\Delta S = k \cdot \ln \left(\frac{A \cdot (1.1 \cdot L_0)^2}{A \cdot L_0^2} \right) = \frac{(1.1 \cdot L_0)^2}{N \cdot \lambda^2} - \frac{L_0^2}{N \cdot \lambda^2}$$

$$\Delta S = k \cdot \ln(1.1^2) = \frac{(1.1 \cdot L_0)^2 - L_0^2}{N \cdot \lambda^2} \quad \Delta S = k \cdot \ln(1.1^2) = \frac{L_0^2 \cdot (1.1^2 - 1)}{N \cdot \lambda^2}$$

Substituting in for L_0 :

$$L_0 = \lambda \cdot \sqrt{N} \quad \Delta S = k \cdot \ln(1.1^2) = \frac{N \cdot \lambda^2 \cdot (1.1^2 - 1)}{N \cdot \lambda^2}$$

For one mole of chains:

$$k = 1.38066 \cdot 10^{-23} \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad L = 6.02 \cdot 10^{23}$$

$$\Delta S = k \cdot L \cdot \ln(1.1^2) = (1.1^2 - 1) \quad \Delta S = 0.161 \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

SECTION 5.2

5.23

To find the total energy, we use eq. (5.11):

$$i = 0 \dots 3$$

ϵ_i	n_{A_i}	n_{B_i}	n_{C_i}
0-K	33	31	32
100-K	15	17	16
200-K	7	9	8
300-K	5	5	4

$$E_A = \sum_i n_{A_i} \cdot \epsilon_i \quad E_A = 4400 \cdot K$$

$$E_B = \sum_i n_{B_i} \cdot \epsilon_i \quad E_B = 4400 \cdot K$$

$$E_C = \sum_i n_{C_i} \cdot \epsilon_i \quad E_C = 4400 \cdot K$$

Thus, all three have the same energy. To calculate the number of configurations, we use eq. (5.13):

$$W_A = \frac{\sum_i n_{A_i}!}{\prod_i n_{A_i}!}$$

$$W_A = 1.212 \cdot 10^{27}$$

$$W_B = \frac{\sum_i n_{B_i}!}{\prod_i n_{B_i}!}$$

$$W_B = 1.307 \cdot 10^{27}$$

$$W_C = \frac{\sum_i n_{C_i}!}{\prod_i n_{C_i}!}$$

$$W_C = 1.562 \cdot 10^{27}$$

For a Boltzmann distribution, the ration of populations is given by:

$$\frac{n_i}{n_j} = \exp \left(-\frac{\Delta \epsilon}{k \cdot T} \right) \quad \text{For equally spaced levels, this means that:} \quad \frac{p_2}{p_1} = \frac{p_3}{p_2}$$

The only set of populations which mets this condition is set C, so set C is a Boltzmann distribution and is more probable than A or B.

5.25

The Boltzmann distribution is given by eq. (5.21)

$$i = 0 \dots 2$$

$$p(T) = \frac{e^{-\frac{\theta_i}{T}}}{\sum_i e^{-\frac{\theta_i}{T}}}$$

θ_i
0-K
100-K
200-K

p(50)	p(500)	p(5000)
0.867	0.402	0.34
0.117	0.329	0.333
0.016	0.269	0.327

At very high temperatures, all of the energy levels will be equally accessible. The high temperature limit is to have 1/3 of the molecules in each level.

5.27

For systems with degeneracy, we use eq. (5.24). The partition function is defined by eq. (5.23).

$$i = 0..1 \quad T = 987 \cdot K$$

$$\begin{array}{c} \text{theta}_i \\ \hline 0 \cdot K \\ 367 \cdot K \end{array} \quad \begin{array}{c} g_i \\ \hline 2 \\ 4 \end{array} \quad z = \sum_i g_i \cdot e^{-\frac{\text{theta}_i}{T}} \quad \begin{array}{c} \text{theta}_i \\ \hline 0 \cdot K \\ 367 \cdot K \end{array} \quad \begin{array}{c} g_i \cdot e^{-\frac{\text{theta}_i}{T}} \\ \hline p_i \end{array} \quad \begin{array}{c} \text{theta}_i \\ \hline 0 \cdot K \\ 367 \cdot K \end{array} \quad \begin{array}{c} g_i \cdot e^{-\frac{\text{theta}_i}{T}} \\ \hline z \end{array}$$

$$\begin{array}{c} p_i \\ \hline 0.4704 \\ 0.5296 \end{array}$$

The average energy is obtained by dividing the total energy, eq. (5.11), by the total number of particles. Since we are working with population ratios, the total number of particles is 1.

$$E = \sum_i \text{theta}_i \cdot p_i \quad E = 300.3 \cdot K$$

We can get this in terms of J/mole by multiplying by R:

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot K} \quad E \cdot R = 2497 \cdot \frac{\text{joule}}{\text{mole}}$$

SECTION 5.3

5.29

The partition function is defined by eq. (5.22). For the system of problem 5.25:

$$i = 0..2$$

$$\theta_i$$

0·K
100·K
200·K

$$z(T) = \sum_i e^{-\frac{\theta_i}{T}}$$

$$z(50) = 1.154$$

$$z(500) = 2.489$$

$$z(5000) = 2.941$$

The high temperature limit is $z = 3$.

5.31

The heat capacity at constant volume is defined as:

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v$$

The relationship between the partition function, z , and the internal energy, U , is given by eq. (5.26). We take the derivative with respect to temperature to obtain C_v :

$$U - U_o = RT^2 \left(\frac{\partial \ln z}{\partial T} \right)_v$$

$$C_v = \frac{\partial}{\partial T} \left[RT^2 \left(\frac{\partial \ln z}{\partial T} \right)_v + U_o \right]$$

$$C_v = 2RT \left(\frac{\partial \ln z}{\partial T} \right)_v + RT^2 \left(\frac{\partial^2 \ln z}{\partial T^2} \right)_v$$

$$R = Nk$$

$$C_v = 2NkT \left(\frac{\partial \ln z}{\partial T} \right)_v + NkT^2 \left(\frac{\partial^2 \ln z}{\partial T^2} \right)_v$$

SECTION 5.4

5.33

Equation (5.31) gives z_{tr} :

$$z_{tr} = \frac{(2 \cdot \pi \cdot m \cdot k \cdot T)^{3/2} \cdot V}{h^3}$$

The SI units are:

$$m \quad \text{kg} \quad k \quad \frac{\text{joule}}{\text{K}} \quad T \quad \text{K} \quad V \quad \text{m}^3 \quad h \quad \text{joule} \cdot \text{sec}$$

$$z_{tr} = \frac{\text{kg} \cdot \frac{\text{joule}}{\text{K}} \cdot \text{K}^2 \cdot \text{m}^3}{(\text{joule} \cdot \text{sec})^3}$$

$$z_{tr} = \frac{\text{kg}^{1.5} \cdot \text{joule}^{1.5} \cdot \text{K}^{1.5} \cdot \text{m}^3}{\text{joule}^3 \cdot \text{sec}^3}$$

$$z_{tr} = \frac{\text{kg}^{1.5} \cdot \text{joule}^{1.5} \cdot \text{m}^3}{\text{joule}^3 \cdot \text{sec}^3}$$

$$z_{tr} = \frac{\text{kg}^{1.5} \cdot \text{m}^3}{\text{joule}^{1.5} \cdot \text{sec}^3}$$

A joule is defined as $\text{joule} = \frac{\text{kg} \cdot \text{m}^2}{\text{sec}^2}$ Substituting this in:

$$z_{tr} = \frac{\text{kg}^{1.5} \cdot \text{m}^3 \cdot \text{sec}^3}{\text{kg}^{1.5} \cdot \text{m}^3 \cdot \text{sec}^3} = 1$$

Thus, z_{tr} is unitless.

5.35

Following example 5.16 in the text, we use the Sackur-Tetrode equation, eq. (5.35), with the constants substituted in. This gives us:

$$R = 8.31451 \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T = 298.15 \cdot \text{K} \quad M = 4.022602 \frac{\text{gm}}{\text{mole}}$$

$$S = 1.5 \cdot R \cdot \ln \frac{M}{1 \cdot \text{gm} \cdot \text{mole}^{-1}} + 2.5 \cdot R \cdot \ln \frac{T}{1 \cdot \text{K}} + 1.15167 \cdot R$$

$$S = 126.216 \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

Following example 5.16 in the text, we use the Sackur-Tetrode equation, eq. (5.35), with the constants substituted in. This gives us:

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad m = 9.109390 \cdot 10^{-28} \cdot \text{gm} \quad L = 6.022137 \cdot 10^{23} \cdot \frac{1}{\text{mole}} \quad T = 1000 \cdot \text{K}$$

$$S = 1.5 \cdot R \cdot \ln \left[\frac{m \cdot L}{1 \cdot (\text{gm} \cdot \text{mole}^{-1})} \right] + 2.5 \cdot R \cdot \ln \left(\frac{T}{1 \cdot \text{K}} \right) + 1.15167 \cdot R \quad S = 40.371 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

SECTION 5.5

5.39

This problem is similar to example 5.19. We use eq. (5.39) to calculate the vibrational partition function. The constant for vibration for HCl can be found on Table 5.1. Boltzmann's law gives the fraction of the molecules in the lower state.

$$\theta_v = 4301.6 \quad n = 0$$

$$T = 300\text{ K} \quad z_{\text{vib}} = \frac{1}{1 - \exp\left(-\frac{\theta_v}{T}\right)} \quad p = \frac{\exp\left(-n \cdot \frac{\theta_v}{T}\right)}{z_{\text{vib}}}$$

$$z_{\text{vib}} = 1.000000593 \quad p = 0.999999407$$

$$T = 3000\text{ K} \quad z_{\text{vib}} = \frac{1}{1 - \exp\left(-\frac{\theta_v}{T}\right)} \quad p = \frac{\exp\left(-n \cdot \frac{\theta_v}{T}\right)}{z_{\text{vib}}}$$

$$z_{\text{vib}} = 1.313 \quad p = 0.7616$$

5.41

As T goes to infinity, the expression becomes indeterminate. We can either use L'Hopital's rule or expand the function in a Taylor series. Here, we will expand in a series for the exponents:

$$C_v = \frac{R \left(\frac{\theta}{T}\right)^2 e^{\theta/T}}{(e^{\theta/T} - 1)^2} = \frac{R \left(\frac{\theta}{T}\right)^2 e^{\theta/T}}{e^{3\theta/T} - 2e^{\theta/T} + 1}$$

$$C_v = \frac{R \left(\frac{\theta}{T} \right)^2 \left(1 + \frac{\theta}{T} + \frac{\theta^2}{2T^2} + \frac{\theta^3}{6T^3} + \dots \right)}{\left(1 + \frac{2\theta}{T} + \frac{4\theta^2}{2T^2} + \frac{8\theta^3}{6T^3} + \dots \right) - \left(2 + \frac{2\theta}{T} + \frac{2\theta^2}{2T^2} + \frac{2\theta^3}{6T^3} + \dots \right) + 1}$$

We combine terms in the denominator to obtain:

$$C_v = \frac{R \left(\frac{\theta}{T} \right)^2 \left(1 + \frac{\theta}{T} + \frac{\theta^2}{2T^2} + \frac{\theta^3}{6T^3} + \dots \right)}{\frac{2\theta^2}{2T^2} + \frac{4\theta^3}{6T^3} + \dots}$$

Multiplying top and bottom by $(T/\theta)^2$:

$$C_v = \frac{R \left(1 + \frac{\theta}{T} + \frac{\theta^2}{2T^2} + \frac{\theta^3}{6T^3} + \dots \right)}{1 + \frac{4\theta}{6T} + \dots}$$

Now, if we take the limit as T goes to infinity, all of the terms in the sum in the denominator will be zero except for the leading 1, and all the terms in the denominator will be zero except for the leading one. This gives us:

$$C_v = R$$

5.43

Equation (5.43) is the high temperature approximation of the rotational partition function. The molecular constants for oxygen can be found on Table 5.1. For oxygen, a linear, symmetric molecule, the symmetry number is 2:

$$\theta_r = 2.08 \quad \sigma = 2 \quad T = 20.8 \cdot K$$

$$z_{\text{rot}} = \frac{T}{\sigma \cdot \theta_r} \quad z_{\text{rot}} = 5$$

By direct summation of eq. (5.42):

$$n = 0..10$$

$$J_n = 2 \cdot n + 1$$

$$z_{\text{rot}} = \frac{1}{\sigma} \sum_n (2J_n + 1) \cdot \exp \left[-J_n \cdot (J_n + 1) \cdot \frac{\theta_r}{T} \right] \quad z_{\text{rot}} = 2.585$$

5.45

Equation (5.43) is the high temperature approximation of the rotational partition function. The molecular constants for HF can be found on Table 5.1. For HCl, a linear, unsymmetric molecule, the symmetry number is 1.

$$\theta_r = 30.127 \quad \sigma = 1 \quad T = 300 \cdot \text{K}$$

$$z_{\text{rot}} = \frac{T}{\sigma \cdot \theta_r} \quad z_{\text{rot}} = 9.958$$

The percent population is given by Boltzmann's law (see example 5.24):

$$J = 0..7 \quad p_J = \frac{(2J + 1) \cdot \exp \left[-J \cdot (J + 1) \cdot \frac{\theta_r}{T} \right]}{z_{\text{rot}}}$$

J	p _J
0	0.1
1	0.246
2	0.275
3	0.211
4	0.121
5	0.054
6	0.019
7	0.005

5.47

This problem is similar to example 5.27 in the text. We must write out the partition function explicitly. The electronic energy levels are listed in Table 5.2.

$$T = 10000\text{ K} \quad i = 0..3 \quad R = 8.31451 \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad \text{kJ} = 1000 \cdot \text{joule}$$

$$g_i = \theta e_i$$

4	0
6	27658.7
4	27671.7
6	41492.4

$$z_{\text{elec}} = \sum_i g_i \cdot \exp\left(-\frac{\theta e_i}{T}\right) \quad p_i = \frac{g_i \cdot \exp\left(-\frac{\theta e_i}{T}\right)}{z_{\text{elec}}}$$

$$z_{\text{elec}} = 4.723545$$

i	p _i
0	0.846822
1	0.079925
2	0.053214
3	0.02004

$$U_{\text{elec}} = R \cdot \sum_i p_i \cdot \theta e_i \quad U_{\text{elec}} = 37.537 \frac{\text{kJ}}{\text{mole}}$$

5.49

As in example 5.27, eq. (5.27) can be used to calculate the entropy. For a species in which only the ground state contributes, the electronic entropy will be equal to $R \ln(g_0)$.

$$R = 8.31451 \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T = 1500 \cdot \text{K} \quad M = 22.98977$$

$$S_{\text{elec}} = R \cdot \ln(2) \quad S_{\text{elec}} = 5.763 \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

The entropy also has a contribution from translational motion:

$$S_{\text{trans}} = 1.5 \cdot R \cdot \ln(M) + 2.5 \cdot R \cdot \ln(T) = 1.15167 \cdot R \quad S_{\text{trans}} = 181.539 \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

Since we are dealing with an atomic species, there are not contributions from vibration or rotation. The total entropy is:

$$S = S_{\text{elec}} + S_{\text{trans}} \quad S = 187.302 \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

5.51

Since there is no degeneracy, the partition function is just a sum over all the energy levels:

$$z = \sum_m e^{-m^2 \theta_x / T}$$

At high temperatures, we would expect many levels to be populated, so the sum can be approximated as an integral up to infinity. This integral can be computed using an integral table:

$$z = \int_0^\infty e^{-m^2 \theta_x / T} dm = \frac{1}{2} \sqrt{\frac{\pi T}{\theta_x}}$$

Equation (5.26) relates the partition function to the internal energy:

$$U = RT^2 \left(\frac{\partial \ln z}{\partial T} \right)_V + U_0$$

$$\ln z = \ln \left(\frac{1}{2} \right) + \frac{1}{2} [\ln \pi + \ln T - \ln \theta_x]$$

$$\left(\frac{\partial \ln z}{\partial T} \right)_V = \frac{1}{2T}$$

$$U = RT^2 \left(\frac{1}{2T} \right) + U_0$$

$$U = \frac{RT}{2} + U_0$$

The heat capacity at constant volume is defined as:

$$C_v = \left(\frac{\partial U}{\partial T} \right)_V$$

$$C_v = \left(\frac{\partial U}{\partial T} \right)_V = \frac{R}{2}$$

5.53

The partition function for this system is:

$$z = \sum_m m^2 e^{-m\theta_x/T}$$

At high temperatures, we would expect many levels to be populated, so the sum can be approximated as an integral up to infinity. This integral can be computed using an integral table:

$$z = \int_0^\infty m^2 e^{-m\theta_x/T} dm \qquad \int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$$

$$z = \int_0^\infty m^2 e^{-m\theta_x/T} dm = \frac{2}{a^3}$$

Equation (5.26) relates the partition function to the internal energy:

$$U = RT^2 \left(\frac{\partial \ln z}{\partial T} \right)_V + U_0$$

$$\ln z = \ln 2 + 3 \ln \left(\frac{T}{\theta_x} \right)$$

$$\left(\frac{\partial \ln z}{\partial T} \right)_V = \frac{3}{T} \qquad U = RT^2 \left(\frac{3}{T} \right) + U_0 \qquad U = 3RT + U_0$$

The heat capacity at constant volume is defined as:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 3R$$

SECTION 5.6

5.55

We use the formulas on Table 5.3 for a linear molecule.

$$R = 8.31451 \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T = 298.15 \cdot \text{K} \quad \theta_v = 3323 \cdot \text{K} \quad \text{kJ} = 1000 \cdot \text{joule}$$

$$U = 1.5 \cdot R \cdot T + R \cdot T \cdot \left(\frac{R \cdot \theta_v}{\theta_v} \exp \left(-\frac{\theta_v}{T} \right) + 1 \right) \quad U = 6.199 \cdot \frac{\text{kJ}}{\text{mole}}$$

To compute the enthalpy, we use the definition, $H = U + PV$. For an ideal gas, $PV = RT$, so we have $H = U + RT$.

$$H = U + R \cdot T \quad H = 8.677 \cdot \frac{\text{kJ}}{\text{mole}}$$

5.57

We use the formulas on Table 5.3 for a nonlinear molecule.

$$i = 0..3 \quad \theta_{v_i} = \quad g_i = \quad R = 8.31451 \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T = 500 \cdot \text{K}$$

1131 · K
374 · K
1470 · K
604 · K

1
2
3
3

$$u_i = \frac{\theta_{v_i}}{T}$$

$$C_{vm} = 1.5 \cdot R + 1.5 \cdot R \cdot \sum_i \frac{g_i \cdot R \cdot (u_i)^2 \cdot e^{u_i}}{(e^{u_i} - 1)^2}$$

$$C_{vm} = 81.087 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

For an ideal gas,

$$C_{pm} = C_{vm} + R$$

$$C_{pm} = 89.402 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

5.59

We use the formulas on Table 5.3 for a nonlinear molecule. Also, because Table 5.1 indicates that NO₂ has a ground electronic state of 2, we must add on a term of $R \ln(g_0)$ to the entropy.

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$M = 46.0067$$

$$T = 298.15 \cdot \text{K}$$

$$\sigma = 2$$

$$i = 0..2$$

$$\theta_a \theta_b \theta_c = 4.24244 \cdot \text{K}^3 \quad \theta_{v_i}$$

$$z_r = \frac{\pi \cdot T^{1.5}}{\sigma \cdot \theta_a \theta_b \theta_c}$$

1953.55 · K
1088.85 · K
2396.25 · K

$$S = 1.5 \cdot R \cdot \ln(M) + 2.5 \cdot R \cdot \ln(T) - 1.15167 \cdot R + 1.5 \cdot R + R \cdot \ln(z_r) + \dots$$

$$+ \sum_i \left[\frac{R \cdot \frac{\theta_{v_i}}{T}}{\exp\left(\frac{\theta_{v_i}}{T}\right) - 1} - R \cdot \ln\left(1 - \exp\left(-\frac{\theta_{v_i}}{T}\right)\right) \right] + R \cdot \ln(2)$$

$$S = 240.031 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

This agrees well with the literature value of 239.9 J/moleK.

SECTION 5.7

5.61

Since we only have a table of energy levels, we must use direct sums to compute the desired quantities. We use eqs. (5.47) and (5.48).

$$i = 0..9 \quad T = 600 \cdot K$$

$$\theta_i = \frac{R}{k_B} \cdot \frac{\epsilon_i}{T} \quad z = \sum_i \exp(-\theta_i) \quad p_i = \frac{\exp(-\theta_i)}{z}$$

0·K
155·K
310·K
465·K
620·K
775·K
930·K
1085·K
1240·K
1395·K

$$u_{av} = \sum_i u_i \cdot p_i$$

$$u_{rms} = \sqrt{\sum_i u_i^2 \cdot p_i}$$

$$C_v = R \cdot (u_{rms}^2 - u_{av}^2)$$

$$C_v = 3.365 \cdot \frac{\text{joule}}{\text{mole} \cdot K}$$

$$\frac{C_v}{R} = 0.405$$

SECTION 5.8

5.63

Because we are concerned with an atomic species, we will only have contributions from translational motion and electrical energy. The formulas for the free energy function can be found on Table 5.3. Equation (5.53) gives the electronic contribution to the free energy function.

$$i = 0..3 \quad R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad M = 15.9994$$

θ_{e_i}	g_i
0·K	5
227.705·K	3
326.594·K	1
22830·K	5

$$z_{\text{elec}}(T) = \sum_i g_i \cdot \exp\left(-\frac{\theta_{e_i}}{T}\right) \quad \phi_{\text{elec}}(T) = R \cdot \ln(z_{\text{elec}}(T))$$

$$\phi(T) = 1.5 \cdot R \cdot \ln(M) + 2.5 \cdot R \cdot \ln(T) - 3.65167 \cdot R + \phi_{\text{elec}}(T)$$

$$\phi(298.15 \cdot \text{K}) = 138.504 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad \phi(2000 \cdot \text{K}) = 180.031 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\phi(500 \cdot \text{K}) = 150.062 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

5.65

We use the equations on Table 5.3 for a linear molecule.

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad M = 2 \cdot 14.0067 \quad \theta_v = 3395 \cdot \text{K} \quad \theta_r = 2.89 \cdot \text{K} \quad \sigma = 2$$

$$z_r(T) = \frac{T}{\sigma \cdot \theta_r}$$

$$\phi(T) = 1.5 \cdot R \cdot \ln(M) + 2.5 \cdot R \cdot \ln(T) - 3.65167 \cdot R + R \cdot \ln(z_r(T)) - R \cdot \ln\left(1 - \exp\left(-\frac{\theta_v}{T}\right)\right)$$

$$\phi(298.15 \cdot \text{K}) = 162.42 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad \phi(1500 \cdot \text{K}) = 210.349 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

5.67

We use the equations on Table 5.3 for a linear molecule. For oxygen, we must include the electronic contribution, eq. (5.53).

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad M = 2 \cdot 15.9994 \quad \theta_v = 2274 \cdot \text{K} \quad \theta_r = 2.08 \cdot \text{K} \quad \sigma = 2$$

$$i = 0..2 \quad z_r(T) = \frac{T}{\sigma \cdot \theta_r}$$

$$\theta_{e_i} \quad g_i$$

0 · K
11392 · K
18984 · K

3
2
1

$$z_{\text{elec}}(T) = \sum_i g_i \cdot \exp\left(-\frac{\theta_{e_i}}{T}\right) \quad \phi_{\text{elec}}(T) = R \cdot \ln(z_{\text{elec}}(T))$$

$$\phi(T) = 1.5 \cdot R \cdot \ln(M) + 2.5 \cdot R \cdot \ln(T) - 3.65167 \cdot R + R \cdot \ln z_r(T) - R \cdot \ln \left(1 - \exp \left(-\frac{\theta_v}{T} \right) \right) + \phi_{\text{elec}}(T)$$

$$\phi(298.15 \cdot \text{K}) = 175.952 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad \phi(1500 \cdot \text{K}) = 225.028 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\phi(1000 \cdot \text{K}) = 212.068 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

SECTION 5.9

5.69

At low temperatures, the state of the system is dominated by energy considerations. Thus, at low temperatures, a graph of the order parameter versus the configurational free energy would have a minimum in the middle at $J = 0$, since in this state there are mainly A-B interactions. This is exactly the opposite of the low-temperature graph in Figure 5.11. At higher temperatures, entropy begins to play a role. The entropy will want to drive the system towards a disordered state, where $J = 0$, so the shape of the high temperature graph in Figure 5.11 will stay the same. However, a disordered state is already favorable from an energetics point of view. So we will probably not see an order-disorder transition if A-B interactions are higher in energy than A-A and B-B interactions. If this seems confusing, reread section 5.9.

5.71

The order parameter is given by eq. (5.61):

$$T \cdot \ln \left(\frac{1+J}{1-J} \right) = \frac{4 \cdot J \cdot (\epsilon_{AA} + \epsilon_{BB} - 2 \cdot \epsilon_{AB})}{k}$$

Solving for T , we obtain:

$$J = 0.5 \quad \theta_{AA} = 100 \cdot K \quad \theta_{BB} = 200 \cdot K \quad \theta_{AB} = 50 \cdot K$$

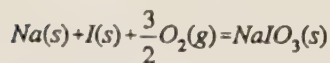
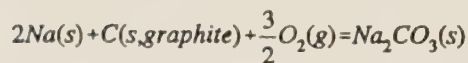
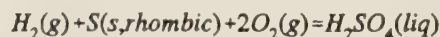
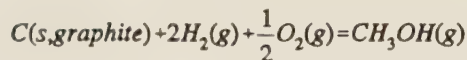
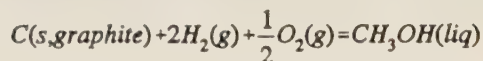
$$T = \frac{4 \cdot J \cdot (\theta_{AA} + \theta_{BB} - 2 \cdot \theta_{AB})}{\ln \left(\frac{1+J}{1-J} \right)} \quad T = 364 \cdot K$$

CHAPTER 6 *Chemical Reactions*

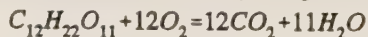
SECTION 6.2

6.1

Formation reactions of compounds are written using the component elements in their most stable forms at 1 bar and a given (usually room) temperature.

6.3

Combustion products are usually a combination of CO_2 , SO_2 , and H_2O (liq).



6.5

The standard enthalpy change is the heat of reaction (at standard conditions), and thus can be calculated from eq. 6.4 in the text. Stoichiometric coefficients are positive for products and negative for reactants. Heats of formation are given in Table 6.1 at 298.15 K.

$$\Delta_f H_{\text{N}_2\text{H}_4\text{gas}} = 95.40 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta_f H_{\text{O}_2} = 0 \cdot \frac{\text{kJ}}{\text{mole}} \quad \text{kJ} \approx 1000 \cdot \text{joule}$$

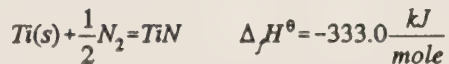
$$\Delta_f H_{\text{NO}_2} = 33.18 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta_f H_{\text{H}_2\text{Ogas}} = 241.818 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta_{\text{rxn}} H = 2 \cdot \Delta_f H_{\text{NO}_2} + 2 \cdot \Delta_f H_{\text{H}_2\text{Ogas}} - \Delta_f H_{\text{N}_2\text{H}_4\text{gas}} - 3 \cdot \Delta_f H_{\text{O}_2}$$

$$\Delta_{\text{rxn}} H = -512.68 \cdot \frac{\text{kJ}}{\text{mole}}$$

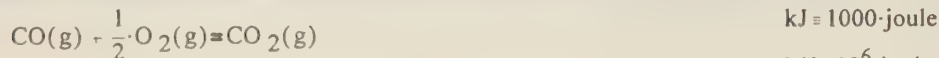
6.7

The formation reaction of TiN can be obtained by reversing the second equation and adding it to the first equation. The heat of the formation reaction can be obtained using Hess's law of heat summation (remembering to reverse the sign of the enthalpy change for the second equation because we flipped it). The result is



6.9

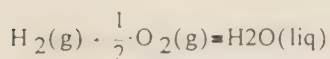
The only components that can undergo combustion are CO and H₂. The heats of combustion of these do not appear in Table 6.2, but they can be calculated using heats of formation given in Table 6.1. (Heats of formation of elements in their most stable form at standard conditions are defined to be zero.)



$$\text{MJ} = 10^6 \cdot \text{joule}$$

$$\Delta fH_{\text{CO}_2} = 393.509 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta fH_{\text{CO}} = -110.525 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta cH_{\text{CO}} = \Delta fH_{\text{CO}_2} - \Delta fH_{\text{CO}}$$



combustion reactions.

$$\Delta fH_{\text{H}_2\text{O}} = -285.830 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta cH_{\text{H}_2} = \Delta fH_{\text{H}_2\text{O}}$$

For 1 kg of water gas,

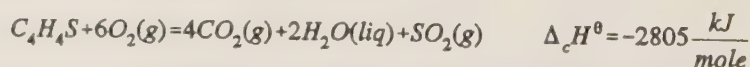
$$\text{moles CO} = \frac{0.40 \cdot (1 \cdot \text{kg})}{28.0104 \cdot \frac{\text{gm}}{\text{mole}}} \quad \text{moles H}_2 = \frac{0.52 \cdot (1 \cdot \text{kg})}{2.01588 \cdot \frac{\text{gm}}{\text{mole}}}$$

$$\Delta cH_{\text{watergas}} = \text{moles CO} \cdot \Delta cH_{\text{CO}} + \text{moles H}_2 \cdot \Delta cH_{\text{H}_2}$$

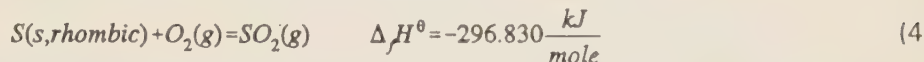
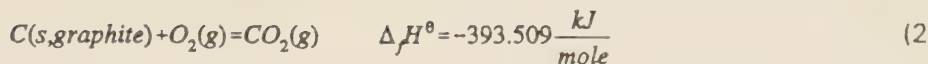
$$\Delta cH_{\text{watergas}} = -78 \cdot \text{MJ}$$

6.11

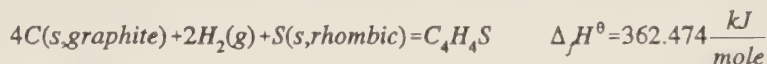
Table 6.2 gives the heat of combustion of thiophene



This can be converted to the formation reaction of thiophene using the following formation reaction (Table 6.1)



The formation reaction of thiophene can be obtained by adding 4 times eq.(2), 2 times eq.(3), eq.(4) and the reverse of eq.(1). The result is



6.13

Eq. 6.8 in the text gives a formula to calculate the temperature dependence of the heat of reaction. If $\Delta_{rxn} C_p$ (defined by eq. 6.6) is constant, this equation simplifies to

$$\Delta_{rxn} H(T_2) = \Delta_{rxn} H(T_1) + \Delta_{rxn} C_p (T_2 - T_1)$$

It will be most convenient to take $T_1 = 298.15$ K because that is where we can most easily calculate the heat of reaction (using heats of formation from Table 6.1).

$$\Delta_{rxn} H(298.15) = \Delta_f H^\theta(CO_2, g) + \Delta_f H^\theta(Cl_2, g) - \Delta_f H^\theta(COCl_2, g)$$

$$\Delta_{rxn} H(298.15) = -110.525 + 0 - (-218.8) = 108.275 \frac{kJ}{mole}$$

Similarly, we can use the heat capacities in Table 6.1 to determine $\Delta_{rxn} C_p$

$$\Delta_{rxn} C_p = C_{p,m}(CO_2, g) + C_{p,m}(Cl_2, g) - C_{p,m}(COCl_2, g)$$

$$\Delta_{rxn} C_p = 29.142 + 33.907 - 57.66 = 5.389 \frac{J}{mole \cdot K}$$

Thus

$$\Delta_{\text{rxn}} H^{\circ}(T) = 108275 + (5.389)(T - 298.15)$$

$$\Delta_{\text{rxn}} H^{\circ}(T) = (106668 + 5.389T) \frac{J}{\text{mole}}$$

6.15

We can use eq. 6.8 in the text to derive an accurate formula for the enthalpy of the reaction. It is easiest to take $T_1 = 298.15$ K because then we can use Table 6.1 to calculate the heat of reaction at T_1 .

$$\Delta_{\text{rxn}} H_{298.15} = -241.818 \frac{\text{kJ}}{\text{mole}}$$

$$\text{kJ} = 1000 \cdot \text{joule}$$

Table 2.2 gives the heat capacities needed to calculate $\Delta_{\text{rxn}} C_p$.

$$C_{\text{pm}} \text{H}_2\text{O}(T) = \left(26.06 + 17.7 \cdot 10^{-3} \cdot T - 2.63 \cdot 10^{-6} \cdot T^2 + \frac{2.20 \cdot 10^5}{T^2} \right) \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$C_{\text{pm}} \text{H}_2(T) = \left(26.36 + 4.35 \cdot 10^{-3} \cdot T - 0.245 \cdot 10^{-6} \cdot T^2 + \frac{1.15 \cdot 10^5}{T^2} \right) \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$C_{\text{pm}} \text{O}_2(T) = \left(29.30 + 6.14 \cdot 10^{-3} \cdot T - 0.88 \cdot 10^{-6} \cdot T^2 - \frac{1.59 \cdot 10^5}{T^2} \right) \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\Delta_{\text{rxn}} C_p(T) = C_{\text{pm}} \text{H}_2\text{O}(T) - C_{\text{pm}} \text{H}_2(T) - \frac{1}{2} \cdot C_{\text{pm}} \text{O}_2(T)$$

$$\Delta_{\text{rxn}} H(T) = \Delta_{\text{rxn}} H_{298.15} + \int_{298.15}^T \Delta_{\text{rxn}} C_p(T) dT$$

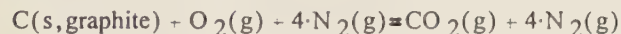
$$\Delta_{\text{rxn}} H(T) = \left(-2.37182 \cdot 10^5 - 14.95 \cdot T + 0.00514 \cdot T^2 - 6.483 \cdot 10^{-7} \cdot T^3 - \frac{1.845 \cdot 10^5}{T} \right) \cdot \frac{\text{joule}}{\text{mole}}$$

SECTION 6.3

6.17

The adiabatic flame temperature is the temperature at which the reaction products have absorbed all of the heat generated by the reaction. However, in these calculations, the "reaction products" include any species that are present after the reaction has taken place, including inerts and unreacted reactants as well as the "new" products. The adiabatic flame temperature can be found by finding the temperature that satisfies eq. 6.9.

The overall reaction can be written as



$$\Delta_{\text{rxn}}H_{\theta} = -393509 \text{ joule/mole} \quad \text{from Table 6.1}$$

Heat capacities are given by Table 2.2 as follows

$$C_{\text{pm CO}_2}(T) = 41.58 + 15.6 \cdot 10^{-3} \cdot T - 2.95 \cdot 10^{-6} \cdot T^2 - \frac{7.97 \cdot 10^5}{T^2}$$

$$C_{\text{pm N}_2}(T) = 25.79 + 8.09 \cdot 10^{-3} \cdot T - 1.46 \cdot 10^{-6} \cdot T^2 + \frac{0.88 \cdot 10^5}{T^2}$$

$$C_{\text{p prod}}(T) = C_{\text{pm CO}_2}(T) + 4 \cdot C_{\text{pm N}_2}(T)$$

Solving eq. 6.9:

$$T_{\text{guess}} = 2000$$

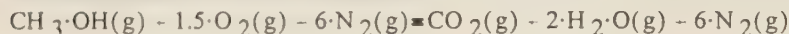
$$T_{\text{flame}} = \text{root} \left(\Delta_{\text{rxn}}H_{\theta} - \int_{298.15}^{T_{\text{guess}}} C_{\text{p prod}}(T) dT, T_{\text{guess}} \right)$$

$$T_{\text{flame}} = 2376 \text{ Kelvin}$$

6.19

The adiabatic flame temperature is the temperature at which the reaction products have absorbed all of the heat generated by the reaction. However, in these calculations, the "reaction products" include any species that are present after the reaction has taken place, including inerts and unreacted reactants as well as the "new" products. The adiabatic flame temperature can be found by finding the temperature that satisfies eq. 6.9.

The overall reaction can be written as



$$\Delta_{\text{rxn}}H_{\theta} = (-393509) + 2(-241818) - (-200660) \quad \text{joule/mole} \quad \text{from Table 6.1}$$

Heat capacities are given by Table 2.2 as follows

$$C_{\text{pm CO}_2}(T) = 41.58 + 15.6 \cdot 10^{-3} \cdot T - 2.95 \cdot 10^{-6} \cdot T^2 - \frac{7.97 \cdot 10^5}{T^2}$$

$$C_{\text{pm H}_2\text{O}}(T) = 26.06 + 17.7 \cdot 10^{-3} \cdot T - 2.63 \cdot 10^{-6} \cdot T^2 + \frac{2.20 \cdot 10^5}{T^2}$$

$$C_{\text{pm N}_2}(T) = 25.79 + 8.09 \cdot 10^{-3} \cdot T - 1.46 \cdot 10^{-6} \cdot T^2 - \frac{0.88 \cdot 10^5}{T^2}$$

$$C_{\text{p prod}}(T) = C_{\text{pm CO}_2}(T) + 2 \cdot C_{\text{pm H}_2\text{O}}(T) + 6 \cdot C_{\text{pm N}_2}(T)$$

Solving eq. 6.9:

$$T_{\text{guess}} = 2000$$

$$T_{\text{flame}} = \text{root} \left[\Delta_{\text{rxn}}H_{\theta} + \int_{298.15}^{T_{\text{guess}}} C_{\text{p prod}}(T) dT, T_{\text{guess}} \right]$$

$$T_{\text{flame}} = 2270 \text{ Kelvin}$$

6.21

Again, eq. 6.9 in the text is the basis for the solution. From Table 6.1 we have the following data

$$\Delta fH_{\text{NO}} = 90250 \quad \Delta fH_{\text{SO}_3} = -395720 \quad \Delta fH_{\text{NO}_2} = 33180 \quad \Delta fH_{\text{SO}_2} = -296830$$

All are in joule/mole. Thus, the standard heat of reaction is

$$\Delta_{\text{rxn}}H_{\theta} = \Delta fH_{\text{NO}} - \Delta fH_{\text{SO}_3} - \Delta fH_{\text{NO}_2} - \Delta fH_{\text{SO}_2}$$

$$\Delta_{\text{rxn}}H_{\theta} = -4.182 \cdot 10^4$$

Heat capacities are given by Table 6.1 as follows

$$C_{\text{pm NO}} = 29.844 \quad C_{\text{pm SO}_3} = 50.67 \quad \text{Both are in joule/mole/K}$$

$$C_{\text{p prod}}(T) = C_{\text{pm NO}} - C_{\text{pm SO}_3}$$

Solving eq. 6.9:

$$T_{\text{guess}} = 1000$$

$$T_{\text{max}} = \text{root} \left(\Delta_{\text{rxn}}H_{\theta} - \int_{373}^{T_{\text{guess}}} C_{\text{p prod}}(T) dT, T_{\text{guess}} \right)$$

$$T_{\text{max}} = 892 \text{ Kelvin}$$

SECTION 6.4

6.23

Given: $P = 1 \cdot \text{atm}$ $P_{\theta} = 10^5 \cdot \text{Pa}$

$X_{\text{CS}_2} = 0.85$ $X_{\text{S}_2} = 1 - X_{\text{CS}_2}$ There is no graphite in the gas phase.

The equilibrium constant is defined by eq. 6.13 and 6.15 in the text.

$$K_a = \frac{a_{\text{CS}_2}}{a_{\text{C}} \cdot a_{\text{S}_2}}$$

The activity of any solid can be approximated as one at reasonable pressures. If we assume ideal gas behavior, then the activity of each gas is its partial pressure divided by the standard pressure. Dalton's law can be used to express the partial pressures as the mole fraction times the total pressure.

$$a_{\text{C}} = 1$$

$$K_a = \frac{\frac{X_{\text{CS}_2} \cdot P}{P_{\theta}}}{a_{\text{C}} \cdot \left(\frac{X_{\text{S}_2} \cdot P}{P_{\theta}} \right)} \quad K_a = \frac{X_{\text{CS}_2}}{X_{\text{S}_2}} \quad K_a = 5.67$$

We can see that with the ideal gas assumption and Dalton's law of partial pressures, the resulting expression for K_a does not depend on the reaction pressure. Therefore, the percentage of CS_2 at 10 atm will still be 85%. The reason is there is no change in the number of moles of gas during the reaction. You may recall from Le Chatelier's Principle that increasing the pressure drives equilibrium toward the direction of fewer moles of gas. Since the number of moles of gas does not change, the equilibrium does not change either (with the assumptions made).

6.25

(a) Given: $P = 0.5523 \cdot \text{bar}$ $P_{\theta} = 1 \cdot \text{bar}$ $\text{bar} = 10^5 \cdot \text{Pa}$

$X_{\text{H}_2\text{O}} = 0.5$ $X_{\text{CO}_2} = 0.5$ Water vapor and carbon dioxide are formed in equimolar amounts.

The equilibrium constant is defined by eq. 6.13 and 6.15 in the text.

$$K_a = \frac{a_{\text{Na}_2\text{CO}_3} \cdot a_{\text{H}_2\text{O}} \cdot a_{\text{CO}_2}}{a_{\text{NaHCO}_3}^2}$$

The activity of any solid can be approximated as one at reasonable pressures. If we assume ideal gas behavior, then the activity of each gas is its partial pressure divided by the standard pressure. Dalton's law can be used to express the partial pressures as the mole fraction times the total pressure.

$$a_{\text{Na}_2\text{CO}_3} = 1 \quad a_{\text{NaHCO}_3} = 1$$

$$K_a = \frac{a_{\text{Na}_2\text{CO}_3} \cdot \left(\frac{X_{\text{H}_2\text{O}} \cdot P}{P_{\theta}} \right) \cdot \left(\frac{X_{\text{CO}_2} \cdot P}{P_{\theta}} \right)}{a_{\text{NaHCO}_3}^2} \quad K_a = 0.076259$$

(b) $P_{\text{CO}_2}(\xi) = 1.6500 \cdot \text{bar} + \xi$ $P_{\text{H}_2\text{O}}(\xi) = \xi$

The equilibrium constant can be expressed in terms of the partial pressures

$$K_a = \frac{P_{\text{CO}_2} \cdot P_{\text{H}_2\text{O}}}{P_{\theta}^2}$$

$$\xi_{\text{guess}} = 0.5 \cdot \text{bar}$$

$$\xi = \text{root} \left(\frac{P_{\text{CO}_2}(\xi_{\text{guess}}) \cdot P_{\text{H}_2\text{O}}(\xi_{\text{guess}})}{P_{\theta}^2} - K_a \cdot \xi_{\text{guess}} \right)$$

$$P_{\text{H}_2\text{O}}(\xi) = 0.0450 \cdot \text{bar}$$

$$P_{\text{total}} = P_{\text{CO}_2}(\xi) + P_{\text{H}_2\text{O}}(\xi)$$

$$P_{\text{total}} = 1.7400 \cdot \text{bar}$$

SECTION 6.5

6.27

From Table 6.1 we can calculate the free energy change for the reaction, $\text{CCl}_4(\text{liq}) = \text{CCl}_4(\text{g})$

$$\begin{aligned}\Delta fG_{\text{CCl}_4\text{liq}} &= -65.21 \cdot \frac{\text{kJ}}{\text{mole}} & \Delta fG_{\text{CCl}_4\text{gas}} &= -60.59 \cdot \frac{\text{kJ}}{\text{mole}} & \text{kJ} &= 1000 \cdot \text{joule} \\ R &= 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \\ \Delta_{\text{rxn}}G_{\theta} &= \Delta fG_{\text{CCl}_4\text{gas}} - \Delta fG_{\text{CCl}_4\text{liq}} & T &= 298.15 \cdot \text{K}\end{aligned}$$

We can use eq. 6.15 in the text to calculate the equilibrium constant.

$$K_a = \exp\left(\frac{\Delta_{\text{rxn}}G_{\theta}}{-R \cdot T}\right) \quad K_a = 0.155$$

In this reaction, K_a is equal to the activity of the vapor divided by the activity of the liquid. Because liquids are largely incompressible, their activities can be assumed to be one at reasonable pressures. The activity of the vapor can be estimated as the vapor pressure divided by the standard pressure (assuming an ideal gas).

$$K_a = \frac{P_{\text{vap}}}{P_{\theta}} \quad P_{\text{vap}} = K_a \cdot P_{\theta} \quad P_{\theta} = 10^5 \cdot \text{Pa}$$

$$P_{\text{vap}} = 116.3 \cdot \text{torr}$$

The methods of chapter 4 can also be used to estimate the vapor pressure. The data from Table 4.2 give the normal boiling point of carbon tetrachloride and the heat of vaporization at the normal boiling point.

$$T_1 = 349.9 \cdot \text{K} \quad P_1 = 1 \cdot \text{atm} \quad \Delta_{\text{v}}H = 30.0 \cdot \frac{\text{kJ}}{\text{mole}}$$

The Clausius-Clapeyron equation (eq. 4.20) gives the dependence of the vapor pressure-temperature relation on the heat of vaporization. For a constant heat of vaporization, this equation can be integrated to give eq. 4.22. This will allow us to predict the vapor pressure of carbon tetrachloride at 25 C.

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta_v H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$T_2 = 298.15 \cdot K$$

$$P_2 = \exp\left[\frac{-(\Delta_v H \cdot T_1 - \Delta_v H \cdot T_2)}{R \cdot (T_2 \cdot T_1)}\right] \cdot P_1$$

$$P_2 = 126.9 \cdot \text{torr}$$

In order to tell which answer is more accurate, we have to look at the assumptions that accompany both solutions. Using the methods of chapter 6, we assumed that the liquid activity was one and that the vapor could be treated as an ideal gas. The first is a very good assumption, and the second is reasonable. Using the methods of chapter 4, we assumed that the heat of vaporization did not vary with temperature over approximately a 50 K range. This assumption turns out to cause the greatest error. Therefore, the first answer is most accurate. The actual vapor pressure is about 115 torr.

6.31

Eq. 6.25 can be used to calculate the equilibrium constant at 1000 K. In order to use this it is necessary the standard free energy of reaction and the standard enthalpy of reaction (both at 298.15 K) using data from Table 6.1

$$\Delta_f G_{\text{ClO}} = 98.11 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta_f G_{\text{CO}_2} = -394.359 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta_f G_{\text{CCl}_4} = -60.59 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta_f G_{\text{O}_2} = 0 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta_{\text{rxn}} G_{\text{ref}} = 4 \cdot \Delta_f G_{\text{ClO}} + \Delta_f G_{\text{CO}_2} - \Delta_f G_{\text{CCl}_4} - 3 \cdot \Delta_f G_{\text{O}_2}$$

$$\Delta_f H_{\text{ClO}} = 101.84 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta_f H_{\text{CO}_2} = -393.509 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta_f H_{\text{CCl}_4} = -102.9 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta_f H_{\text{O}_2} = 0 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta_{\text{rxn}} H_{\text{ref}} = 4 \cdot \Delta_f H_{\text{ClO}} + \Delta_f H_{\text{CO}_2} - \Delta_f H_{\text{CCl}_4} - 3 \cdot \Delta_f H_{\text{O}_2}$$

We also need to consider the temperature dependence of the enthalpy

$$C_{\text{pm}} \text{ClO} = 31.46 \cdot \frac{\text{joule}}{\text{K} \cdot \text{mole}} \quad C_{\text{pm}} \text{CO}_2 = 37.11 \cdot \frac{\text{joule}}{\text{K} \cdot \text{mole}}$$

$$C_{\text{pm}} \text{CCl}_4 = 83.30 \cdot \frac{\text{joule}}{\text{K} \cdot \text{mole}} \quad C_{\text{pm}} \text{O}_2 = 29.355 \cdot \frac{\text{joule}}{\text{K} \cdot \text{mole}}$$

$$\Delta_{\text{rxn}} C_p = 4 \cdot C_{\text{pm}} \text{ClO} + C_{\text{pm}} \text{CO}_2 - C_{\text{pm}} \text{CCl}_4 - 3 \cdot C_{\text{pm}} \text{O}_2$$

$$\text{kJ} = 1000 \cdot \text{joule}$$

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$T_{\text{ref}} = 298.15 \cdot K$$

$$\Delta_{\text{rxn}}H(T) = \Delta_{\text{rxn}}H_{\text{ref}} + \int_{T_{\text{ref}}}^T \Delta_{\text{rxn}}C_p dT$$

$$\Delta_{\text{rxn}}H(1000\text{K}) = 111 \cdot \frac{\text{kJ}}{\text{mole}}$$

Now we can use eq. 6.25 to calculate the equilibrium constant at 1000 K.

$$K_a(T) = \exp \left[\frac{-\Delta_{\text{rxn}}G_{\text{ref}}}{R \cdot T_{\text{ref}}} + \int_{T_{\text{ref}}}^T \frac{\Delta_{\text{rxn}}H(T)}{R \cdot T^2} dT \right]$$

$$K_a(1000\text{K}) = 7.1 \cdot 10^3$$

6.29

We will use the free energy function based on 298.15 K because Table 6.5 contains the data needed for this problem. The equilibrium constant can then be determined by solving eq. 6.21. Necessary data are

$$\phi_{\text{TiN}} = 68.3 \cdot \frac{\text{joule}}{\text{K}} \quad \phi_{\text{Ti}} = 54.2 \cdot \frac{\text{joule}}{\text{K}} \quad \phi_{\text{N}_2} = 216.2 \cdot \frac{\text{joule}}{\text{K}}$$

$$\Delta\phi = \phi_{\text{TiN}} - \phi_{\text{Ti}} - \frac{1}{2} \phi_{\text{N}_2}$$

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad \text{kJ} = 1000 \cdot \text{joule}$$

$$\Delta fH_{\text{TiN}} = -338 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta fH_{\text{Ti}} = 0 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta fH_{\text{N}_2} = 0 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta H_{\theta} = \Delta fH_{\text{TiN}} - \Delta fH_{\text{Ti}} - \frac{1}{2} \Delta fH_{\text{N}_2}$$

$$T = 1500\text{K}$$

$$K_a = \exp \left(\frac{\Delta\phi}{R} - \frac{\Delta H_{\theta}}{R \cdot T} \right) \quad \text{eq. 6.21}$$

$$K_a = 7.2 \cdot 10^6$$

6.33

The equilibrium constant for this reaction can be expressed as follows if we assume the ideal gas law applies and the activity of solids is one.

$$K_a = \left(\frac{P}{P_\theta} \right)^{10} \quad P = 0.249 \cdot \text{bar} \quad P_\theta = 1 \cdot \text{bar} \quad \text{bar} \equiv 10^5 \cdot \text{Pa} \quad \text{kJ} \equiv 1000 \cdot \text{joule}$$

$$K_a = 9.16 \cdot 10^{-7}$$

The standard free energy of reaction can be calculated using eq. 6.15

$$T = 298.15 \cdot \text{K} \quad R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\Delta_{\text{rxn}} G_\theta = -R \cdot T \cdot \ln(K_a) \quad \Delta_{\text{rxn}} G_\theta = 34.5 \cdot \frac{\text{kJ}}{\text{mole}}$$

6.35

The equilibrium constant can then be determined by solving eq. 6.21. Data at 773 K can be interpolated from the data given by assuming a linear relationship.

$$\phi_{\text{NH}_3} = 49.2456 \cdot \frac{\text{cal}}{\text{K}} \quad \phi_{\text{N}_2} = 48.14856 \cdot \frac{\text{cal}}{\text{K}} \quad \phi_{\text{H}_2} = 33.56326 \cdot \frac{\text{cal}}{\text{K}}$$

$$\Delta\phi = \phi_{\text{NH}_3} - \frac{1}{2} \cdot \phi_{\text{N}_2} - \frac{3}{2} \cdot \phi_{\text{H}_2}$$

$$\Delta fH_{\text{NH}_3} = -10.97 \cdot \frac{\text{kcal}}{\text{mole}} \quad \Delta fH_{\text{N}_2} = 0 \cdot \frac{\text{kcal}}{\text{mole}} \quad \Delta fH_{\text{H}_2} = 0 \cdot \frac{\text{kcal}}{\text{mole}}$$

$$\Delta H_\theta = \Delta fH_{\text{NH}_3} - \frac{1}{2} \cdot \Delta fH_{\text{N}_2} - \frac{3}{2} \cdot \Delta fH_{\text{H}_2}$$

$$T = 773 \cdot \text{K}$$

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad \text{kcal} \equiv 1000 \cdot \text{cal}$$

$$K_a = \exp\left(\frac{\Delta\phi}{R} - \frac{\Delta H_\theta}{R \cdot T}\right) \quad \text{eq. 6.21}$$

$$K_a = 4.0 \cdot 10^{-3}$$

6.37

(a) In order to tell which form is more stable at 25 C and 1 bar, all we have to do is examine the standard free energies of formation in Table 6.1

$$\Delta_f G_{\text{PbOred}} = -188.93 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta_f G_{\text{PbOyel}} = -187.89 \cdot \frac{\text{kJ}}{\text{mole}} \quad \text{kJ} \equiv 1000 \cdot \text{joule}$$

Since red PbO has a lower standard free energy at 25 C, it is the thermodynamically more stable form under these conditions.

(b) Consider the reaction $\text{PbO}(\text{red}) = \text{PbO}(\text{yel})$. The standard free energy of reaction is just the difference between the standard free energies of formation. The temperature dependence of $\Delta_{\text{rxn}} G_\theta$ can be determined assuming $\Delta_{\text{rxn}} H_\theta$ and $\Delta_{\text{rxn}} S_\theta$ are constant. The temperature at which $\Delta_{\text{rxn}} G_\theta$ equals zero represents the point at which the standard free energies of formation are equal, and the temperature above which the yellow form will presumably be more stable.

$$\Delta_f H_{\text{PbOred}} = -218.99 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta_f H_{\text{PbOyel}} = -217.32 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta_{\text{rxn}} H_\theta = \Delta_f H_{\text{PbOyel}} - \Delta_f H_{\text{PbOred}}$$

$$S_{\text{PbOred}} = 66.5 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad S_{\text{PbOyel}} = 68.70 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad \Delta_{\text{rxn}} S_\theta = S_{\text{PbOyel}} - S_{\text{PbOred}}$$

$$\Delta_{\text{rxn}} G_\theta(T) = \Delta_{\text{rxn}} H_\theta - T \cdot \Delta_{\text{rxn}} S_\theta$$

$$T_{\text{guess}} = 500 \cdot \text{K}$$

$$T = \text{root}(\Delta_{\text{rxn}} G_\theta(T_{\text{guess}}), T_{\text{guess}})$$

$$T = 759 \cdot \text{K}$$

Above this temperature, the yellow form of PbO is predicted to be more stable.

Thus far we have only dealt with the standard free energy of reaction, which does not by itself predict whether a reaction is spontaneous or not. Spontaneity is determined by $\Delta_{\text{rxn}} G$, not $\Delta_{\text{rxn}} G_\theta$. Eq. 6.14 in the text relates the two quantities. In this example because we are dealing only with solids, all activities will be equal to one and the distinction is not significant.

6.39

Solving eq. 6.24 in the text is the easiest way to estimate $\Delta_{\text{rxn}}H_{\theta}$.

$$\ln(K_2) = \ln(K_1) - \frac{\Delta_{\text{rxn}}H_{\theta}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\text{kJ} = 1000 \cdot \text{joule}$$

$$K_1 = 5.85 \cdot 10^{-4} \quad T_1 = 1000 \cdot \text{K}$$

$$K_2 = 2.04 \cdot 10^{-5} \quad T_2 = 2000 \cdot \text{K}$$

$$\Delta_{\text{rxn}}H_{\theta} = \frac{\left(\frac{\ln(K_2)}{1} - \frac{\ln(K_1)}{1} \right)}{\left(\frac{1}{R \cdot T_2} - \frac{1}{R \cdot T_1} \right)}$$

$$\Delta_{\text{rxn}}H_{\theta} = -55.8 \cdot \frac{\text{kJ}}{\text{mole}}$$

This value represents the mean reaction enthalpy over the temperature interval 1000 K to 2000 K. Data in Table 6.1 are for 298.15 K. The value given in Table 6.1 is -46.11 kJ/mole. Remember that $\Delta_{\text{rxn}}H_{\theta}$ is a function of temperature through eq. 6.8.

6.41

Eq. 6.23 tells us that the slope of $\ln(K_a)$ versus $1/T$ is equal to $-\Delta_{\text{rxn}}H/R$. For this reaction $K_p = K_a$ since the activity of solids is one and there is no net change in the total moles of gas.

points = 5 i = 0..points - 1

$$T_i = \quad K_{a_i} =$$

831
857
878
906
918

0.0154
0.0170
0.0182
0.0202
0.0215

$$x_i = \frac{1}{T_i} \quad y_i = \ln(K_{a_i})$$

We are now ready to perform the regression.

$$m = \text{slope}(x, y) \quad m = -2.861 \cdot 10^3 \quad m \text{ is the slope of the } \ln K_a \text{ vs. } 1/T \text{ graph}$$

$$r = \text{corr}(x, y) \quad r = -0.997168 \quad r \text{ is the correlation factor related to the goodness of fit}$$

$$b = \text{intercept}(x, y) \quad b = -0.737 \quad b \text{ is the intercept of the } \ln K_a \text{ vs } 1/T \text{ graph}$$

The standard deviation of the slope may be calculated using eq. A1.25 of the Appendix.

$$\sigma_m = \frac{m}{r} \cdot \sqrt{\frac{1 - r^2}{\text{points} - 2}} \quad \sigma_m = 124.56 \quad R = 8.31451$$

$$\Delta_{\text{rxn}} H_{\theta} = -m \cdot R \cdot \frac{\text{joule}}{\text{mole}} \quad \Delta_{\text{rxn}} H_{\theta} = 23.786 \cdot \frac{\text{kJ}}{\text{mole}} \quad \text{kJ} \approx 1000 \cdot \text{joule}$$

$$\sigma_{\Delta_{\text{rxn}} H_{\theta}} = \sigma_m \cdot R \cdot \frac{\text{joule}}{\text{mole}} \quad \sigma_{\Delta_{\text{rxn}} H_{\theta}} = 1.036 \cdot \frac{\text{kJ}}{\text{mole}}$$

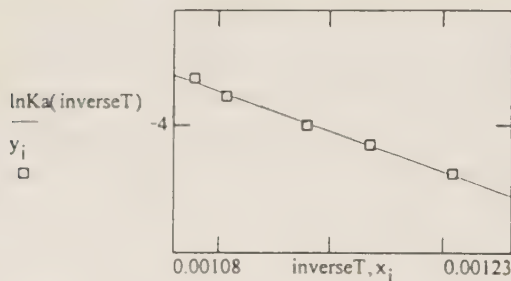
The confidence interval is defined by eq. A1.27 of the Appendix. In this problem there are 5 points and 2 parameters, which means there are 3 degrees of freedom. For 90% confidence, $t_c = 2.35$. Therefore, the confidence interval, λ , is

$$t_c = 2.35 \quad \lambda_{90\%} = t_c \cdot \sigma_{\Delta_{\text{rxn}} H_{\theta}} \quad \lambda_{90\%} = 2.434 \cdot \frac{\text{kJ}}{\text{mole}}$$

It may be helpful to see a plot of the data and regressed fit on a $\ln K_a$ vs $1/T$ graph.

$$\ln K_a(x) = m \cdot x + b$$

$$\text{inverseT} = 0.00100, 0.00101 \dots 0.00130$$



This graph shows the fit of the $\ln K_a$ vs $1/T$ data. The slope of this line is $-\Delta_{\text{rxn}} H_{\theta}/R$ according to eq. 6.23

Summary

$$\Delta_{\text{rxn}} H_{\theta} = 24 \cdot \frac{\text{kJ}}{\text{mole}} \quad \lambda_{90\%} = 2 \cdot \frac{\text{kJ}}{\text{mole}} \quad \sigma_{\Delta_{\text{rxn}} H_{\theta}} = 1 \cdot \frac{\text{kJ}}{\text{mole}}$$

SECTION 6.6

6.43

Since the given equation of state is explicit in volume, we can use eq. 6.29 to calculate the fugacity coefficient, and hence the fugacity.

$$\ln \phi = \frac{1}{RT} \int_0^P \left(V_m - \frac{RT}{P} \right) dP$$

Substituting the given equation of state for V_m gives

$$\ln \phi = \frac{1}{RT} \int_0^P (\beta + \gamma P) dP$$

$$\ln \phi = \frac{1}{RT} \left(\beta P + \frac{\gamma P^2}{2} \right)_0^P$$

$$\phi = \exp \left(\frac{\beta P}{RT} + \frac{\gamma P^2}{2RT} \right)$$

$$f = P \exp \left(\frac{\beta P}{RT} + \frac{\gamma P^2}{2RT} \right)$$

6.45

Eq. 6.30 in the text can be used to calculate the fugacity coefficient. A cubic spline will be used to fit the data.

$i = 0..20$

$P_i =$

$z_i =$

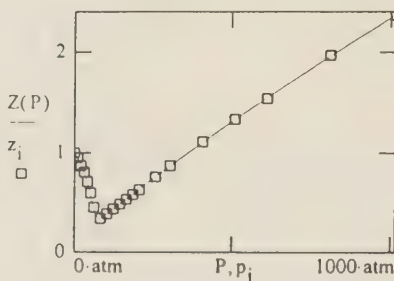
1-atm	0.994
10-atm	0.937
20-atm	0.8683
30-atm	0.7928
40-atm	0.7034
50-atm	0.5936
60-atm	0.4515
80-atm	0.3429
100-atm	0.3767
120-atm	0.4259
140-atm	0.4753
160-atm	0.5252
180-atm	0.5752
200-atm	0.6246
250-atm	0.7468
300-atm	0.8663
400-atm	1.098
500-atm	1.3236
600-atm	1.5409
800-atm	1.9626
1000-atm	2.3684

$\text{fit} = \text{cspline}(p, z)$

$\text{atm} \equiv 101325$

$Z(P) = \text{interp}(\text{fit}, p, z, P)$

$P = 0\text{-atm}, 1\text{-atm}.. 1000\text{-atm}$



$$\phi(P) = \exp \left(\int_0^P \frac{Z(P) - 1}{P} dP \right)$$

$$\phi(100\text{-atm}) = 0.471$$

$$\phi(200\text{-atm}) = 0.327$$

$$\phi(500\text{-atm}) = 0.317$$

$$\phi(1000\text{-atm}) = 0.552$$

6.47

Eq. 6.30 in the text can be used to calculate the fugacity coefficient. A cubic spline will be used to fit the data.

$i = 0..24$

$P_i =$

$z_i =$

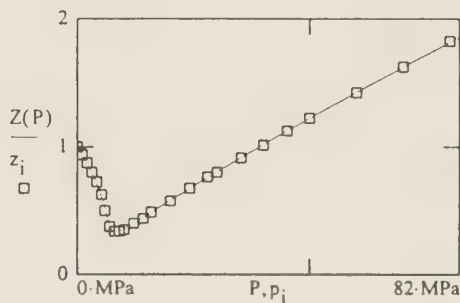
0.1·MPa	0.9943
1·MPa	0.9410
2·MPa	0.8768
3·MPa	0.8055
4·MPa	0.7241
5·MPa	0.6266
6·MPa	0.5013
7·MPa	0.3701
8·MPa	0.3338
9·MPa	0.3398
10·MPa	0.3560
12·MPa	0.3974
14·MPa	0.4424
16·MPa	0.4884
20·MPa	0.5803
24·MPa	0.6709
28·MPa	0.7600
30·MPa	0.8040
35·MPa	0.9123
40·MPa	1.0186
45·MPa	1.1231
50·MPa	1.226
60·MPa	1.4278
70·MPa	1.6251
80·MPa	1.8188

$\text{fit} = \text{cspline}(p, z)$

$\text{MPa} = 10^6$

$Z(P) = \text{interp}(\text{fit}, p, z, P)$

$P = 0.1 \cdot \text{MPa}, 0.2 \cdot \text{MPa} \dots 82 \cdot \text{MPa}$



$$\phi(P) = \exp \left(\int_0^P \frac{Z(P) - 1}{P} dP \right)$$

$$\phi(5 \cdot \text{MPa}) = 0.726$$

$$\phi(10 \cdot \text{MPa}) = 0.485$$

$$\phi(20 \cdot \text{MPa}) = 0.329$$

$$\phi(40 \cdot \text{MPa}) = 0.270$$

$$\phi(80 \cdot \text{MPa}) = 0.394$$

6.49

(a) For an incompressible solid, we can use eq. 6.31 to calculate the activity

$$P = 1000 \cdot \text{atm} \quad P_{\theta} = 1 \cdot \text{bar} \quad R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad \text{bar} = 10^5 \cdot \text{Pa}$$

$$T = 298.15 \cdot \text{K} \quad V_m = 7.1 \cdot \text{cm}^3$$

$$\Gamma = \exp \left[\frac{(P - P_{\theta}) \cdot V_m}{R \cdot T} \right] \quad \Gamma = 1.336$$

(b) If we no longer assume the molar volume is constant, then we have to integrate the following equation

$$R \cdot T \cdot d(\ln(\Gamma)) = V_m(P) \cdot dP$$

The dependence of the molar volume on pressure is given by eq. 1.51

$$V_m(P) = V_m \left[1 - \kappa_T (P - P_{\theta}) \right] \quad \kappa_T = \frac{1.5 \cdot 10^{-7}}{\text{atm}}$$

$$\int_1^{\Gamma} \frac{1}{\Gamma} d\ln(\Gamma) = \int_{P_{\theta}}^{1000 \cdot \text{atm}} \frac{V_m(P)}{R \cdot T} dP$$

$$\Gamma = \exp \left[\int_{P_{\theta}}^{1000 \cdot \text{atm}} \frac{V_m(P)}{R \cdot T} dP \right] \quad \Gamma = 1.336$$

6.51

K_p is defined by the following equation

$$K_p = \frac{K_a \cdot P_{\theta}^{\Delta v_g}}{K_{\phi}}$$

where Δv_g represents the change in moles of gas for the reaction and K_{ϕ} represents the collection of fugacity coefficients (and activity coefficients for solids).

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$$K_a = 0.46 \quad \Delta v_g = -1 \quad P = 1000 \cdot \text{atm} \quad P_\theta = 1 \cdot \text{bar} \quad T = 873 \cdot \text{K}$$

$$\text{bar} = 10^5 \cdot \text{Pa}$$

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\text{MPa} = 10^6 \cdot \text{Pa}$$

$$K_\phi = \frac{\phi_{\text{CH}_4}}{\Gamma_C \cdot \phi_{\text{H}_2}^2}$$

Estimation of fugacity (or activity) coefficients:

Carbon

$$\rho = 2.26 \cdot \frac{\text{gm}}{\text{cm}^3} \quad \text{MW} = 12.011 \cdot \frac{\text{gm}}{\text{mole}} \quad V_m = \frac{\text{MW}}{\rho}$$

$$\Gamma_C = \exp \left[\frac{(P - P_\theta) \cdot V_m}{R \cdot T} \right] \quad \Gamma_C = 1.077$$

Hydrogen

$$T_{c \text{ H}_2} = 33.2 \cdot \text{K} \quad P_{c \text{ H}_2} = 1.297 \cdot \text{MPa}$$

$$T_{r \text{ H}_2} = \frac{T}{T_{c \text{ H}_2}} \quad P_{r \text{ H}_2} = \frac{P}{P_{c \text{ H}_2}}$$

$$T_{r \text{ H}_2} = 26.295 \quad P_{r \text{ H}_2} = 78.123$$

$$\phi_{\text{H}_2} = 1.36 \quad \text{from Figure 6.8}$$

Methane

$$T_{c \text{ CH}_4} = 190.6 \cdot \text{K} \quad P_{c \text{ CH}_4} = 4.641 \cdot \text{MPa}$$

$$T_{r \text{ CH}_4} = \frac{T}{T_{c \text{ CH}_4}} \quad P_{r \text{ CH}_4} = \frac{P}{P_{c \text{ CH}_4}}$$

$$T_{r \text{ CH}_4} = 4.58 \quad P_{r \text{ CH}_4} = 21.833$$

$$\phi_{\text{CH}_4} = 1.43 \quad \text{from Figure 6.8}$$

Therefore

$$K_\phi = \frac{\phi_{\text{CH}_4}}{\Gamma_C \cdot \phi_{\text{H}_2}^2} \quad K_\phi = 0.718$$

$$K_p = \frac{K_a \cdot P_\theta^{\Delta v_g}}{K_\phi} \quad K_p = 0.649 \cdot \text{atm}^{-1}$$

We can easily solve for mole fraction of methane using K_p .

$$K_p = \frac{P_{\text{CH}_4}}{P_{\text{H}_2}^2} \quad P_{\text{CH}_4} (X_{\text{CH}_4}) = X_{\text{CH}_4} \cdot P \quad P_{\text{H}_2} (X_{\text{CH}_4}) = (1 - X_{\text{CH}_4}) \cdot P$$

$$X_{\text{guess}} = 0.5$$

$$X_{\text{CH}_4} = \text{root} \left(P_{\text{CH}_4} (X_{\text{guess}}) - K_p \cdot P_{\text{H}_2} (X_{\text{guess}})^2, X_{\text{guess}} \right)$$

$$X_{\text{CH}_4} = 96.0\%$$

SECTION 6.7

6.53

The most systematic way to approach equilibrium problems is to set up a mass balance table. With no loss of generality we may assume that there is one mole of CO and two moles of H_2 initially. ξ is the extent of reaction.

	moles initial	moles at equilibrium	
CO	1	$1 - \xi$	
H_2	2	$2 \cdot (1 - \xi)$	
CH_3OH	0	ξ	$totalmoles(\xi) = 3 - 2 \cdot \xi$
$X_{CO}(\xi) = \frac{1 - \xi}{totalmoles(\xi)}$ $X_{H_2}(\xi) = \frac{2 \cdot (1 - \xi)}{totalmoles(\xi)}$ $X_{CH_3OH}(\xi) = \frac{\xi}{totalmoles(\xi)}$			

The equilibrium constant may be expressed as follows using Dalton's Law of Partial Pressures.

$$K_p(\xi) = \frac{X_{CH_3OH}(\xi) \cdot P}{(X_{CO}(\xi) \cdot P) \cdot (X_{H_2}(\xi) \cdot P)^2}$$

$$P = 56 \cdot atm$$

$$TOL = 0.001$$

$$K_{given} = 0.00608 \cdot atm^{-2}$$

Solving for ξ and X_{CH_3OH} :

$$\xi_{guess} = 0.9$$

$$\xi = root [X_{CH_3OH}(\xi_{guess}) \cdot P - (X_{CO}(\xi_{guess}) \cdot P) \cdot (X_{H_2}(\xi_{guess}) \cdot P)^2 \cdot K_{given} \cdot \xi_{guess}]$$

$$\xi = 0.715$$

$$X_{CH_3OH}(\xi) = 0.456$$

$$Recalculate K_p \text{ to check: } K_p(\xi) = 0.00608 \cdot atm^{-2}$$

Adjust tolerance until the calculated value of K_p matches the given one. It may also be necessary to refine the initial guess if convergence problems are encountered.

6.55

The equilibrium constant can easily be calculated with data from Table 6.1 and eq. 6.15 in the text.

$$\Delta_f G_{\text{NO}_2} = 51.31 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta_f G_{\text{N}_2\text{O}_4} = 97.89 \cdot \frac{\text{kJ}}{\text{mole}} \quad \text{kJ} = 1000 \cdot \text{joule} \quad R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\Delta_{\text{rxn}} G_{\theta} = 2 \cdot \Delta_f G_{\text{NO}_2} - \Delta_f G_{\text{N}_2\text{O}_4} \quad T = 298.15 \cdot \text{K}$$

$$K_{a \text{ calc}} = \exp\left(-\frac{\Delta_{\text{rxn}} G_{\theta}}{R \cdot T}\right) \quad K_{a \text{ calc}} = 0.148$$

The most systematic way to solve equilibrium problems is to set up a mass balance table. We may assume that there is one mole of N_2O_4 initially. α is the degree of dissociation.

	moles initial	moles at equilibrium	
N_2O_4	1	$1 - \alpha$	
NO_2	0	$2 \cdot \alpha$	total moles(α) = $1 + \alpha$
$X_{\text{N}_2\text{O}_4}(\alpha)$	$= \frac{1 - \alpha}{\text{total moles}(\alpha)}$		
$X_{\text{NO}_2}(\alpha)$	$= \frac{2 \cdot \alpha}{\text{total moles}(\alpha)}$		

If we neglect non-idealities, the activities and equilibrium constant may be expressed as follows

$$a_{\text{N}_2\text{O}_4}(\alpha) = \frac{X_{\text{N}_2\text{O}_4}(\alpha) \cdot P}{P_{\theta}} \quad a_{\text{NO}_2}(\alpha) = \frac{X_{\text{NO}_2}(\alpha) \cdot P}{P_{\theta}} \quad P = 1 \cdot \text{bar} \quad \text{bar} = 10^5 \cdot \text{Pa} \\ P_{\theta} = 1 \cdot \text{bar}$$

$$K_a(\alpha) = \frac{a_{\text{NO}_2}(\alpha)^2}{a_{\text{N}_2\text{O}_4}(\alpha)}$$

Solving for α :

$$\alpha_{\text{guess}} = 0.5$$

$$\alpha = \text{root}\left(a_{\text{NO}_2}(\alpha_{\text{guess}})^2 - K_{a \text{ calc}} \cdot a_{\text{N}_2\text{O}_4}(\alpha_{\text{guess}}), \alpha_{\text{guess}}\right)$$

$$\alpha = 0.189$$

$$\text{Recalculate } K_a \text{ to check: } K_a(\alpha) = 0.148$$

$$\text{TOL} = 10^{-4}$$

Adjust tolerance until the calculated value of K_a matches the given one. It may also be necessary to refine the initial guess if convergence problems are encountered.

6.57

The most systematic way to approach equilibrium problems is to set up a mass balance table. With no loss of generality we may assume that there is one mole each of NO_2 and SO_2 initially. ξ is the extent of reaction, which is also the conversion of SO_2 to SO_3 .

	moles initial		moles at equilibrium		
NO_2	1		$1 - \xi$		
SO_2	1		$1 - \xi$		
NO	0		ξ		
SO_3	0		ξ	total moles	2
$X_{\text{NO}_2}(\xi)$	$\frac{1 - \xi}{\text{total moles}}$		$X_{\text{SO}_2}(\xi)$	$\frac{1 - \xi}{\text{total moles}}$	
			$X_{\text{NO}}(\xi)$	$\frac{\xi}{\text{total moles}}$	
			$X_{\text{SO}_3}(\xi)$	$\frac{\xi}{\text{total moles}}$	

The equilibrium constant may be expressed as follows. Notice that because there is no net change in the moles of gas, the pressure does not appear in K_p .

$$K_p(\xi) = \frac{X_{\text{NO}}(\xi) \cdot X_{\text{SO}_3}(\xi)}{X_{\text{NO}_2}(\xi) \cdot X_{\text{SO}_2}(\xi)}$$

$$\text{TOL} = 0.001$$

$$K_{\text{given}} = 15.8 \cdot 10^3$$

Solving for ξ :

$$\xi_{\text{guess}} = 0.9$$

$$\xi_{\text{root}} = \text{root}(X_{\text{NO}}(\xi_{\text{guess}}) \cdot X_{\text{SO}_3}(\xi_{\text{guess}}) - X_{\text{NO}_2}(\xi_{\text{guess}}) \cdot X_{\text{SO}_2}(\xi_{\text{guess}}) \cdot K_{\text{given}}, \xi_{\text{guess}})$$

$$\xi = 99.2\%$$

$$\text{Recalculate } K_p \text{ to check: } K_p(\xi) = 1.58 \cdot 10^4$$

Adjust tolerance until the calculated value of K_p matches the given one. It may also be necessary to refine the initial guess if convergence problems are encountered.

6.59

The most systematic way to approach equilibrium problems is to set up a mass balance table. ξ is the extent of reaction.

	moles initial	moles at equilibrium	
HCl	4	$4 \cdot (1 - \xi)$	
O ₂	1	$1 - \xi$	
Cl ₂	0	$2 \cdot \xi$	
H ₂ O	0	$2 \cdot \xi$	total moles(ξ) = $5 - \xi$
<hr/>			
$X_{\text{HCl}}(\xi)$	$\frac{4 \cdot (1 - \xi)}{\text{total moles}(\xi)}$	$X_{\text{O}_2}(\xi)$	$\frac{1 - \xi}{\text{total moles}(\xi)}$
$X_{\text{Cl}_2}(\xi)$	$\frac{2 \cdot \xi}{\text{total moles}(\xi)}$	$X_{\text{H}_2\text{O}}(\xi)$	$\frac{2 \cdot \xi}{\text{total moles}(\xi)}$

The equilibrium constant may be expressed as follows using Dalton's Law.

$$K_p(\xi) = \frac{(X_{\text{Cl}_2}(\xi) \cdot P)^2 \cdot (X_{\text{H}_2\text{O}}(\xi) \cdot P)^2}{(X_{\text{HCl}}(\xi) \cdot P)^4 \cdot (X_{\text{O}_2}(\xi) \cdot P)}$$

$P = 5 \cdot \text{atm}$
TOL = 0.001

$$K_{\text{given}} = 23.14 \cdot \text{atm}^{-1}$$

Solving for ξ :

$$\xi_{\text{gss}} = 0.9$$

$$\xi_{\text{root}} = \text{root} \left((X_{\text{Cl}_2}(\xi_{\text{gss}}) \cdot P)^2 \cdot (X_{\text{H}_2\text{O}}(\xi_{\text{gss}}) \cdot P)^2 - (X_{\text{HCl}}(\xi_{\text{gss}}) \cdot P)^4 \cdot (X_{\text{O}_2}(\xi_{\text{gss}}) \cdot P) \cdot K_{\text{given}}, \xi_{\text{gss}} \right)$$

$$\xi = 0.762$$

$$P_{\text{Cl}_2}(\xi) = X_{\text{Cl}_2}(\xi) \cdot P$$

$$P_{\text{Cl}_2}(\xi) = 1.80 \cdot \text{atm}$$

$$\text{Recalculate } K_p \text{ to check: } K_p(\xi) = 23.14 \cdot \text{atm}^{-1}$$

6.61

The equilibrium constant for the reaction $4 S_2 = S_8$ can be calculated with free energy function data from Table 6.5 and eq. 6.21 in the text.

$$\begin{aligned} \phi_{S_2} 1000K &= 245.7 \cdot \frac{\text{joule}}{\text{mole} \cdot K} & \phi_{S_2} 1500K &= 256.7 \cdot \frac{\text{joule}}{\text{mole} \cdot K} & \Delta fH_{S_2} &= 129.0 \cdot \frac{\text{kJ}}{\text{mole}} & R &= 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot K} \\ \phi_{S_8} 1000K &= 516.1 \cdot \frac{\text{joule}}{\text{mole} \cdot K} & \phi_{S_8} 1500K &= 569.8 \cdot \frac{\text{joule}}{\text{mole} \cdot K} & \Delta fH_{S_8} &= 101.3 \cdot \frac{\text{kJ}}{\text{mole}} & \text{kJ} &= 1000 \cdot \text{joule} \\ \Delta \phi 1000K &= \phi_{S_8} 1000K - 4 \cdot \phi_{S_2} 1000K & \Delta H &= \Delta fH_{S_8} - 4 \cdot \Delta fH_{S_2} \\ \Delta \phi 1500K &= \phi_{S_8} 1500K - 4 \cdot \phi_{S_2} 1500K \end{aligned}$$

$$K_a 1000K = \exp \left(\frac{\Delta \phi 1000K}{R} - \frac{\Delta H}{R \cdot 1000 \cdot K} \right) \quad K_a 1000K = 1.923 \cdot 10^{-3}$$

$$K_a 1500K = \exp \left(\frac{\Delta \phi 1500K}{R} - \frac{\Delta H}{R \cdot 1500 \cdot K} \right) \quad K_a 1500K = 3.717 \cdot 10^{-10}$$

The most systematic way to solve equilibrium problems is to set up a gas phase mass balance table. We may assume that there are 4 moles of S_2 initially. ξ is the extent of reaction.

	moles initial	moles at equilibrium	
S_2	4	$4 \cdot (1 - \xi)$	
S_8	0	ξ	$\text{totalmoles}(\xi) = 4 - 3 \cdot \xi$
$X_{S_2}(\xi)$	$\frac{4 \cdot (1 - \xi)}{\text{totalmoles}(\xi)}$		$X_{S_8}(\xi) = \frac{\xi}{\text{totalmoles}(\xi)}$

If we neglect non-idealities, the activities and equilibrium constant may be expressed as follows

$$\begin{aligned} a_{S_2}(\xi) &= \frac{X_{S_2}(\xi) \cdot P}{P_\theta} & a_{S_8}(\xi) &= \frac{X_{S_8}(\xi) \cdot P}{P_\theta} & P &= 3 \cdot \text{atm} & \text{bar} &= 10^5 \cdot \text{Pa} \\ & & & & P_\theta &= 1 \cdot \text{bar} \\ K_a(\xi) &= \frac{a_{S_8}(\xi)}{a_{S_2}(\xi)^4} \end{aligned}$$

Solving for ξ at 1000K:

$$\xi_{\text{guess}} = 0.5$$

$$\xi_{1000\text{K}} = \text{root}(a_{\text{S8}}(\xi_{\text{guess}}) - a_{\text{S2}}(\xi_{\text{guess}})^4 \cdot K_{\text{a } 1000\text{K}}, \xi_{\text{guess}}) \quad \text{TOL} = 10^{-9}$$

$$\xi_{1000\text{K}} = 0.158$$

$$X_{\text{S8}}(\xi_{1000\text{K}}) = 0.045$$

Adjust tolerance until the calculated value of K_{a} matches the given one. It may also be necessary to refine the initial guess if convergence problems are encountered.

Solving for ξ at 1500K:

$$\xi_{\text{guess}} = 0.5$$

$$\xi_{1500\text{K}} = \text{root}(a_{\text{S8}}(\xi_{\text{guess}}) - a_{\text{S2}}(\xi_{\text{guess}})^4 \cdot K_{\text{a } 1500\text{K}}, \xi_{\text{guess}})$$

$$\xi_{1500\text{K}} = 4.176 \cdot 10^{-8}$$

$$X_{\text{S8}}(\xi_{1500\text{K}}) = 1.0 \cdot 10^{-8}$$

$$\text{Recalculate } K_{\text{a}} \text{ to check: } K_{\text{a}}(\xi_{1000\text{K}}) = 1.923 \cdot 10^{-3} \quad K_{\text{a}}(\xi_{1500\text{K}}) = 3.717 \cdot 10^{-10}$$

6.63

The most systematic way to approach equilibrium problems is to set up a mass balance table. ξ is the extent of reaction, which is also the fractional conversion of A to B.

	moles initial	moles at equilibrium	
A	1	$1 - \xi$	
I ₂	1	$1 - \xi$	
HI	0	$2 \cdot \xi$	
B	0	ξ	totalmoles(ξ) = $2 - \xi$
$X_{\text{A}}(\xi)$	$\frac{1 - \xi}{\text{totalmoles}(\xi)}$	$X_{\text{I}_2}(\xi) = \frac{1 - \xi}{\text{totalmoles}(\xi)}$	$X_{\text{HI}}(\xi) = \frac{2 \cdot \xi}{\text{totalmoles}(\xi)}$
			$X_{\text{B}}(\xi) = \frac{\xi}{\text{totalmoles}(\xi)}$

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The equilibrium constant may be expressed as follows using Dalton's Law of Partial Pressures.

$$K_p(\xi) = \frac{(X_{HI}(\xi) \cdot P)^2 \cdot (X_B(\xi) \cdot P)}{(X_A(\xi) \cdot P) \cdot (X_{I2}(\xi) \cdot P)}$$

$$P = 2 \cdot \text{atm}$$

$$\text{TOL} = 0.001$$

$$K_{\text{given}} = 0.30 \cdot \text{atm}$$

Solving for ξ :

$$\xi_{\text{guess}} = 0.9$$

$$\xi_{\text{root}} = \text{root} \left[X_{HI}(\xi_{\text{guess}}) \cdot P^2 \cdot X_B(\xi_{\text{guess}}) \cdot P - (X_A(\xi_{\text{guess}}) \cdot P) \cdot (X_{I2}(\xi_{\text{guess}}) \cdot P) \cdot K_{\text{given}}, \xi_{\text{guess}} \right]$$

$$\xi = 34.0\%$$

$$\text{Recalculate } K_p \text{ to check: } K_p(\xi) = 0.30 \cdot \text{atm}$$

Adjust tolerance until the calculated value of K_p matches the given one. It may also be necessary to refine the initial guess if convergence problems are encountered.

6.65

We can determine the equilibrium constant from free energy function data in Tables 6.4 and 6.5 for 1500 K.

$$\phi_C = 17.5 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} + \frac{1.050 \cdot \frac{\text{kJ}}{\text{mole}}}{1500 \cdot \text{K}}$$

Equation 5.27 was used to convert ϕ based on 0 K to ϕ based on 298.15 K.

$$\phi_{Ti} = 54.2 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\phi_{TiC} = 60.8 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\text{kJ} \equiv 1000 \cdot \text{joule}$$

$$R \approx 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\Delta fH_{Ti} = 0 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta fH_{TiC} = -185 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta fH_C = 0 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$T = 1500 \cdot \text{K}$$

$$\Delta \phi = \phi_{TiC} - \phi_C - \phi_{Ti}$$

$$\Delta H = \Delta fH_{TiC} - \Delta fH_C - \Delta fH_{Ti}$$

$$K_a = \exp \left[\frac{\Delta \phi}{R} - \frac{\Delta H}{R \cdot T} \right] \quad \text{eq. 6.21}$$

$$K_a = 6.858 \cdot 10^5$$

We can calculate $\Delta_{\text{rxn}}G_{\theta}$ using equation 6.15

$$\Delta_{\text{rxn}}G_{\theta} = -R \cdot T \cdot \ln(K_a) \quad \Delta_{\text{rxn}}G_{\theta} = -167.6 \cdot \frac{\text{kJ}}{\text{mole}}$$

However, it is $\Delta_{\text{rxn}}G$, not $\Delta_{\text{rxn}}G_{\theta}$, that determines spontaneity. The two are related by eq. 6.14. Since we are dealing only with solids, the activity quotient is one (and $\ln Q = 0$). Thus, for this case the two are equal.

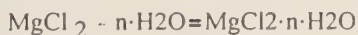
$$Q = 1$$

$$\Delta_{\text{rxn}}G = \Delta_{\text{rxn}}G_{\theta} + R \cdot T \cdot \ln(Q) \quad \Delta_{\text{rxn}}G = -167.6 \cdot \frac{\text{kJ}}{\text{mole}}$$

Since $\Delta_{\text{rxn}}G < 0$, the reaction is spontaneous under these conditions.

6.67

The most stable hydrate is the one which minimizes free energy. The general reaction for hydrate formation is given below. We will first calculate $\Delta_{\text{rxn}}G_{\theta}$, and then use eq. 6.14 to calculate $\Delta_{\text{rxn}}G$. (Lone subscripts refer to the degree of hydration of MgCl_2 .)



kJ : 1000·joule

$$\Delta_{\text{f}}G_0 = 592.33 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta_{\text{f}}G_1 = 862.36 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta_{\text{f}}G_2 = 1118.5 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta_{\text{f}}G_4 = 1633.8 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta_{\text{f}}G_6 = 1278.8 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta_{\text{f}}G_{\text{H}_2\text{O}} = 228.572 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta_{\text{rxn}}G_{\theta 1} = \Delta_{\text{f}}G_1 - \Delta_{\text{f}}G_0 - \Delta_{\text{f}}G_{\text{H}_2\text{O}} \quad \Delta_{\text{rxn}}G_{\theta 1} = 41.458 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta_{\text{rxn}}G_{\theta 2} = \Delta_{\text{f}}G_2 - \Delta_{\text{f}}G_0 - 2 \cdot \Delta_{\text{f}}G_{\text{H}_2\text{O}} \quad \Delta_{\text{rxn}}G_{\theta 2} = 69.026 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta_{\text{rxn}}G_{\theta 4} = \Delta_{\text{f}}G_4 - \Delta_{\text{f}}G_0 - 4 \cdot \Delta_{\text{f}}G_{\text{H}_2\text{O}} \quad \Delta_{\text{rxn}}G_{\theta 4} = -127.182 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta_{\text{rxn}}G_{\theta 6} = \Delta_{\text{f}}G_6 - \Delta_{\text{f}}G_0 - 6 \cdot \Delta_{\text{f}}G_{\text{H}_2\text{O}} \quad \Delta_{\text{rxn}}G_{\theta 6} = 684.962 \cdot \frac{\text{kJ}}{\text{mole}}$$

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Because the only non-condensed phase in this reaction is $\text{H}_2\text{O}(\text{g})$, the activity quotient found in eq. 6.14 simplifies to $(P_\theta/P_{\text{H}_2\text{O}})^n$.

$$T = 298.15 \cdot \text{K} \quad P_{\text{H}_2\text{O}} = 0.8 \cdot (23.76 \cdot \text{torr}) \quad P_\theta = 1 \cdot \text{atm} \quad R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\Delta_{\text{rxn}}G_1 = \Delta_{\text{rxn}}G_{\theta 1} \cdot R \cdot T \cdot \ln \frac{P_\theta}{P_{\text{H}_2\text{O}}} \quad \Delta_{\text{rxn}}G_1 = 32.314 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta_{\text{rxn}}G_2 = \Delta_{\text{rxn}}G_{\theta 2} \cdot R \cdot T \cdot \ln \frac{P_\theta^2}{P_{\text{H}_2\text{O}}} \quad \Delta_{\text{rxn}}G_2 = 50.739 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta_{\text{rxn}}G_4 = \Delta_{\text{rxn}}G_{\theta 4} \cdot R \cdot T \cdot \ln \frac{P_\theta^4}{P_{\text{H}_2\text{O}}} \quad \Delta_{\text{rxn}}G_4 = 90.608 \cdot \frac{\text{kJ}}{\text{mole}} \quad \text{MgCl}_2 \cdot 4\text{H}_2\text{O} \text{ minimizes } \Delta_{\text{rxn}}G \text{ and is therefore the most stable.}$$

$$\Delta_{\text{rxn}}G_6 = \Delta_{\text{rxn}}G_{\theta 6} \cdot R \cdot T \cdot \ln \frac{P_\theta^6}{P_{\text{H}_2\text{O}}} \quad \Delta_{\text{rxn}}G_6 = 739.824 \cdot \frac{\text{kJ}}{\text{mole}}$$

CHAPTER 7 Solutions

SECTION 7.1

7.1

It is easiest to calculate the mole fractions of both components first, and then use eq. 7.3 to obtain the molality.

$$\text{mass}_{\text{acetone}} = 10.0 \cdot \text{gm} \qquad \text{mass}_{\text{ethanol}} = 450 \cdot \text{gm} \qquad \text{MW}_{\text{acetone}} = 58.08 \cdot \frac{\text{gm}}{\text{mole}}$$

$$\text{moles}_{\text{acetone}} = \frac{\text{mass}_{\text{acetone}}}{\text{MW}_{\text{acetone}}} \qquad \text{moles}_{\text{ethanol}} = \frac{\text{mass}_{\text{ethanol}}}{\text{MW}_{\text{ethanol}}} \qquad \text{MW}_{\text{ethanol}} = 46.07 \cdot \frac{\text{gm}}{\text{mole}}$$

$$\text{moles}_{\text{total}} = \text{moles}_{\text{acetone}} + \text{moles}_{\text{ethanol}}$$

$$X_{\text{acetone}} = \frac{\text{moles}_{\text{acetone}}}{\text{moles}_{\text{total}}} \qquad X_{\text{ethanol}} = \frac{\text{moles}_{\text{ethanol}}}{\text{moles}_{\text{total}}}$$

$$X_{\text{acetone}} = 0.017 \qquad X_{\text{ethanol}} = 0.983$$

$$m(X_2, M_1) = \frac{1000 \cdot \text{gm}}{M_1} \cdot \frac{X_2}{1 - X_2} \qquad \text{eq. 7.3}$$

$$m(X_{\text{acetone}}, \text{MW}_{\text{ethanol}}) = 0.383 \quad \text{Units are moles of acetone per kg ethanol}$$

7.3

We'll calculate the mole fraction of sucrose first, and then use eq. 7.3 to obtain the molality.

$$\text{mass}_{\text{sucrose}} = 25.5 \cdot \text{gm} \qquad \text{mass}_{\text{water}} = 250 \cdot \text{gm} \qquad \text{MW}_{\text{sucrose}} = 342.300 \cdot \frac{\text{gm}}{\text{mole}}$$

$$\text{moles}_{\text{sucrose}} = \frac{\text{mass}_{\text{sucrose}}}{\text{MW}_{\text{sucrose}}} \qquad \text{moles}_{\text{water}} = \frac{\text{mass}_{\text{water}}}{\text{MW}_{\text{water}}} \qquad \text{MW}_{\text{water}} = 18.015 \cdot \frac{\text{gm}}{\text{mole}}$$

$$X_{\text{sucrose}} = \frac{\text{moles}_{\text{sucrose}}}{\text{moles}_{\text{sucrose}} + \text{moles}_{\text{water}}}$$

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$$X_{\text{sucrose}} = 0.00534$$

$$m(X_2, M_1) = \frac{1000 \cdot \text{gm}}{M_1} \cdot \frac{X_2}{1 - X_2} \quad \text{eq. 7.3}$$

$$m(X_{\text{sucrose}}, \text{MW}_{\text{water}}) = 0.298 \quad \text{Units are moles of sucrose per kg water.}$$

The molality could also be determined by multiplying the given amounts of sucrose and water by 4. The result is 102 g of sucrose in 1000 g of water. 102 g of sucrose is 0.298 moles.

7.5

Since we have 60.12 g of NaCl in 1 kg of water, all we have to do to find the molality is determine how many moles of NaCl there are.

$$\text{MW}_{\text{NaCl}} = 58.443 \frac{\text{gm}}{\text{mole}} \quad \text{mass NaCl} = 60.12 \cdot \text{gm}$$

$$\text{moles NaCl} = \frac{\text{mass NaCl}}{\text{MW}_{\text{NaCl}}}$$

$$m = \text{moles NaCl}$$

$$m = 1.0287 \quad \text{Molality units are moles of solute per kg of solvent.}$$

Concentration is moles of solute per liter of solution. We can use the density and total mass of the solution to determine the total volume of solution. Then, the concentration is easily determined.

$$\rho = 1.03887 \frac{\text{gm}}{\text{cm}^3} \quad \text{mass total} = 1 \cdot \text{kg} + 60.12 \cdot \text{gm}$$

$$V_{\text{total}} = \frac{\text{mass total}}{\rho} \quad V_{\text{total}} = 1.020 \cdot \text{liter}$$

$$c = \frac{\text{moles NaCl}}{V_{\text{total}}} \quad c = 1.00807 \frac{\text{mole}}{\text{liter}}$$

SECTION 7.2

7.7

The volume change on mixing can be estimated using eq. 7.10. V_{pm} denotes a partial molar volume. V_m denotes a pure component molar volume.

$$\text{Water} \quad MW_{\text{water}} = 18.015 \frac{\text{gm}}{\text{mole}} \quad \text{moles}_{\text{water}} = 2 \cdot \text{mole} \quad \rho_{\text{water}} = 0.997 \frac{\text{gm}}{\text{cm}^3}$$

$$V_m_{\text{water}} = \frac{MW_{\text{water}}}{\rho_{\text{water}}} \quad V_{pm_{\text{water}}} = 17 \frac{\text{cm}^3}{\text{mole}}$$

$$\text{Ethanol} \quad MW_{\text{ethanol}} = 46.069 \frac{\text{gm}}{\text{mole}} \quad \text{moles}_{\text{ethanol}} = \text{moles}_{\text{water}} \cdot \left(\frac{0.4}{0.6} \right) \quad \rho_{\text{ethanol}} = 0.7893 \frac{\text{gm}}{\text{cm}^3}$$

$$V_m_{\text{ethanol}} = \frac{MW_{\text{ethanol}}}{\rho_{\text{ethanol}}} \quad V_{pm_{\text{ethanol}}} = 57 \frac{\text{cm}^3}{\text{mole}}$$

$$\Delta_{\text{mix}}V = \text{moles}_{\text{water}} \cdot (V_{pm_{\text{water}}} - V_m_{\text{water}}) + \text{moles}_{\text{ethanol}} \cdot (V_{pm_{\text{ethanol}}} - V_m_{\text{ethanol}}) \quad \text{eq. 7.10}$$

$$\Delta_{\text{mix}}V = 4.0 \cdot \text{cm}^3$$

SECTION 7.3

7.9

Let's first list all of the distinct chemical species that we can identify: 1) water, 2) Ag^+ ion, 3) Cl^- ion, 4) AgCl , 5) AgBr , 6) Cl^- ion, 7) Br^- ion.

The number of components is the number of distinct species minus the number of constraints on the system. Constraints include things such as mass balance, electrical neutrality, and chemical equilibrium requirements.

Constraints here are 1) mass balance/electrical neutrality between Ag^+ ions and all negative ions, 2) equilibrium between solid AgCl and the dissociated salt, 3) equilibrium between solid AgBr and the dissociated salt. Thus, $7 - 3 = 4$ components.

You may be wondering why the first constraint was not three constraints. After all, there are three mass balance/electrical neutrality requirements that must be satisfied individually by each of the three salts (AgNO_3 , AgCl , AgBr). This is perfectly valid. However, if this is how you choose constraints, you have to distinguish between Ag^+ derived from each salt. Thus, Ag^+ becomes three components. Then there would be 9 components, 5 constraints, and still 4 components.

The different phases present are 1) aqueous solution, 2) vapor, 3) solid AgCl , and 4) solid AgBr .

Gibbs' Phase Rule gives the degrees of freedom as $F = \text{components} + 2 - \text{phases} = 2$. Thus, if P is fixed, the temperature can still vary.

7.11

(a) There is only one component because the two species present, the monomer and the dimer, are constrained by the reaction equilibrium between the two. The gas phase is the only phase present.

(b) There is only one component which can be independently varied because the three species present are bound by two constraints: 1) the reaction equilibrium and 2) mass balance between CO and Cl_2 (they must be formed in equal amounts if none is added). The gas phase is the only phase present.

(c) There are two components because the second constraint discussed in part (b) is not present. The gas phase is the only phase.

(d) There are two components because there are 3 distinct species and 1 constraint (the reaction equilibrium of $\text{NH}_4\text{Cl} = \text{HCl} + \text{NH}_3$). There is no mass balance linking HCl and NH_3 since there are arbitrary amounts of these gases. There are two phases, solid NH_4Cl and gas.

7.13

There are three distinct species: 1) ammonia (g), 2) carbon dioxide (g), and 3) ammonium carbamate (s). There is one constraint, that of reaction equilibrium. Thus there are two components. There are also two phases, solid and gas. The degree of freedom is $F = c + 2 - p = 2$.

SECTION 7.5

7.15

(a) An ideal solution is one that obeys Raoult's Law, eq. 7.21. From the given data, we can calculate the partial pressures for each component using this equation. The total pressure is just the sum of the two partial pressures. Pure component pressures are denoted here as P^* . All data and calculations are for 80 °C.

$$P^*_{\text{benzene}} = 760 \cdot \text{torr}$$

$$P^*_{\text{toluene}} = 350 \cdot \text{torr}$$

$$P_{\text{benzene}}(X_{\text{benzene}}) = X_{\text{benzene}} \cdot P^*_{\text{benzene}} \quad P_{\text{toluene}}(X_{\text{benzene}}) = (1 - X_{\text{benzene}}) \cdot P^*_{\text{toluene}}$$

$$P_{\text{benzene}}(0.2) = 152 \cdot \text{torr}$$

$$P_{\text{toluene}}(0.2) = 280 \cdot \text{torr}$$

$$P_{\text{total}}(X_{\text{benzene}}) = P_{\text{benzene}}(X_{\text{benzene}}) + P_{\text{toluene}}(X_{\text{benzene}})$$

$$P_{\text{total}}(0.2) = 432 \cdot \text{torr}$$

(b) Boiling occurs when the total vapor pressure equals the ambient pressure.

$$X_{\text{guess}} = 0.5$$

$$X_{\text{benzene}} = \text{root}(P_{\text{total}}(X_{\text{guess}}) - 500 \cdot \text{torr}, X_{\text{guess}})$$

$$X_{\text{benzene}} = 0.366$$

$$X_{\text{toluene}} = 1 - X_{\text{benzene}}$$

$$X_{\text{toluene}} = 0.634$$

7.17

Raoult's Law, eq. 7.21, predicts partial pressures based on liquid mole fractions and pure component vapor pressures. Pure component vapor pressures are denoted here as P^* .

$$P^*(a, b, T) = 10^{\frac{0.05223 \cdot a}{T} + b} \cdot \text{torr} \quad T = 296.15 \cdot \text{K}$$

$$a_{\text{bromide}} = 32430 \quad b_{\text{bromide}} = 7.821$$

$$a_{\text{chloride}} = 28894 \quad b_{\text{chloride}} = 7.593$$

$$P^*_{\text{bromide}} = P^*(a_{\text{bromide}}, b_{\text{bromide}}, T)$$

$$P^*_{\text{chloride}} = P^*(a_{\text{chloride}}, b_{\text{chloride}}, T)$$

$$P^*_{\text{bromide}} = 126.339 \cdot \text{torr}$$

$$P^*_{\text{chloride}} = 314.165 \cdot \text{torr}$$

Calculation of partial pressures:

$$X_{\text{bromide}} = 0.381$$

$$X_{\text{chloride}} = 1 - X_{\text{bromide}}$$

$$P_{\text{bromide}} = X_{\text{bromide}} \cdot P_{\text{star bromide}}$$

$$P_{\text{chloride}} = X_{\text{chloride}} \cdot P_{\text{star chloride}}$$

$$P_{\text{bromide}} = 48.135 \cdot \text{torr}$$

$$P_{\text{chloride}} = 194.468 \cdot \text{torr}$$

$$P_{\text{total}} = P_{\text{bromide}} + P_{\text{chloride}} \quad P_{\text{total}} = 243 \cdot \text{torr}$$

7.19

(a) The activities may be estimated using eq. 7.25, assuming the fugacity may be estimated as the partial pressure. Dalton's Law can be used to estimate the partial pressure. The activity coefficient can be estimated using eq. 7.26.

$$X_1 = 0.9006 \quad P_{\text{star } 1} = 130.4 \cdot \text{torr} \quad P_{\text{star } 2} = 43.9 \cdot \text{torr}$$

$$Y_1 = 0.6667 \quad P = 185.9 \cdot \text{torr}$$

$$a_1 = \frac{Y_1 \cdot P}{P_{\text{star } 1}} \quad a_1 = 0.950 \quad a_2 = \frac{(1 - Y_1) \cdot P}{P_{\text{star } 2}} \quad a_2 = 1.411$$

$$\gamma_1 = \frac{a_1}{X_1} \quad \gamma_1 = 1.055 \quad \gamma_2 = \frac{a_2}{(1 - X_1)} \quad \gamma_2 = 14.20$$

(b) Raoult's Law is eq. 7.21 in the text

$$P_{1\text{RL}} = X_1 \cdot P_{\text{star } 1} \quad P_{2\text{RL}} = (1 - X_1) \cdot P_{\text{star } 2}$$

$$P_{1\text{RL}} = 117.438 \cdot \text{torr} \quad P_{2\text{RL}} = 4.364 \cdot \text{torr}$$

$$P_{\text{RL}} = P_{1\text{RL}} + P_{2\text{RL}}$$

$$P_{\text{RL}} = 121.8 \cdot \text{torr}$$

(a) Using eqs. 7.25 and 7.26, the activity coefficient may be estimated as $\gamma_i = P_i / (P_{\text{star}_i} \cdot X_i)$, where P_{star} represents the pure component vapor pressure.

$$i = 1..7$$

$$P_i =$$

942.6·torr
909.6·torr
883.3·torr
868.4·torr
830.2·torr
786.8·torr
758.7·torr

$$X_{2_i} =$$

0.1312
0.2040
0.2714
0.3360
0.4425
0.5578
0.6036

$$Y_{2_i} =$$

0.0243
0.0300
0.0342
0.0362
0.0411
0.0451
0.0489

$$X_{1_i} = 1 - X_{2_i}$$

$$P_{\text{star}_1} = 1008 \cdot \text{torr}$$

$$P_{1_i} = Y_{1_i} \cdot P_i$$

$$\gamma_{1_i} = \frac{P_{1_i}}{P_{\text{star}_1} \cdot X_{1_i}}$$

$$Y_{1_i} = 1 - Y_{2_i}$$

$$P_{\text{star}_2} = 48.3 \cdot \text{torr}$$

$$P_{2_i} = Y_{2_i} \cdot P_i$$

$$\gamma_{2_i} = \frac{P_{2_i}}{P_{\text{star}_2} \cdot X_{2_i}}$$

$$\gamma_{1_i}$$

1.050
1.100
1.162
1.250
1.417
1.686
1.806

$$\gamma_{2_i}$$

3.615
2.769
2.305
1.937
1.596
1.317
1.273

(b) We can use eq. 7.27 to calculate $\Delta_{\text{mix}} G_{\text{ex}}$ if we divide through by $(n_1 + n_2)$. Thus, the moles become mole fractions. But what is the mole fraction? Since we are not given data on the sizes of the liquid and vapor phases, we'll assume the majority is in the liquid phase and thus use the liquid mole fractions.

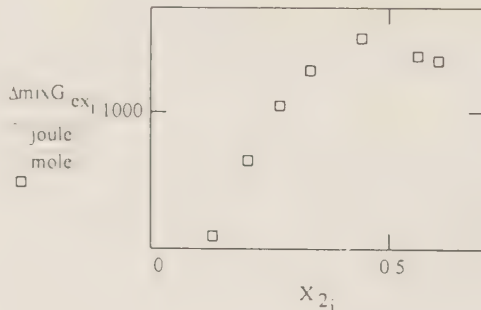
$$\Delta_{\text{mix}} G_{\text{ex}_i} = R \cdot T \cdot (X_{1_i} \cdot \ln(\gamma_{1_i}) + X_{2_i} \cdot \ln(\gamma_{2_i}))$$

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$T = 363.15 \cdot \text{K}$$

$$\Delta_{\text{mix}} G_{\text{ex}_i}$$

joule
(mole)
637.472
855.725
$1.014 \cdot 10^3$
$1.119 \cdot 10^3$
$1.211 \cdot 10^3$
$1.161 \cdot 10^3$
$1.147 \cdot 10^3$



7.23

Table 7.2 gives values for w , the first derivative with respect to T , and the second derivative with respect to T . If we start with the second derivative, we can gradually integrate these derivatives back to give $w(T)$.

$$\left(\frac{\partial^2 w}{\partial T^2}\right) = -0.046$$

Integrating with respect to T gives

$$\left(\frac{\partial w}{\partial T}\right) = -0.046T + c_1$$

We can determine the value of the integration constant, c_1 , using the known value for the first derivative. Table 7.2 gives the first derivative as -7.03 at $T = 293$ K. This means $c_1 = 6.448$.

$$\left(\frac{\partial w}{\partial T}\right) = -0.046T + 6.448$$

Integrating again gives

$$w = -0.023T^2 + 6.448T + c_2$$

Since Table 7.2 gives $w = 1275$ at $T = 293$ K, $c_2 = 1360.263$.

$$w(T) = 1360.263 + 6.448T - 0.023T^2$$

7.25

(a) If we assume an ideal solution, then Raoult's Law, eq. 7.21, applies. P_{star} denotes the pure component vapor pressure.

$$P_{\text{star } 1} = 118 \cdot \text{torr} \quad X_1 = 0.25 \quad P_1 = X_1 \cdot P_{\text{star } 1} \quad P_1 = 29.5 \cdot \text{torr}$$

$$P_{\text{star } 2} = 122 \cdot \text{torr} \quad X_2 = 0.75 \quad P_2 = X_2 \cdot P_{\text{star } 2} \quad P_2 = 91.5 \cdot \text{torr}$$

$$P_{\text{total}} = P_1 + P_2 \quad P_{\text{total}} = 121 \cdot \text{torr}$$

(b) Regular solution theory tries to correct for the differing interactions between like-like and like-unlike molecules. The parameter, w , was derived as a function of temperature in problem 7.23, and can be used here to calculate w at 303 K.

$$w(T) = (1360.263 + 6.448 \cdot T - 0.023 \cdot T^2) \cdot \frac{\text{joule}}{\text{mole}} \quad w(303) = 1.202 \cdot 10^3 \cdot \frac{\text{joule}}{\text{mole}}$$

The predicted activity coefficients are given by eq. 7.28.

$$\gamma_1 = \exp\left(\frac{X_2^2 \cdot w(303)}{R \cdot T}\right)$$

$$\gamma_1 = 1.308$$

$$\gamma_2 = \exp\left(\frac{X_1^2 \cdot w(303)}{R \cdot T}\right)$$

$$\gamma_2 = 1.03$$

$$T = 303 \cdot K$$

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot K}$$

The partial pressures are then given by eqs. 7.25 and 7.26.

$$P_1 = X_1 \cdot \gamma_1 \cdot P_{\text{star } 1}$$

$$P_2 = X_2 \cdot \gamma_2 \cdot P_{\text{star } 2}$$

$$P_1 = 38.585 \cdot \text{torr}$$

$$P_2 = 94.271 \cdot \text{torr}$$

$$P_{\text{total}} = P_1 + P_2$$

$$P_{\text{total}} = 133 \cdot \text{torr}$$

SECTION 7.6

7.27

The Henry's Law constant is defined by eq. 7.31. If we plot P_2/X_2 as a function of X_2 , k_x can be found by extrapolating back to $X_2 = 0$.

$$i = 0..4$$

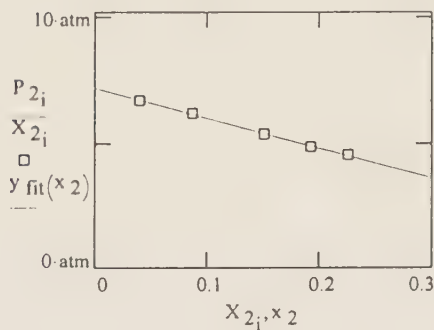
$$P_{2,i} = \quad X_{2,i} = \quad y_i = \frac{P_{2,i}}{X_{2,i}}$$

200·torr	0.040
400·torr	0.087
600·torr	0.151
700·torr	0.193
760·torr	0.226

$$k_x = \text{intercept}(X_2, y) \quad m = \text{slope}(X_2, y)$$

$$k_x = 7.05 \cdot \text{atm} \quad y_{\text{fit}}(x_2) = k_x + m \cdot x_2$$

$$x_2 = 0, 0.1 \dots 1$$



The Henry's Law constant is $k_x = 7.05 \text{ atm}$.

7.29

Henry's Law, eq. 7.30, gives us the Kr liquid phase mole fraction. Keep in mind that the 100 atm is the partial pressure of Kr.

$$k_x = 2.00 \cdot 10^4 \cdot \text{atm} \quad P_2 = 100 \cdot \text{atm}$$

$$X_2 = \frac{P_2}{k_x} \quad X_2 = 0.00500$$

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Now we just have to find how many grams of Kr is equivalent to this mole fraction in 1000 g of water.

$$M_1 = 18.015 \frac{\text{gm}}{\text{mole}} \quad M_2 = 83.80 \frac{\text{gm}}{\text{mole}} \quad \text{TOL} = 10^{-5}$$

$$n_1 = \frac{1000 \cdot \text{gm}}{M_1} \quad n_{2\text{guess}} = 1 \cdot \text{mole}$$

$$n_2 = \text{root} \left(\frac{n_{2\text{guess}}}{n_1 + n_{2\text{guess}}} - X_{2,n_{2\text{guess}}} \right)$$

$$n_2 = 0.279$$

$$\text{mass}_{\text{Kr}} = n_2 \cdot M_2$$

$$\text{mass}_{\text{Kr}} = 23.4 \cdot \text{gm}$$

SECTION 7.7

7.31

The osmotic coefficient data can be fit to a polynomial, and the activity coefficients of n-octane can be estimated with eq. 7.37. A curve fitting program gives

$$\phi(m) = 1 - 0.397281 \cdot m + 0.0359014 \cdot m^2 + 0.117675 \cdot m^3 - 0.00871332 \cdot m^4$$

$$\gamma_{2m}(m) = \exp \left(\phi(m) - 1 + \int_0^m \frac{\phi(mx) - 1}{mx} dm \right)$$

$$\gamma_{2m}(0.01) = 0.992 \quad \gamma_{2m}(0.1) = 0.925 \quad \gamma_{2m}(0.5) = 0.695$$

7.33

We can use eq. 7.36 to estimate the osmotic coefficient. The solvent activity may be estimated as the partial pressure over the pure component pressure (Pstar). The solute molality is given in the problem.

$$P_{\text{H}_2\text{O}} = 23.6798 \cdot \text{torr} \quad P_{\text{star H}_2\text{O}} = 23.7675 \cdot \text{torr} \quad M_1 = 18.015$$

$$a_1 = \frac{P_{\text{H}_2\text{O}}}{P_{\text{star H}_2\text{O}}} \quad a_1 = 0.996 \quad m = 0.15$$

$$\phi = \frac{-1000 \cdot \ln(a_1)}{m \cdot M_1} \quad \phi = 1.368$$

7.35

The osmotic coefficient can be calculated with eq. 7.36 (using $v = 1$ for nonelectrolytes). Then, the quantity $(\phi-1)/m$ can be fit to a linear function of m , which can be used in eq. 7.37 to calculate the desired activity coefficients.

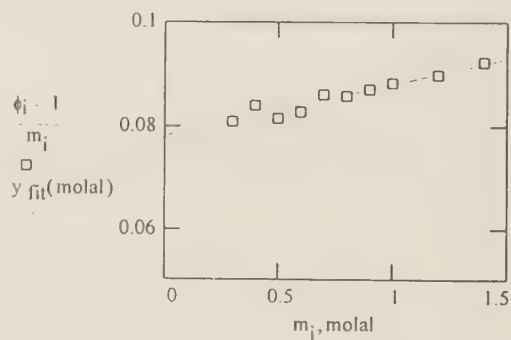
$i = 0..9$	m_i	a_{\pm}	$\phi_i = \frac{-1000 \cdot \ln(a_{\pm})}{m_i \cdot M_1}$	$M_1 = 18.015$
			$y_i = \frac{\phi_i - 1}{m_i}$	
	0.3	0.99448		
	0.4	0.99258		
	0.5	0.99067		
	0.6	0.98872		
	0.7	0.98672		
	0.8	0.98472		
	0.9	0.98267		
	1.0	0.98059		
	1.2	0.97634		
	1.4	0.97193		
			$s = \text{slope}(m, y)$	$b = \text{intercept}(m, y)$
			$s = 0.010$	$b = 0.078$
			$y_{\text{fit}}(m) = b + s \cdot m$	
			$\phi_{\text{fit}}(m) = y_{\text{fit}}(m) \cdot m + 1$	molal 0, 0.1 .. 1.5

$$\gamma_{2m}(m) = \exp \left(\phi_{\text{fit}}(m) - 1 - \int_0^m y_{\text{fit}}(mx) \, dm \right)$$

$$\gamma_{2m}(0.1) = 1.016$$

$$\gamma_{2m}(0.5) = 1.085$$

$$\gamma_{2m}(1.0) = 1.186$$



SECTION 7.8

7.37

The first thing we have to do is calculate the molality of ethanol in this solution, since the freezing point depression equations use molality. In 1000 g of water, we need 1000/9 g of ethanol to make a 10% ethanol solution by weight.

$$\text{mass ethanol} = \frac{1000 \cdot \text{gm}}{9} \quad \text{MW ethanol} = 46.069 \cdot \frac{\text{gm}}{\text{mole}}$$

$$m = \frac{\text{mass ethanol}}{\text{MW ethanol}} \quad m = 2.412$$

Now we can use eq. 7.4 to determine the freezing point depression.

$$K_f = 1.860 \quad T_{\text{star } f} = 273.15 \cdot \text{K}$$

$$\theta = K_f m \quad \theta = 4.5$$

$$T_f = T_{\text{star } f} - \theta \cdot \text{K}$$

$$T_f = 268.66 \cdot \text{K}$$

7.39

The boiling point elevation derivation directly parallels the freezing point depression derivation in the text. We can start with

$$\mu_1(\text{vap}) = \mu_1(\text{solution})$$

With eqs. 7.16, 7.17, and the Raoult's Law reference state (pure liquid), the solution chemical potential becomes

$$\mu_1^v = \mu_1^* + RT \ln(a_1)$$

Solving for $\ln(a_1)$,

$$\ln(a_1) = \frac{1}{RT} (\mu_1^v - \mu_1^*)$$

Taking the partial derivative with respect to T gives the following (remember that T and μ are functions of temperature),

$$\left(\frac{\partial \ln a_1}{\partial T} \right) = -\frac{1}{RT^2} (\mu_1^v - \mu_1^*) + \frac{1}{RT} \left[\left(\frac{\partial \mu_1^v}{\partial T} \right) - \left(\frac{\partial \mu_1^*}{\partial T} \right) \right]$$

Using $\mu = G = H - TS$ and $\left(\frac{\partial G}{\partial T}\right)_P = -S$ gives the following

$$\frac{\partial \ln a_1}{\partial T} = -\frac{1}{RT^2}(H_1^v - H_1^*)$$

$$\frac{\partial \ln a_1}{\partial T} = -\frac{\Delta_{vap}H}{RT^2}$$

Integrating from T_b^* and $a_1 = 1$ to T_b and a_1 gives

$$\ln a_1 = \int_{T_b^*}^{T_b} -\frac{\Delta_{vap}H}{RT^2} dT$$

If we assume the boiling point elevation is small, then the integrand may be assumed to be constant and T may be replaced with T_b^* . Defining $\theta = T_b - T_b^*$, we now have

$$\ln a_1 = -\frac{\Delta_{vap}H}{RT_b^{*2}}\theta$$

The osmotic coefficient was given by eq. 7.36 as

$$\phi = \frac{-1000(g/kg)\ln a_1}{mM_1}$$

Substituting eq. (1) into eq. (2) gives

$$\phi = \left[\frac{1000(g/kg)\Delta_{vap}H}{M_1RT_b^{*2}} \right] \frac{\theta}{m}$$

The grouping in the brackets can be used to define a boiling point elevation constant, K_b

$$K_b = \frac{M_1RT_b^{*2}}{1000(g/kg)\Delta_{vap}H}$$

Thus, eq. (3) becomes

$$\phi = \frac{\theta}{K_b m}$$

Since ϕ approaches one in dilute solution, we have finally

$$\theta = K_b m$$

7.41

The necessary data for ethanol can be obtained from Table 4.2. Equations for boiling point elevation were derived in problem 7.39.

$$T_{\text{star } b} = 351.7 \cdot \text{K} \quad \Delta vH = 38.58 \cdot \frac{\text{kJ}}{\text{mole}} \quad M_1 = 46.069 \cdot \frac{\text{gm}}{\text{mole}} \quad \text{kJ} \equiv 1000 \cdot \text{joule}$$

$$m = 0.825 \cdot \frac{\text{mole}}{\text{kg}} \quad R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$K_b = \frac{M_1 \cdot R \cdot T_{\text{star } b}^2}{\left(\frac{1000 \cdot \text{gm}}{\text{kg}}\right) \cdot \Delta vH} \quad K_b = 1.228 \cdot \frac{\text{K} \cdot \text{kg}}{\text{mole}}$$

$$\Delta T_b = K_b \cdot m \quad \Delta T_b = 1.0 \cdot \text{K}$$

$$T_b = T_{\text{star } b} + \Delta T_b$$

$$T_b = 352.7 \cdot \text{K}$$

7.43

The average molecular weight can be calculated using eq. 7.43, noting that the "c" is a molar concentration. We are given mass concentrations, and the two are related by the molecular weight. Thus, we may estimate the molecular weight as (mass concentration * R * T / osmotic pressure) at each data point, and then extrapolate back to infinite dilution.

$$i = 0.3$$

$$c_{\text{mass}_i} =$$

$$P_{i_i} =$$

$$MW_i = \frac{c_{\text{mass}_i} \cdot R \cdot T}{P_{i_i}} \quad T = 298.15 \cdot \text{K} \quad R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$20.0 \cdot \frac{\text{gm}}{\text{liter}}$$

$$210.3 \cdot \text{Pa}$$

$$15.0 \cdot \frac{\text{gm}}{\text{liter}}$$

$$150.4 \cdot \text{Pa}$$

$$10.0 \cdot \frac{\text{gm}}{\text{liter}}$$

$$100.5 \cdot \text{Pa}$$

$$5.0 \cdot \frac{\text{gm}}{\text{liter}}$$

$$49.5 \cdot \text{Pa}$$

$$m = \text{slope}(c_{\text{mass}}, MW)$$

$$b = \text{intercept}(c_{\text{mass}}, MW)$$

$$m = 867.245 \cdot \frac{\text{liter}}{\text{mole}}$$

$$b = 2.559 \cdot 10^5 \cdot \frac{\text{gm}}{\text{mole}}$$

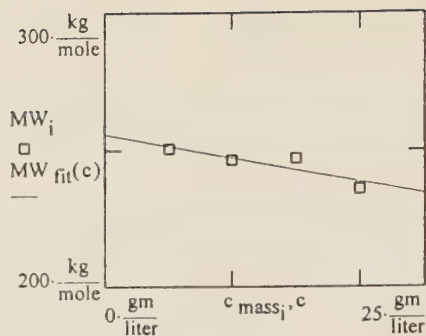
$$MW_{\text{fit}(c)} = b + m \cdot c$$

$$c = 0 \cdot \frac{\text{gm}}{\text{liter}}, 1 \cdot \frac{\text{gm}}{\text{liter}} \dots 30 \cdot \frac{\text{gm}}{\text{liter}}$$

The molecular weight extrapolated to infinite dilution is just the y-intercept of the straight line fit.

$$MW = b$$

$$MW = 256 \cdot \frac{\text{kg}}{\text{mole}}$$



7.45

The hydrostatic pressure is given by ρgh , while the osmotic pressure is given in the problem. All we have to do is find the depth at which the two become equal.

$$\rho = 1.03 \cdot \frac{\text{gm}}{\text{cm}^3} \quad g = 9.81 \cdot \frac{\text{m}}{\text{sec}^2} \quad P_{\text{static}}(h) = \rho \cdot g \cdot h \quad P_{\text{osmotic}} = 23 \cdot \text{atm}$$

$$h_{\text{guess}} = 10 \cdot \text{m}$$

$$h = \text{root}(P_{\text{static}}(h_{\text{guess}}) - P_{\text{osmotic}}, h_{\text{guess}})$$

$h = 231 \cdot \text{m}$ At a depth below 231 m, the hydrostatic pressure would exceed the osmotic pressure, and fresh water would flow into the pipe.

7.47

The osmotic pressure is approximated by eq. 7.43.

$$c = 0.2 \cdot \frac{\text{mole}}{\text{liter}} \quad R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T = 293.15 \cdot \text{K}$$

$$P_i = c \cdot R \cdot T \quad P_i = 4.81 \cdot \text{atm}$$

This is reasonably close to the observed value of 5.06 atm.

SECTION 7.9

7.49

The equilibrium constant is the ratio of the activities of boric acid in the various solvents. At infinite dilution, the Henry's law activity (concentration scale) is just the concentration. Thus, the equilibrium constant is just the ratio of the concentrations in the limit of infinite dilution. We can plot $c(\text{acid in H}_2\text{O}) / c(\text{acid in alcohol})$ as a function of either concentration and then extrapolate to zero.

$$i = 0..1$$

$$c_{\text{acid H}_2\text{O}_i} =$$

0.02602
0.05140

$$c_{\text{acid alcohol}_i} =$$

0.00805
0.01545

$$K_{a_i} = \frac{c_{\text{acid H}_2\text{O}_i}}{c_{\text{acid alcohol}_i}}$$

$$m = \text{slope}(c_{\text{acid alcohol}}, K_a)$$

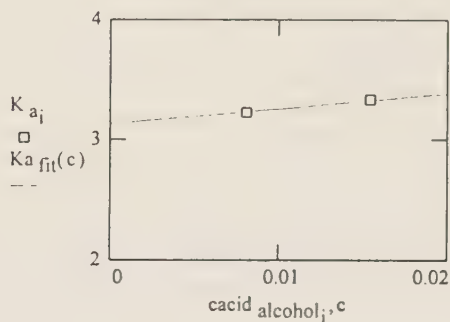
$$b = \text{intercept}(c_{\text{acid alcohol}}, K_a)$$

$$K_{a_{\text{fit}}}(c) = b + m \cdot c$$

$$c = 0, 0.001 .. 0.020$$

$$K_a = K_{a_{\text{fit}}}(0)$$

$$K_a = 3.13$$



7.51

For the "reaction" $\text{I}_2(\text{solid}) = \text{I}_2(\text{ao})$, we can calculate $\Delta_{\text{rxn}}G_0(T)$ using data from Tables 6.1 and 8.3.

Table 6.1 gives data for pure components, while Table 8.3 gives data for components in solution (HL molality scale). Since we are asked to calculate the solubility at several temperatures, we need to derive a temperature dependent expression for $\Delta_{\text{rxn}}G_0(T)$. This can be done by assuming constant

$\Delta_{\text{rxn}}H_0$ and $\Delta_{\text{rxn}}S_0$.

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$$\Delta fH_{I2(solid)} = 0 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta fH_{I2(aq)} = 22.6 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$S_{I2(solid)} = 116.135 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$S_{I2(aq)} = 137.2 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\text{kJ} = 1000 \cdot \text{joule}$$

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\Delta_{rxn}H_{\theta} = \Delta fH_{I2(aq)} - \Delta fH_{I2(solid)}$$

$$\Delta_{rxn}S_{\theta} = S_{I2(aq)} - S_{I2(solid)}$$

$$\Delta_{rxn}H_{\theta} = 22.6 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta_{rxn}S_{\theta} = 21.065 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\Delta_{rxn}G_{\theta}(T) = \Delta_{rxn}H_{\theta} - T \cdot \Delta_{rxn}S_{\theta}$$

The equilibrium constant can easily be calculated from the $\Delta_{rxn}G_{\theta}$ using eq. 6.15

$$K_a(T) = \exp\left(\frac{-\Delta_{rxn}G_{\theta}(T)}{R \cdot T}\right)$$

K_a is the ratio of activities. For solid I_2 , the activity is one. For aqueous I_2 , the activity is $(\gamma m)/(m^{\theta})$, since Table 8.3 uses the Henry's Law molality scale reference state. We are going to assume dilute solution, so the activity coefficient will be approximated as one. Once we find the answer, we'll see that the dilute solution approximation is justified.

Thus K_a becomes just

$$K_a = \frac{m}{m_{\theta}}$$

$$m_{\theta} = 1 \cdot \frac{\text{mole}}{\text{kg}}$$

$$m(T) = K_a(T) \cdot m_{\theta}$$

$$m(273.15 \cdot \text{K}) = 0.00060 \cdot \frac{\text{mole}}{\text{kg}} \quad m(298.15 \cdot \text{K}) = 0.0014 \cdot \frac{\text{mole}}{\text{kg}} \quad m(373.15 \cdot \text{K}) = 0.0086 \cdot \frac{\text{mole}}{\text{kg}}$$

7.53

For the "reaction" $\text{Xe}(g) = \text{Xe}(aq)$, we can calculate $\Delta_{rxn}G_{\theta}(T)$ by assuming constant $\Delta_{rxn}H_{\theta}$ and $\Delta_{rxn}S_{\theta}$.

$$\Delta_{rxn}H_{\theta} = -17.6 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta_{rxn}S_{\theta} = -103.98 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\text{kJ} = 1000 \cdot \text{joule}$$

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\Delta_{rxn}G_{\theta}(T) = \Delta_{rxn}H_{\theta} - T \cdot \Delta_{rxn}S_{\theta}$$

The equilibrium constant can easily be calculated from the $\Delta_{rxn}G_{\theta}$ using eq. 6.15

$$K_a(T) = \exp\left(\frac{-\Delta_{\text{rxn}}G_{\theta}(T)}{R \cdot T}\right)$$

K_a is the ratio of activities. For Xe (g), the activity is (P/P^{θ}) . For Xe (aq), the activity is $(\gamma m)/(m^{\theta})$. We are going to assume dilute solution, so the activity coefficient will be approximated as one. Once we find the answer, we'll see that the dilute solution approximation is justified.

Thus K_a becomes just

$$K_a = \frac{P_{\theta}}{P} \cdot \frac{m}{m_{\theta}} \quad P = 1 \cdot \text{bar} \quad P_{\theta} = 1 \cdot \text{bar} \quad m_{\theta} = 1 \cdot \frac{\text{mole}}{\text{kg}}$$

$$m(T) = K_a(T) \cdot m_{\theta} \cdot \frac{P}{P_{\theta}} \quad \text{bar} = 10^5 \cdot \text{Pa}$$

$$m(273.15 \cdot \text{K}) = 0.0086 \cdot \frac{\text{mole}}{\text{kg}} \quad m(298.15 \cdot \text{K}) = 0.0045 \cdot \frac{\text{mole}}{\text{kg}} \quad m(373.15 \cdot \text{K}) = 0.0011 \cdot \frac{\text{mole}}{\text{kg}}$$

7.55

The first thing we need to do is calculate the equilibrium constant, K_a . For the reaction $\text{H}_2\text{S}(\text{g}) = \text{H}_2\text{S}(\text{aq})$, the equilibrium constant is

$$K_a = \frac{a(\text{H}_2\text{S}, \text{aq})}{a(\text{H}_2\text{S}, \text{g})} = \left(\frac{\gamma \cdot m}{m_{\theta}}\right) \cdot \left(\frac{P_{\theta}}{P_{\text{H}_2\text{S}}}\right)$$

In the limit of infinite dilution, the activity coefficient is one. We will calculate K_a for each data point using the above expression (with $\gamma = 1$). Then, K_a at infinite dilution will be found by regressing the calculated K_a values vs molarity and finding the intercept at $m=0$.

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$$i = 0.4$$

$$m_i$$

$$P_{H_2S_i}$$

0.050	mole kg
0.101	mole kg
0.150	mole kg
0.204	mole kg
0.254	mole kg

0.486	atm
0.992	atm
1.474	atm
2.049	atm
2.514	atm

$$K_{a_i} = \left(\frac{m_i}{m_\theta} \right) \cdot \left(\frac{P_\theta}{P_{H_2S_i}} \right)$$

$$s = \text{slope}(m, K_a)$$

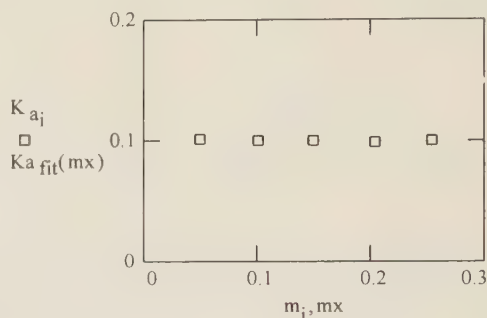
$$b = \text{intercept}(m, K_a)$$

$$K_{a_{fit}}(mx) = b + s \cdot mx$$

$$P_\theta = 10^5 \cdot \text{Pa}$$

$$m_\theta = 1 \cdot \frac{\text{mole}}{\text{kg}}$$

$$mx = 0 \cdot \frac{\text{mole}}{\text{kg}}, 0.05 \cdot \frac{\text{mole}}{\text{kg}} \dots 0.30 \cdot \frac{\text{mole}}{\text{kg}}$$



$$K_a = b = K_a = 0.1018$$

The equilibrium constant is related to $\Delta_{rxn}G^\theta$ by eq. 6.15. However, we also know that $\Delta_{rxn}G^\theta$ for this reaction is $\Delta fG^\theta(aq) - \Delta fG^\theta(g)$. $\Delta fG^\theta(g)$ can be found in Table 6.1, so we may readily solve for $\Delta fG^\theta(aq)$.

$$\Delta_{rxn}G_\theta = R \cdot T \cdot \ln(K_a) \quad \Delta_{rxn}G_\theta = 5.663 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$T = 298.15 \cdot \text{K}$$

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\Delta fG_{\theta gas} = 33.56 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\text{kJ} : 1000 \cdot \text{joule}$$

$$\Delta fG_{\theta aq} = \Delta_{rxn}G_\theta + \Delta fG_{\theta gas} \quad \Delta fG_{\theta aq} = 27.90 \cdot \frac{\text{kJ}}{\text{mole}}$$

This is in excellent agreement with the value given in Table 8.3, -27.83 kJ/mole.

7.57

The first thing we need to do is calculate the equilibrium constant, K_a . For the reaction glycine (s) = glycine (aq), the equilibrium constant is

$$K_a = \frac{\gamma_{2m} \cdot m}{m_{\theta}} \quad \gamma_{2m} = 0.872 \quad m = 3.3 \cdot \frac{\text{mole}}{\text{kg}} \quad m_{\theta} = 1 \cdot \frac{\text{mole}}{\text{kg}}$$

$$K_a = 2.878$$

The equilibrium constant is related to $\Delta_{\text{rxn}}G^{\theta}$ by eq. 6.15. However, we also know that $\Delta_{\text{rxn}}G^{\theta}$ for this reaction is $\Delta fG^{\theta}(\text{aq}) - \Delta fG^{\theta}(\text{s})$. $\Delta fG^{\theta}(\text{s})$ can be found in Table 7.7, so we may readily solve for $\Delta fG^{\theta}(\text{aq})$.

$$\Delta_{\text{rxn}}G_{\theta} = -R \cdot T \cdot \ln(K_a) \quad \Delta_{\text{rxn}}G_{\theta} = -2.62 \cdot \frac{\text{kJ}}{\text{mole}} \quad T = 298.15 \cdot \text{K} \quad R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\Delta fG_{\theta \text{solid}} = -370.7 \cdot \frac{\text{kJ}}{\text{mole}} \quad \text{kJ} = 1000 \cdot \text{joule}$$

$$\Delta fG_{\theta \text{aq}} = \Delta_{\text{rxn}}G_{\theta} + \Delta fG_{\theta \text{solid}} \quad \Delta fG_{\theta \text{aq}} = -373.3 \cdot \frac{\text{kJ}}{\text{mole}}$$

This is in excellent agreement with the value given in Table 7.7, -373.0 kJ/mole.

7.59

Given

$$X_2(T) = \exp \left[-6.0579 - \frac{1152.5}{\left(\frac{T}{\text{K}} \right)} \right] \quad P = 1 \cdot \text{atm} \quad P_{\theta} = 10^5 \cdot \text{Pa}$$

For the reaction, $\text{He(g)} = \text{He(NMA)}$, the equilibrium constant can be written as follows assuming an ideal solution (HL, X scale).

$$K_a(T) = \frac{X_2(T)}{\left(\frac{P}{P_{\theta}} \right)}$$

With an expression for the equilibrium constant, eq. 6.15 can be used to obtain $\Delta_{\text{rxn}}G_{\theta}(T)$.

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$$\Delta_{\text{rxn}}G_{\theta}(T) = R \cdot T \cdot \ln(K_a(T)) \quad R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

An expression for $\Delta_{\text{rxn}}H_{\theta}(T)$ can be found using eq. 6.23. Taking the derivative of $\ln(K_a(T))$ with respect to $1/T$ gives $-\Delta_{\text{rxn}}H_{\theta}/R$.

$$\Delta_{\text{rxn}}H_{\theta} = -R \cdot (-1152.5 \cdot \text{K})$$

The "reaction" here is just the formation reaction for He in solution in NMA, since He(g) is already in its most stable form at standard conditions. Therefore, $\Delta_f G(\text{He}, \text{NMA}:\text{X}) = \Delta_{\text{rxn}}G_{\theta}$ and

$$\Delta_f H(\text{He}, \text{NMA}:\text{X}) = \Delta_{\text{rxn}}H_{\theta}$$

$$\Delta_f G(T) = \Delta_{\text{rxn}}G_{\theta}(T)$$

$$\Delta_f H = \Delta_{\text{rxn}}H_{\theta}$$

$$\text{kJ} \equiv 1000 \cdot \text{joule}$$

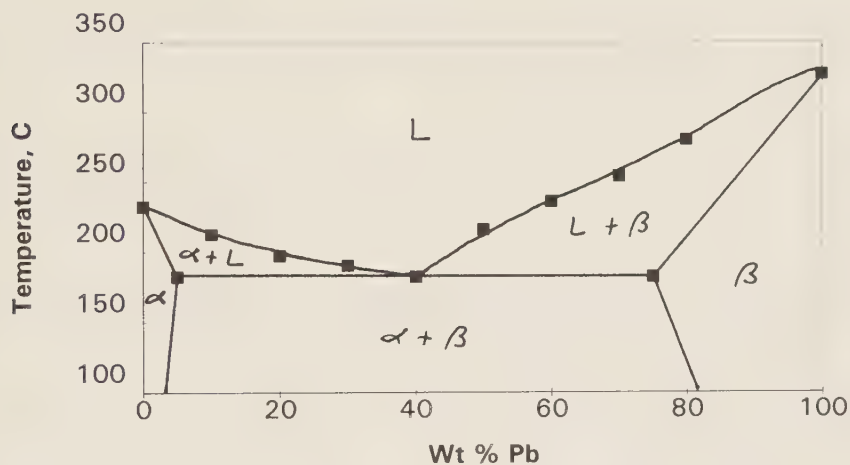
$$\Delta_f G(298.15 \cdot \text{K}) = 24.63 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta_f H = 9.58 \cdot \frac{\text{kJ}}{\text{mole}}$$

SECTION 7.10

7.61

This system is similar to that shown in Figure 7.19(c).



7.63

α represents the solution that is rich in component A. β represents the solutions that is rich in component B.

- (1) α
- (2) $\alpha + \text{vapor}$
- (3) $\text{vapor} + \beta$
- (4) β
- (5) $\alpha + \beta$

Cooling histories:

Degrees of Freedom (F) = $c + 2 - p$.

Composition of single phase regions are given by extending dotted line down to composition axis.
Compositions of two phase regions are given by the ends of horizontal tie lines spanning that area at that temperature.

All samples start as a homogenous vapor ($F = 2 + 2 - 1 = 3$).

(a) As the sample moves into area (2), the phases present are α and the vapor ($F = 2$). When the sample passes into area (1), the only phase is α ($F = 3$). As the sample passes into area (5), there are two immiscible phases α and β present ($F = 2$).

(b) When the sample reaches the intersection of areas (2), (3), and (5), there are three phases present: vapor, α , and β . At this point $F = 1$; this degree of freedom was used when constant pressure was specified in creating the T vs X phase diagram. As the sample passes into area (5), the two phases present are immiscible α and β ($F = 2$).

(c) When the sample passes into area (3), the phases present are vapor and β ($F = 2$). As the sample passes into area (5), the phases are α and β ($F = 2$).

CHAPTER 8 *Ionic Solutions*

SECTION 8.1

8.1

From eq. 8.1, we can calculate the "osmotic factor," i . We are given the molality of the acid, and the freezing point depression constant of water is found in Table 7.6.

$$K_f = 1.860 \frac{\text{K}}{\left(\frac{\text{mole}}{\text{kg}}\right)} \quad \theta = 0.0208 \cdot K \quad m = 0.01 \frac{\text{mole}}{\text{kg}}$$
$$i = \frac{\theta}{K_f m} \quad i = 1.118$$

The degree of ionization (or dissociation) can be found using eq. 8.2. $v=2$ since a weak acid should only dissociate into two ions at most.

$$v = 2 \quad \alpha = \frac{i - 1}{v} \quad \alpha = 0.118$$

8.3

The activity coefficients can be evaluated by using eq. 7.37, but we first need an expression for $j(m)$. We can use the given freezing point depression data to estimate the osmotic coefficient ϕ , using eq. 8.8 ignoring the b term. j is calculated as $1-\phi$. Finally, the desired fit for $j(m)$ can be found by regressing (j/m) vs $1/\text{sqrt}(m)$.

$$i = 0.5$$

$$m_i = \quad \theta_i = \quad v = 2 \quad K_f = 1.860 \quad \phi_i = \frac{\theta_i}{v \cdot K_f m_i} \quad j_i = 1 - \phi_i$$

0.003612	0.01316
0.006690	0.02421
0.009872	0.03509
0.016215	0.05712
0.030369	0.10541
0.048335	0.16359

$$x_i = \frac{1}{\sqrt{m_i}} \quad y_i = \frac{j_i}{m_i}$$

$$s = \text{slope}(x,y) \quad b = \text{intercept}(x,y)$$

$$y_{\text{fit}}(\text{molal}) = b + s \cdot \frac{1}{\sqrt{\text{molal}}}$$

$$\text{molal} = 0.003, 0.004 \dots 0.050$$

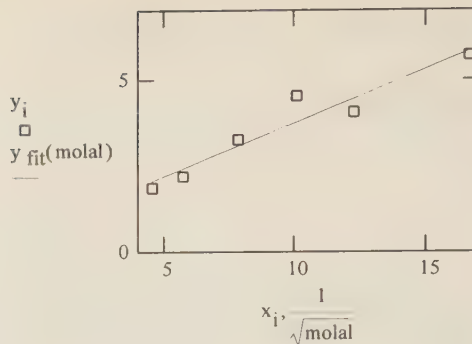
$$j_{\text{fit}}(\text{molal}) = \text{molal} \cdot \gamma_{\text{fit}}(\text{molal})$$

$$\gamma_{\text{mean}}(m) = \exp \left(-j_{\text{fit}}(m) - \int_0^m \frac{j_{\text{fit}}(m)}{m} dm \right)$$

$$\gamma_{\text{mean}}(0.001) = 0.971$$

$$\gamma_{\text{mean}}(0.01) = 0.901$$

$$\gamma_{\text{mean}}(0.05) = 0.762$$



8.5

The distance of closest approach is the a_0 parameter in the Debye-Huckel equation, eq. 8.10. For a 1:1 electrolyte like KCl, $z_+ = z_- = 1$, and $I = m$. With these simplifications and a little rearrangement, eq. 8.10 becomes

$$\ln(\gamma_{\text{mean}}) = \frac{B \cdot a_0}{\alpha} \frac{1}{\alpha \cdot \sqrt{m}}$$

Thus, a_0 can be determined by regressing $1/\ln(\gamma_{\text{mean}})$ vs $1/\sqrt{m}$ and finding the intercept. Only experimental activity coefficients up to $m = 0.1$ mol/kg will be used since the DH equation is only valid in this range. Values for α and B can be found in Table 8.2 for 25 C.

$$i = 0.5$$

$$\alpha = 1.177 \quad B = 0.329$$

m_i	$\gamma_{\text{mean},i}$
0.001	0.9648
0.005	0.927
0.01	0.901
0.02	0.868
0.05	0.816
0.1	0.769

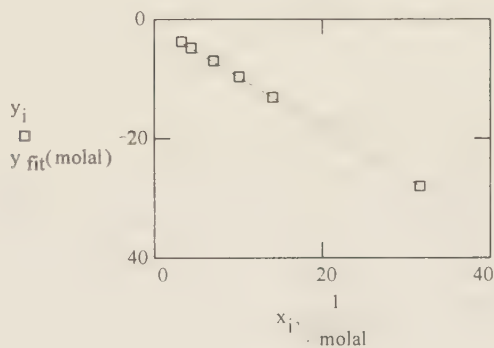
$$x_i = \frac{1}{\sqrt{m_i}} \quad y_i = \frac{1}{\ln(\gamma_{\text{mean},i})}$$

$$s = \text{slope}(x, y) \quad b = \text{intercept}(x, y) \quad y_{\text{fit}}(\text{molal}) = b + s \cdot \frac{1}{\text{molal}}$$

molal = 0.001, 0.002 .. 0.1

$$a_0 = \frac{-b \cdot \alpha}{B}$$

$$a_0 = 4.0 \quad \text{This is in Angstroms (see Table 8.2).}$$



8.7

(a) The DHG equation is given by eq. 8.13. For a 1:1 electrolyte, the DHG equation can be solved for β to give

$$\beta = \frac{1}{2 \cdot m} \cdot \left(\ln(\gamma_{\text{mean}}) + \frac{\alpha \cdot \sqrt{m}}{1 + \sqrt{m}} \right) \quad m = 0.05 \quad \alpha = 1.177 \quad \gamma_{\text{mean}} = 0.830$$

$$\beta = 0.288$$

(b) The DHG equation can be used to predict activity coefficients at other molalities with this β value.

$$\gamma_{\text{mean}}(m) = \exp \left(\frac{-\alpha \cdot \sqrt{m}}{1 + \sqrt{m}} + 2 \cdot \beta \cdot m \right)$$

$i = 0.5$	$m_i =$	$\gamma_{\text{mean}}(m_i)$	$\gamma_{\text{actual},i}$
	0.01	0.904	0.904
	0.02	0.874	0.875
	0.05	0.830	0.830
	0.1	0.798	0.796
	0.2	0.780	0.767
	0.5	0.819	0.757

Remember, the DHG equation does not work well for ionic strengths greater than 0.1 mole/kg.

8.9

The hydrogen ion activity is given by the mean ionic activity coefficient * hydrogen ion molality. Table 8.1 gives the activity coefficient for this case.

$$\gamma_{\text{mean}} = 0.809 \quad m_{\text{H}} = 1 \quad a_{\text{H}} = \gamma_{\text{mean}} \cdot m_{\text{H}} \quad a_{\text{H}} = 0.809$$

pH is defined as the negative base 10 log of hydrogen ion activity.

$$\text{pH} = -\log(a_{\text{H}}) \quad \text{pH} = 0.0921$$

8.11

The ionic strength is given by eq. 8.9. For a 1:1 electrolyte like KCl,

$$m = 0.0250 \quad I = \frac{1}{2} \cdot (m + m) \quad I = 0.0250$$

The DHG equation gives the mean ionic activity coefficient

$$\gamma_{\text{mean}}(\alpha) = \exp\left(\frac{\alpha \cdot v \cdot I}{1 + \sqrt{I}}\right)$$

From Table 8.2, $\alpha_0 = 1.133$

$$\alpha_{25} = 1.177$$

$$\alpha_{100} = 1.372$$

$$\gamma_{\text{mean}}(\alpha_0) = 0.857$$

$$\gamma_{\text{mean}}(\alpha_{25}) = 0.852$$

$$\gamma_{\text{mean}}(\alpha_{100}) = 0.829$$

The mean ionic activity is given by $a_{\text{mean}} = (m_{\text{plus}} \cdot m_{\text{minus}} \cdot \gamma_{\text{mean}})^{\frac{1}{v}}$

Since $m_{\text{plus}} = m$ $m_{\text{minus}} = m$ $v = 2$

$$a_{\text{mean}}(\alpha) = (m_{\text{plus}} \cdot m_{\text{minus}} \cdot \gamma_{\text{mean}}(\alpha))^{\frac{1}{v}}$$

$$a_{\text{mean}}(\alpha_0) = 0.0214$$

$$a_{\text{mean}} \alpha_{25} = 0.0213$$

$$a_{\text{mean}} \alpha_{100} = 0.0207$$

8.13

The ionic strength is given by eq. 8.9. For a 3:2 electrolyte like $\text{La}_2(\text{SO}_4)_3$,

$$m = 0.00150 \quad I = \frac{1}{2} [3^2 \cdot 2 \cdot m + 2^2 \cdot (3 \cdot m)] \quad I = 0.0225$$

The DHG equation gives the mean ionic activity coefficient

$$\gamma_{\text{mean}} := \exp \left(\frac{\alpha \cdot 3 \cdot 2 \cdot \sqrt{I}}{1 + \sqrt{I}} \right)$$

$$\text{From Table 8.2, } \alpha = 1.177$$

$$\gamma_{\text{mean}} = 0.398$$

SECTION 8.2

8.15

For the reaction, $\text{DCAH} = \text{DCA} + \text{H}$, the equilibrium constant is

$$K_a = \frac{(\gamma_{\text{mean}} \cdot m_{\text{DCA}}) \cdot (\gamma_{\text{mean}} \cdot m_{\text{H}})}{\gamma_{\text{DCAH}} \cdot m_{\text{DCAH}}} \quad K_a = 3.32 \cdot 10^{-2}$$

(a) Assuming ideal solution, all activity coefficients are one. We can introduce ξ as the degree of dissociation.

$$m_0 = 0.125 \quad m_{\text{DCA}}(\xi) = \xi \cdot m_0 \quad m_{\text{H}}(\xi) = \xi \cdot m_0 \quad m_{\text{DCAH}}(\xi) = (1 - \xi) \cdot m_0$$

$$\xi_{\text{guess}} := 0.5$$

$$\xi_{\text{ideal}} := \text{root} \left(\frac{m_{\text{DCA}}(\xi_{\text{guess}}) \cdot m_{\text{H}}(\xi_{\text{guess}})}{m_{\text{DCAH}}(\xi_{\text{guess}})} - K_a, \xi_{\text{guess}} \right)$$

$$\xi_{\text{ideal}} = 0.40$$

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(b) Using DHG for the mean ionic activity coefficient, we'll still assume ideal solution for the neutral acid. The DHG equation requires the ionic strength, which depends on the degree of dissociation, so iterative solution is required.

$$I(\xi) = \frac{1}{2} \cdot m_{\text{DCA}}(\xi) + m_{\text{H}}(\xi) \quad \gamma_{\text{mean}}(\xi) = \exp \left(\frac{\alpha \cdot \sqrt{I(\xi)}}{1 + \sqrt{I(\xi)}} \right) \quad \alpha = 1.177$$

from Table 8.2

First Approximation, Ideal dissociation

$$\gamma_{\text{mean}}(\xi_{\text{ideal}}) = 0.807$$

$$\xi_{1\text{st}} = \text{root} \left(\frac{m_{\text{DCA}}(\xi_{\text{ideal}}) \cdot m_{\text{H}}(\xi_{\text{ideal}}) \cdot \gamma_{\text{mean}}(\xi_{\text{ideal}})^2}{m_{\text{DCAH}}(\xi_{\text{ideal}})} - K_{\text{a}}, \xi_{\text{ideal}} \right)$$

$$\xi_{1\text{st}} = 0.469$$

Second Approximation

$$\gamma_{\text{mean}}(\xi_{1\text{st}}) = 0.795$$

$$\xi_{2\text{nd}} = \text{root} \left(\frac{m_{\text{DCA}}(\xi_{1\text{st}}) \cdot m_{\text{H}}(\xi_{1\text{st}}) \cdot \gamma_{\text{mean}}(\xi_{1\text{st}})^2}{m_{\text{DCAH}}(\xi_{1\text{st}})} - K_{\text{a}}, \xi_{1\text{st}} \right)$$

$$\xi_{2\text{nd}} = 0.472$$

Third Approximation

$$\gamma_{\text{mean}}(\xi_{2\text{nd}}) = 0.795$$

$$\xi_{3\text{rd}} = \text{root} \left(\frac{m_{\text{DCA}}(\xi_{2\text{nd}}) \cdot m_{\text{H}}(\xi_{2\text{nd}}) \cdot \gamma_{\text{mean}}(\xi_{2\text{nd}})^2}{m_{\text{DCAH}}(\xi_{2\text{nd}})} - K_{\text{a}}, \xi_{2\text{nd}} \right)$$

$$\xi_{3\text{rd}} = 0.472$$

The iteration has converged.

pH is defined as the $-\log_{10}(a_{\text{H}})$

$$\text{pH} = -\log \gamma_{\text{mean}}(\xi_{3\text{rd}}) \cdot m_{\text{H}}(\xi_{3\text{rd}}) \quad \text{pH} = 1.33$$

Recalculate the equilibrium constant to check:

$$K_{\text{a check}} = \frac{m_{\text{DCA}}(\xi_{3\text{rd}}) \cdot m_{\text{H}}(\xi_{3\text{rd}}) \cdot \gamma_{\text{mean}}(\xi_{3\text{rd}})^2}{m_{\text{DCAH}}(\xi_{3\text{rd}})} \quad K_{\text{a check}} = 3.32 \cdot 10^{-2}$$

8.17

For the reaction given, the equilibrium constant can be calculated from data in Tables 6.1 and 8.3.

$$\Delta fG_{\text{CH}_3\text{NH}_2} = 20.77 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta fG_{\text{H}_2\text{Oliq}} = -237.129 \cdot \frac{\text{kJ}}{\text{mole}} \quad \text{kJ} = 1000 \cdot \text{joule} \quad R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\Delta fG_{\text{CH}_3\text{NH}_3} = -39.86 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta fG_{\text{OH}^-} = -157.244 \cdot \frac{\text{kJ}}{\text{mole}} \quad T = 298.15 \cdot \text{K}$$

$$\Delta_{\text{rxn}}G_{\theta} = \Delta fG_{\text{CH}_3\text{NH}_3} + \Delta fG_{\text{OH}^-} - \Delta fG_{\text{CH}_3\text{NH}_2} - \Delta fG_{\text{H}_2\text{Oliq}} \quad \Delta_{\text{rxn}}G_{\theta} = 19.255 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$K_a = \exp\left(\frac{-\Delta_{\text{rxn}}G_{\theta}}{R \cdot T}\right) \quad K_a = 4.233 \cdot 10^{-4}$$

The equilibrium constant is given by

$$K_a = \frac{(\gamma_{\text{mean}}^{\text{m CH}_3\text{NH}_3}) \cdot (\gamma_{\text{mean}}^{\text{m OH}^-})}{(\gamma_{\text{CH}_3\text{NH}_2}^{\text{m CH}_3\text{NH}_2}) \cdot a_{\text{H}_2\text{O}}}$$

Water is referenced to the RL reference state. Since $X_{\text{H}_2\text{O}}$ is almost one, we will assume the activity of water is also one. We will also assume the activity coefficient for the neutral base is one. Defining ξ as the degree of dissociation, the molalities are expressed as

$$m_0 := 0.178 \quad m_{\text{CH}_3\text{NH}_3}(\xi) = \xi \cdot m_0 \quad m_{\text{OH}^-}(\xi) = \xi \cdot m_0 \quad m_{\text{CH}_3\text{NH}_2}(\xi) = (1 - \xi) \cdot m_0$$

We will use the DHG equation to estimate the mean ionic activity coefficient. However, this quantity depends on the ionic strength, which in turn depends on the degree of dissociation. Since we don't know what ξ is yet, we will assume an ideal solution first, and then iterate successively.

$$I(\xi) := \frac{1}{2} \cdot (m_{\text{CH}_3\text{NH}_3}(\xi) + m_{\text{OH}^-}(\xi)) \quad \gamma_{\text{mean}}(\xi) = \exp\left(\frac{-\alpha \cdot \sqrt{I(\xi)}}{1 + \sqrt{I(\xi)}}\right) \quad \alpha = 1.177$$

from Table 8.2

$$\xi_{\text{guess}} := 0.5$$

$$\text{TOL} := 10^{-6}$$

$$\xi_{\text{ideal}} = \text{root}\left(\frac{m_{\text{CH}_3\text{NH}_3}(\xi_{\text{guess}}) \cdot m_{\text{OH}^-}(\xi_{\text{guess}})}{m_{\text{CH}_3\text{NH}_2}(\xi_{\text{guess}})} - K_a, \xi_{\text{guess}}\right) \quad \xi_{\text{ideal}} = 0.048$$

First Approximation

$$\gamma_{\text{mean}}(\xi_{\text{ideal}}) = 0.906$$

$$\xi_{1\text{st}} = \text{root}\left(\frac{m_{\text{CH}_3\text{NH}_3}(\xi_{\text{ideal}}) \cdot m_{\text{OH}^-}(\xi_{\text{ideal}}) \cdot \gamma_{\text{mean}}(\xi_{\text{ideal}})^2}{m_{\text{CH}_3\text{NH}_2}(\xi_{\text{ideal}})} - K_a, \xi_{\text{ideal}}\right) \quad \xi_{1\text{st}} = 0.053$$

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Second Approximation

$$\gamma_{\text{mean}}(\xi_{1\text{st}}) = 0.901$$

$$\xi_{2\text{nd}} = \text{root} \left(\frac{m_{\text{CH}_3\text{NH}_3}(\xi_{1\text{st}}) \cdot m_{\text{OH}}(\xi_{1\text{st}}) \cdot \gamma_{\text{mean}}(\xi_{1\text{st}})^2}{m_{\text{CH}_3\text{NH}_2}(\xi_{1\text{st}})} \cdot K_a, \xi_{1\text{st}} \right) \quad \xi_{2\text{nd}} = 0.053$$

The iteration has converged.

Recalculate the equilibrium constant to check:

$$K_{a \text{ check}} = \frac{m_{\text{CH}_3\text{NH}_3}(\xi_{2\text{nd}}) \cdot m_{\text{OH}}(\xi_{2\text{nd}}) \cdot \gamma_{\text{mean}}(\xi_{2\text{nd}})^2}{m_{\text{CH}_3\text{NH}_2}(\xi_{2\text{nd}})} \quad K_{a \text{ check}} = 4.233 \cdot 10^{-4}$$

The concentration of hydroxide ion and the pH of the solution are given by:

$$m_{\text{OH}}(\xi_{2\text{nd}}) = 0.00937 \quad \text{pH} = 14 + \log(\gamma_{\text{mean}}(\xi_{2\text{nd}}) \cdot m_{\text{OH}}(\xi_{2\text{nd}})) \quad \text{pH} = 11.927$$

Remember that $\text{pH} + \text{pOH} = 14$ is a useful rule of thumb. If you didn't know this, just do the calculations for $\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$ and you'll find that $-\log[a(\text{H}^+)] - \log[a(\text{OH}^-)] = 14.00$.

8.19

For the reaction, $\text{HCOOH} = \text{HCOO} + \text{H}$, the equilibrium constant can be calculated from data in Table 8.3.

$$\Delta fG_{\text{HCOOH}} = 372.3 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta fG_{\text{HCOO}} = 351.0 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta fG_{\text{H}} = 0 \cdot \frac{\text{kJ}}{\text{mole}} \quad \begin{array}{l} \text{kJ} : 1000 \cdot \text{joule} \\ R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \end{array}$$

$$\Delta_{\text{rxn}}G_{\theta} = \Delta fG_{\text{HCOO}} + \Delta fG_{\text{H}} - \Delta fG_{\text{HCOOH}}$$

$$\Delta_{\text{rxn}}G_{\theta} = 21.3 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$T = 298.15 \cdot \text{K}$$

$$K_a = \exp \left(-\frac{\Delta_{\text{rxn}}G_{\theta}}{R \cdot T} \right) \quad K_a = 1.855 \cdot 10^{-4}$$

The equilibrium constant can also be expressed as

$$K_a = \frac{(\gamma_{\text{mean}} \cdot m_{\text{HCOO}}) \cdot (\gamma_{\text{mean}} \cdot m_{\text{H}})}{\gamma_{\text{HCOOH}} \cdot m_{\text{HCOOH}}}$$

We can introduce ξ as the degree of dissociation.

$$m_0 = 0.022 \quad m_{\text{HCOOH}}(\xi) = (1 - \xi) \cdot m_0 \quad m_{\text{HCOO}}(\xi) = \xi \cdot m_0 \quad m_{\text{H}}(\xi) = \xi \cdot m_0$$

Using DHG for the mean ionic activity coefficient, we'll assume ideal solution for the neutral acid. The DHG equation requires the ionic strength, which depends on the degree of dissociation, so iterative solution is required. As a starting point, we'll assume ideal solution to calculate the first ξ .

$$I(\xi) = \frac{1}{2} \cdot (m_{\text{HCOO}}(\xi) + m_{\text{H}}(\xi)) \quad \gamma_{\text{mean}}(\xi) = \exp\left(\frac{-\alpha \cdot \sqrt{I(\xi)}}{1 + \sqrt{I(\xi)}}\right) \quad \alpha = 1.177$$

from Table 8.2

$$\xi_{\text{guess}} := 0.5$$

$$\text{TOL} = 10^{-8}$$

$$\xi_{\text{ideal}} = \text{root}\left(\frac{m_{\text{HCOO}}(\xi_{\text{guess}}) \cdot m_{\text{H}}(\xi_{\text{guess}})}{m_{\text{HCOOH}}(\xi_{\text{guess}})} - K_{\text{a}}, \xi_{\text{guess}}\right)$$

$$\xi_{\text{ideal}} = 0.0877$$

First Approximation (using ideal dissociation to calculate γ_{mean})

$$\gamma_{\text{mean}}(\xi_{\text{ideal}}) = 0.952$$

$$\xi_{1\text{st}} = \text{root}\left(\frac{m_{\text{HCOO}}(\xi_{\text{ideal}}) \cdot m_{\text{H}}(\xi_{\text{ideal}}) \cdot \gamma_{\text{mean}}(\xi_{\text{ideal}})^2}{m_{\text{HCOOH}}(\xi_{\text{ideal}})} - K_{\text{a}}, \xi_{\text{ideal}}\right)$$

$$\xi_{1\text{st}} = 0.0921$$

Second Approximation

$$\gamma_{\text{mean}}(\xi_{1\text{st}}) = 0.951$$

$$\xi_{2\text{nd}} = \text{root}\left(\frac{m_{\text{HCOO}}(\xi_{1\text{st}}) \cdot m_{\text{H}}(\xi_{1\text{st}}) \cdot \gamma_{\text{mean}}(\xi_{1\text{st}})^2}{m_{\text{HCOOH}}(\xi_{1\text{st}})} - K_{\text{a}}, \xi_{1\text{st}}\right)$$

$$\xi_{2\text{nd}} = 0.0921$$

The iteration has converged.

Recalculate the equilibrium constant to check:

$$K_{\text{a check}} = \frac{m_{\text{HCOO}}(\xi_{2\text{nd}}) \cdot m_{\text{H}}(\xi_{2\text{nd}}) \cdot \gamma_{\text{mean}}(\xi_{2\text{nd}})^2}{m_{\text{HCOOH}}(\xi_{2\text{nd}})} \quad K_{\text{a check}} = 1.855 \cdot 10^{-4}$$

For the reaction, $\text{CH}_3\text{COOH} = \text{CH}_3\text{COO} + \text{H}$, the equilibrium constant can be calculated from data in Table 8.3

$$\Delta_f G_{\text{CH}_3\text{COOH}} = -396.46 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta_f G_{\text{CH}_3\text{COO}} = -369.31 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta_f G_{\text{H}} = 0 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta_{\text{rxn}} G_{\theta} = \Delta_f G_{\text{CH}_3\text{COO}} + \Delta_f G_{\text{H}} - \Delta_f G_{\text{CH}_3\text{COOH}}$$

$$\text{kJ} \approx 1000 \cdot \text{joule}$$

$$\Delta_{\text{rxn}} G_{\theta} = 27.15 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$R \approx 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$K_a = \exp\left(\frac{-\Delta_{\text{rxn}} G_{\theta}}{R \cdot T}\right) \quad K_a = 1.752 \cdot 10^{-5}$$

$$T = 298.15 \cdot \text{K}$$

The equilibrium constant can also be expressed as

$$K_a = \frac{(\gamma_{\text{mean}} \cdot m_{\text{CH}_3\text{COO}}) \cdot (\gamma_{\text{mean}} \cdot m_{\text{H}})}{\gamma_{\text{CH}_3\text{COOH}} \cdot m_{\text{CH}_3\text{COOH}}}$$

We can introduce ξ as the degree of dissociation and express the molalities as follows. Since HCl is a very strong acid, we can assume that it is totally dissociated.

$$\begin{aligned} m_0 &= 0.012 & m_{\text{CH}_3\text{COOH}}(\xi) &= (1 - \xi) \cdot m_0 & m_{\text{CH}_3\text{COO}}(\xi) &= \xi \cdot m_0 \\ m_{\text{H}}(\xi) &= \xi \cdot m_0 + 0.05 & m_{\text{Cl}} &= 0.05 \end{aligned}$$

Using DHG for the mean ionic activity coefficient, we'll assume ideal solution for the neutral acetic acid. The DHG equation requires the ionic strength, which depends on the degree of dissociation, so iterative solution is required. As a starting point, we'll assume ideal solution to calculate the first ξ .

$$I(\xi) = \frac{1}{2} (m_{\text{CH}_3\text{COO}}(\xi) + m_{\text{H}}(\xi) + m_{\text{Cl}})$$

$$\gamma_{\text{mean}}(\xi) = \exp\left(\frac{\alpha \cdot \sqrt{I(\xi)}}{1 + \sqrt{I(\xi)}}\right)$$

$$\alpha = 1.177$$

from Table 8.2

$$\xi_{\text{guess}} = 0.5$$

$$\text{TOL} = 10^{-8}$$

$$\xi_{\text{ideal}} = \text{root}\left(\frac{m_{\text{CH}_3\text{COO}}(\xi_{\text{guess}}) \cdot m_{\text{H}}(\xi_{\text{guess}})}{m_{\text{CH}_3\text{COOH}}(\xi_{\text{guess}})} - K_a \cdot \xi_{\text{guess}}\right)$$

$$\xi_{\text{ideal}} = 3.5026 \cdot 10^{-4}$$

First Approximation (using ideal dissociation to calculate γ_{mean})

$$\gamma_{\text{mean}}(\xi_{\text{ideal}}) = 0.806$$

$$\xi_{1\text{st}} = \text{root}\left(\frac{m_{\text{CH}_3\text{COO}}(\xi_{\text{ideal}}) \cdot m_{\text{H}}(\xi_{\text{ideal}}) \cdot \gamma_{\text{mean}}(\xi_{\text{ideal}})^2}{m_{\text{CH}_3\text{COOH}}(\xi_{\text{ideal}})} - K_a \cdot \xi_{\text{ideal}}\right)$$

$$\xi_{1\text{st}} = 0.00054$$

Second Approximation

$$\gamma_{\text{mean}}(\xi_{1\text{st}}) = 0.806$$

$$\xi_{2\text{nd}} = \text{root} \left(\frac{m_{\text{CH}_3\text{COO}}(\xi_{1\text{st}}) \cdot m_{\text{H}}(\xi_{1\text{st}}) \cdot \gamma_{\text{mean}}(\xi_{1\text{st}})^2}{m_{\text{CH}_3\text{COOH}}(\xi_{1\text{st}})} - K_a, \xi_{1\text{st}} \right) \quad \xi_{2\text{nd}} = 0.00054$$

The iteration has converged. Recalculate the equilibrium constant to check:

$$K_{a\text{ check}} = \frac{m_{\text{CH}_3\text{COO}}(\xi_{2\text{nd}}) \cdot m_{\text{H}}(\xi_{2\text{nd}}) \cdot \gamma_{\text{mean}}(\xi_{2\text{nd}})^2}{m_{\text{CH}_3\text{COOH}}(\xi_{2\text{nd}})} \quad K_{a\text{ check}} = 1.752 \cdot 10^{-5}$$

The pH is defined as $-\log(a_{\text{H}})$

$$\text{pH} = -\log(\gamma_{\text{mean}}(\xi_{2\text{nd}}) \cdot m_{\text{H}}(\xi_{2\text{nd}})) \quad \text{pH} = 1.394$$

8.23

For the reaction, $\text{Ag}_2\text{SO}_4(\text{s}) = 2\text{Ag}(\text{ao}) + \text{SO}_4(\text{ao})$, the equilibrium constant can be calculated from data in Tables 6.1 and 8.3.

$$\begin{aligned} \Delta fG_{\text{Ag}_2\text{SO}_4} &= -618.41 \cdot \frac{\text{kJ}}{\text{mole}} & \Delta fG_{\text{Ag}} &= 77.107 \cdot \frac{\text{kJ}}{\text{mole}} & \Delta fG_{\text{SO}_4} &= -744.53 \cdot \frac{\text{kJ}}{\text{mole}} & \text{kJ} &\equiv 1000 \cdot \text{joule} \\ \Delta_{\text{rxn}}G_{\theta} &= 2 \cdot \Delta fG_{\text{Ag}} + \Delta fG_{\text{SO}_4} - \Delta fG_{\text{Ag}_2\text{SO}_4} & R &= 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \\ \Delta_{\text{rxn}}G_{\theta} &= 28.094 \cdot \frac{\text{kJ}}{\text{mole}} & T &= 298.15 \cdot \text{K} \end{aligned}$$

$$K_a = \exp \left(\frac{-\Delta_{\text{rxn}}G_{\theta}}{R \cdot T} \right) \quad K_a = 1.197 \cdot 10^{-5}$$

The equilibrium constant can also be expressed as

$$K_a = \frac{(\gamma_{\text{mean}} \cdot m_{\text{Ag}})^2 \cdot (\gamma_{\text{mean}} \cdot m_{\text{SO}_4})}{a_{\text{Ag}_2\text{SO}_4}}$$

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We can introduce S as the moles of Ag_2SO_4 soluble in 1 kg of water. Since CuSO_4 is very soluble in water, we will assume that it is totally dissociated.

$$m_{\text{Ag}}(S) = 2 \cdot S \quad m_{\text{SO}_4}(S) = S + 0.012 \quad m_{\text{Cu}} = 0.012$$

We will use DHG for the mean ionic activity coefficient. The activity of the solid salt is one. The DHG equation requires the ionic strength, which depends on the solubility, so an iterative solution is required. As a starting point, we'll assume ideal solution to calculate the first estimate for S .

$$I(S) = \frac{1}{2} \cdot (1^2 \cdot m_{\text{Ag}}(S) + 2^2 \cdot m_{\text{SO}_4}(S) + 2^2 \cdot m_{\text{Cu}}) \quad \gamma_{\text{mean}}(S) = \exp\left(\frac{-\alpha \cdot 2 \cdot \sqrt{I(S)}}{1 + \sqrt{I(S)}}\right) \quad \alpha = 1.177 \text{ from Table 8.2}$$

$$S_{\text{guess}} = 0.1 \quad \text{TOL} = 10^{-10}$$

$$S_{\text{ideal}} = \text{root}(m_{\text{Ag}}(S_{\text{guess}})^2 \cdot m_{\text{SO}_4}(S_{\text{guess}}) - K_a, S_{\text{guess}}) \quad S_{\text{ideal}} = 0.0113$$

First Approximation (using ideal solubility to calculate γ_{mean})

$$\gamma_{\text{mean}}(S_{\text{ideal}}) = 0.592$$

$$S_{1\text{st}} = \text{root}(m_{\text{Ag}}(S_{\text{ideal}})^2 \cdot m_{\text{SO}_4}(S_{\text{ideal}}) \cdot \gamma_{\text{mean}}(S_{\text{ideal}})^3 - K_a, S_{\text{ideal}}) \quad S_{1\text{st}} = 0.0228$$

Second Approximation

$$\gamma_{\text{mean}}(S_{1\text{st}}) = 0.550$$

$$S_{2\text{nd}} = \text{root}(m_{\text{Ag}}(S_{1\text{st}})^2 \cdot m_{\text{SO}_4}(S_{1\text{st}}) \cdot \gamma_{\text{mean}}(S_{1\text{st}})^3 - K_a, S_{1\text{st}}) \quad S_{2\text{nd}} = 0.0228$$

The iteration has converged.

Recalculate the equilibrium constant to check:

$$K_{a\text{ check}} = m_{\text{Ag}}(S_{2\text{nd}})^2 \cdot m_{\text{SO}_4}(S_{2\text{nd}}) \cdot \gamma_{\text{mean}}(S_{2\text{nd}})^3 \quad K_{a\text{ check}} = 1.197 \cdot 10^{-5}$$

8.25

Since we now have two independent processes by which the salt may solubilize, we have to calculate the individual solubilities and add them together.

For the reaction, $\text{AgCl}(s) = \text{Ag}^+(aq) + \text{Cl}^-(aq)$, the equilibrium constant at 100 C can be calculated from data in Tables 6.1 and 8.3. We will assume $\Delta_{\text{rxn}}H_0$ and $\Delta_{\text{rxn}}S_0$ are independent of T .

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$$\begin{aligned}\Delta_f H_{\text{AgCl}} &= -127.068 \cdot \frac{\text{kJ}}{\text{mole}} & \Delta_f H_{\text{Ag}} &= 105.579 \cdot \frac{\text{kJ}}{\text{mole}} & \Delta_f H_{\text{Cl}} &= -167.159 \cdot \frac{\text{kJ}}{\text{mole}} & \text{kJ} &= 1000 \cdot \text{joule} \\ \Delta_{\text{rxn}} H_{\theta} &= \Delta_f H_{\text{Ag}} + \Delta_f H_{\text{Cl}} - \Delta_f H_{\text{AgCl}} & \Delta_{\text{rxn}} H_{\theta} &= 65.488 \cdot \frac{\text{kJ}}{\text{mole}} & R &= 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \\ S_{\text{AgCl}} &= 96.2 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} & S_{\text{Ag}} &= 72.68 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} & S_{\text{Cl}} &= 56.5 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \\ \Delta_{\text{rxn}} S_{\theta} &= S_{\text{Ag}} + S_{\text{Cl}} - S_{\text{AgCl}} & \Delta_{\text{rxn}} S_{\theta} &= 32.98 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \\ \Delta_{\text{rxn}} G_{\theta}(T) &= \Delta_{\text{rxn}} H_{\theta} - T \cdot \Delta_{\text{rxn}} S_{\theta} & \Delta_{\text{rxn}} G_{\theta}(373.15 \cdot \text{K}) &= 53.182 \cdot \frac{\text{kJ}}{\text{mole}} \\ K_a(T) &= \exp\left(\frac{-\Delta_{\text{rxn}} G_{\theta}(T)}{R \cdot T}\right) & K_a(373.15 \cdot \text{K}) &= 3.595 \cdot 10^{-8}\end{aligned}$$

The equilibrium constant can also be expressed as

$$K_a = \frac{(\gamma_{\text{mean}} \cdot m_{\text{Ag}}) \cdot (\gamma_{\text{mean}} \cdot m_{\text{Cl}})}{a_{\text{AgCl}}}$$

We can introduce S_1 as the moles of AgCl soluble in 1 kg of water by ionization. Since NaNO_3 is very soluble in water, we will assume it is totally dissociated.

$$m_{\text{Ag}}(S_1) = S_1 \quad m_{\text{Cl}}(S_1) = S_1 \quad m_{\text{Na}} = 0.034 \quad m_{\text{NO}_3} = 0.034$$

We will use DHG for the mean ionic activity coefficient. The activity of the solid salt is one. The DHG equation requires the ionic strength, which depends on the solubility, so an iterative solution is required. As a starting point, we'll assume ideal solution to calculate the first estimate for S_1 .

$$I(S_1) = \frac{1}{2} \cdot (m_{\text{Ag}}(S_1) + m_{\text{Cl}}(S_1) + m_{\text{Na}} + m_{\text{NO}_3})$$

$$\gamma_{\text{mean}}(S_1) = \exp\left(\frac{-\alpha \cdot \sqrt{I(S_1)}}{1 + \sqrt{I(S_1)}}\right) \quad \alpha = 1.372 \text{ from Table 8.2 for } 100^\circ\text{C}$$

$$S_{\text{guess}} = 0.1$$

$$\text{TOL} = 10^{-10}$$

$$S_{\text{id}} = \text{root}(m_{\text{Ag}}(S_{\text{guess}}) \cdot m_{\text{Cl}}(S_{\text{guess}}) - K_a(373.15 \cdot \text{K}), S_{\text{guess}})$$

$$S_{\text{id}} = 1.896 \cdot 10^{-4}$$

Successive Approximations

$$S_{1\text{st}} = \text{root}(m_{\text{Ag}}(S_{\text{id}}) \cdot m_{\text{Cl}}(S_{\text{id}}) \cdot \gamma_{\text{mean}}(S_{\text{id}})^2 - K_a(373.15 \cdot \text{K}), S_{\text{id}})$$

$$S_{1\text{st}} = 2.349 \cdot 10^{-4}$$

$$S_{2\text{nd}} = \text{root}(m_{\text{Ag}}(S_{1\text{st}}) \cdot m_{\text{Cl}}(S_{1\text{st}}) \cdot \gamma_{\text{mean}}(S_{1\text{st}})^2 - K_a(373.15 \cdot \text{K}), S_{1\text{st}})$$

$$S_{2\text{nd}} = 2.349 \cdot 10^{-4}$$

The iteration has converged. Recalculate the equilibrium constant to check:

$$K_{a \text{ check}} = m_{\text{Ag}}(S_{2\text{nd}}) \cdot m_{\text{Cl}}(S_{2\text{nd}}) \cdot \gamma_{\text{mean}}(S_{2\text{nd}})^2 \quad K_{a \text{ check}} = 3.595 \cdot 10^{-8}$$

Therefore, the solubility of AgCl through the dissociation is $S_1 = S_{2\text{nd}} \quad S_1 = 2.349 \cdot 10^{-4}$

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For the reaction $\text{AgCl (s)} = \text{AgCl (ao)}$, we can find the equilibrium constant using data in Tables 6.1 and 8.3. We will again assume that $\Delta_{\text{rxn}}H_{\theta}$ and $\Delta_{\text{rxn}}S_{\theta}$ are independent of temperature.

$$\Delta_{\text{f}}H_{\text{AgCl(s)}} = -127.068 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta_{\text{f}}H_{\text{AgCl(ao)}} = -72.8 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta_{\text{rxn}}H_{\theta} = \Delta_{\text{f}}H_{\text{AgCl(ao)}} - \Delta_{\text{f}}H_{\text{AgCl(s)}}$$

$$S_{\text{AgCl(s)}} = 96.2 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad S_{\text{AgCl(ao)}} = 154.0 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad \Delta_{\text{rxn}}S_{\theta} = S_{\text{AgCl(ao)}} - S_{\text{AgCl(s)}}$$

$$\Delta_{\text{rxn}}G_{\theta}(T) = \Delta_{\text{rxn}}H_{\theta} - T \cdot \Delta_{\text{rxn}}S_{\theta}$$

$$K_{\text{a}}(T) = \exp\left(\frac{-\Delta_{\text{rxn}}G_{\theta}(T)}{R \cdot T}\right) \quad K_{\text{a}}(373.15 \cdot \text{K}) = 2.647 \cdot 10^{-5}$$

The equilibrium constant can also be expressed as

$$K_{\text{a}} = \frac{\gamma_{\text{AgCl(ao)}} \cdot m_{\text{AgCl(ao)}}}{a_{\text{AgCl(s)}}}$$

We will assume that the activity of the solid salt and the activity coefficient of the neutral solute are equal to one. (This ideal assumption is not valid for ions.) Thus, we see that the solubility of AgCl through the dissolution of the neutral salt is just K_{a} .

$$S_2 = K_{\text{a}}(373.15 \cdot \text{K}) \quad S_2 = 2.647 \cdot 10^{-5}$$

$$S_{\text{total}} = S_1 + S_2 \quad S_{\text{total}} = 2.614 \cdot 10^{-4} \quad \text{The units are moles of salt per kg water.}$$

8.27

Since there are now three processes by which TiCl can solubilize, we have to calculate the individual solubilities of each process.

Process 1: $\text{TiCl (s)} = \text{TiCl (ao)}$

$$K_1 = 7.167 \cdot 10^{-4}$$

The equilibrium constant can also be expressed as

$$K_1 = \frac{m_{\text{TiCl(ao)}} \cdot \gamma_{\text{TiCl(ao)}}}{a_{\text{TiCl(s)}}}$$

We may assume that the activity of the solid salt is again one. Since there are no ions, it is reasonable to assume an ideal solution so K_1 is the solubility of TiCl through process 1.

$$S_1 = K_1 \quad S_1 = 7.167 \cdot 10^{-4}$$

Process 2: $\text{TiCl (s)} = \text{Ti}^+ (\text{ao}) + \text{Cl}^- (\text{ao})$

$$K_2 = 1.861 \cdot 10^{-4}$$

The equilibrium constant may also be expressed as

$$K_2 = (m_{\text{Ti}} \gamma_{\text{mean}}) \cdot (m_{\text{Cl}} \gamma_{\text{mean}})$$

In writing this expression, we have assumed the activity of the solid salt is one. We will use the DHG equation to calculate the mean ionic activity coefficient. However, since this quantity is dependent on ionic strength and we don't know the ionic strength until we calculate the solubility, an iterative solution is needed.

We can introduce S_2 as the moles of TiCl soluble in 1 kg of water through process 2. Since KCl is very soluble in water, we will assume it is totally ionized.

$$\begin{aligned} m_{\text{Ti}}(S_2) &:= S_2 & m_{\text{Cl}}(S_2) &:= S_2 + 0.05 & m_{\text{K}} &= 0.05 \\ I(S_2) &:= \frac{1}{2} (m_{\text{Ti}}(S_2) + m_{\text{Cl}}(S_2) + m_{\text{K}}) & \gamma_{\text{mean}}(S_2) &= \exp \left(\frac{-\alpha \sqrt{I(S_2)}}{1 + \sqrt{I(S_2)}} \right) & \alpha &= 1.177 \text{ from Table 8.2} \\ & & & & \text{TOL} &= 10^{-8} \end{aligned}$$

Successive Approximations

$$S_{\text{guess}} = 0.001$$

$$S_{1\text{st}} = \text{root} \left(m_{\text{Ti}}(S_{\text{guess}}) \cdot m_{\text{Cl}}(S_{\text{guess}}) \cdot \gamma_{\text{mean}}(S_{\text{guess}})^2 - K_2, S_{\text{guess}} \right) \quad S_{1\text{st}} = 0.0053$$

$$S_{2\text{nd}} = \text{root} \left(m_{\text{Ti}}(S_{1\text{st}}) \cdot m_{\text{Cl}}(S_{1\text{st}}) \cdot \gamma_{\text{mean}}(S_{1\text{st}})^2 - K_2, S_{1\text{st}} \right) \quad S_{2\text{nd}} = 0.0053$$

$$\text{Therefore: } S_2 = S_{2\text{nd}} \quad S_2 = 0.00527$$

The iteration has converged. Recalculate the equilibrium constant to check:

$$K_{2\text{ check}} = m_{\text{Ti}}(S_{2\text{nd}}) \cdot m_{\text{Cl}}(S_{2\text{nd}}) \cdot \gamma_{\text{mean}}(S_{2\text{nd}})^2 \quad K_{2\text{ check}} = 1.861 \cdot 10^{-4}$$

Process 3: $\text{TiCl (s)} + \text{Cl}^- (\text{ao}) = \text{TiCl}_2^- (\text{ao})$

$$K_3 = 2.724 \cdot 10^{-4}$$

The equilibrium constant may be expressed as

$$K_3 = \frac{m_{\text{TiCl}_2} \gamma_{\text{TiCl}_2}}{m_{\text{Cl}} \gamma_{\text{Cl}}}$$

$$S_3 = m_{\text{TICl}_2} \quad S_3 = 1.362 \cdot 10^{-5}$$

Although we assumed the molality of the chloride ion was due only to the KCl, there is actually some interaction between processes 2 and 3. Process 2 produces some chloride ions, while process 3 uses them. Rigorously, each process should take into account the other. However, compared to the chloride ions produced by KCl, neither process changes the chloride molality significantly. Therefore, we can treat the processes as independent.

$$S_{\text{total}} = S_1 + S_2 + S_3 \quad S_{\text{total}} = 0.0060 \quad \text{Units are moles of TICl per kg water.}$$

Although it is not reasonable to assume that ionic activity coefficients equal one, we have to assume that the activity coefficients here are equal, for lack of a better way to estimate them.

$$m_{\text{Cl}} = 0.05 \quad m_{\text{TICl}_2} = K_3 \cdot m_{\text{Cl}}$$

8.29

The solubility of iodine will be calculated separately for each process, and then added together.

Process 1: For the reaction, $\text{I}_2(\text{s}) = \text{I}_2(\text{ao})$, the equilibrium constant can be calculated from data in Tables 6.1 and 8.3.

$$\begin{aligned} \Delta fG_{\text{I}_2\text{solid}} &= 0 \cdot \frac{\text{kJ}}{\text{mole}} & \Delta fG_{\text{I}_2\text{ao}} &= 16.40 \cdot \frac{\text{kJ}}{\text{mole}} & \text{kJ} &= 1000 \cdot \text{joule} \\ \Delta_{\text{rxn}}G_{\theta} &= \Delta fG_{\text{I}_2\text{ao}} - \Delta fG_{\text{I}_2\text{solid}} & \Delta_{\text{rxn}}G_{\theta} &= 16.4 \cdot \frac{\text{kJ}}{\text{mole}} & R &= 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \\ K_a &= \exp\left(\frac{-\Delta_{\text{rxn}}G_{\theta}}{R \cdot T}\right) & K_a &= 1.339 \cdot 10^{-3} & T &= 298.15 \cdot \text{K} \end{aligned}$$

The equilibrium constant can also be expressed as

$$K_a = \frac{\gamma_{\text{I}_2\text{ao}} \cdot m_{\text{I}_2\text{ao}}}{a_{\text{I}_2\text{solid}}} \quad \text{The activity of the solid and the activity coefficient of the neutral solute can be assumed to be one. (This assumption is not valid for ionic solutes.)}$$

Thus, the solubility of iodine through process 1 is just K_a . (Actually, the standard molality of 1 mol/kg should rigorously be included to make the units correct. Units will be added at the end.)

$$m_{\text{I}_2\text{ao}} = K_a \quad m_{\text{I}_2\text{ao}} = 1.339 \cdot 10^{-3}$$

Process 2: For the reaction, $I_2(s) + I^-(ao) = I_3^-(ao)$, the equilibrium constant is calculated as

$$\Delta fG_{I2solid} := 0 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta fG_{Iao} = -51.57 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta fG_{I3ao} := -51.4 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta rxnG_{\theta} := \Delta fG_{I3ao} - \Delta fG_{I2solid} - \Delta fG_{Iao} \quad \Delta rxnG_{\theta} = 170 \cdot \frac{\text{joule}}{\text{mole}}$$

$$K_a := \exp\left(\frac{-\Delta rxnG_{\theta}}{R \cdot T}\right) \quad K_a = 0.934$$

The equilibrium constant can be expressed as

$$K_a = \frac{m_{I3ao} \cdot \gamma_{I3ao}}{a_{I2solid} \cdot m_{Iao} \cdot \gamma_{Iao}}$$

The activity of the solid is one. It will also be assumed that the ionic activity coefficients of I^- and I_3^- are approximately equal. In calculating the molalities, NaI is presumably totally dissociated, since it is very soluble in water.

$$m_{Iao}(m_{I3ao}) = 0.015 - m_{I3ao} \quad \text{since the formation of } I_3^- \text{ consumes } I^-$$

$$m_{\text{guess}} = 0.1$$

$$m_{I3ao} = \text{root}(m_{Iao}(m_{\text{guess}}) \cdot K_a - m_{\text{guess}}, m_{\text{guess}}) \quad \text{This solves the equilibrium expression for the molality of } I_3^-.$$

$$m_{I3ao} = 0.00724$$

The total solubility is the sum of the solubilities for the two processes.

$$S = m_{I2ao} + m_{I3ao} \quad S = 0.00858 \quad \text{Units are mole of iodine per kg of water.}$$

8.31

(a) The equilibrium constant can be calculated using data in Table 8.3 and eq. 6.15.

$$\Delta fG_{Fe2} = -78.90 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta fG_{Cu2} = 65.49 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta fG_{Fe3} = -4.7 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta fG_{Cu1} = 49.98 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta rxnG_{\theta} := \Delta fG_{Fe3} + \Delta fG_{Cu1} - \Delta fG_{Fe2} - \Delta fG_{Cu2} \quad \Delta rxnG_{\theta} = 58.69 \cdot \frac{\text{kJ}}{\text{mole}} \quad T = 298.15 \cdot K$$

$$K_a = \exp\left(\frac{-\Delta rxnG_{\theta}}{R \cdot T}\right) \quad K_a = 5.224 \cdot 10^{-11}$$

$$kJ \approx 1000 \cdot \text{joule}$$

$$R \approx 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot K}$$

(b) The equilibrium constant can be expressed as follows for an ideal solution.

$$K_a = \frac{m_{\text{Fe}^{3+}} \cdot m_{\text{Cu}^{+}}}{m_{\text{Fe}^{2+}} \cdot m_{\text{Cu}^{2+}}}$$

The molalities can be expressed in terms of the extent of reaction, ξ .

$$m_{\text{Fe}^{3+}}(\xi) = \xi \quad m_{\text{Cu}^{+}}(\xi) = \xi \quad m_{\text{Fe}^{2+}}(\xi) = 0.001 - \xi \quad m_{\text{Cu}^{2+}}(\xi) = 0.001 - \xi$$

$$\xi_{\text{guess}} = 0.0005$$

$$\text{TOL} = 10^{-15}$$

$$\xi = \text{root} \left(\frac{m_{\text{Fe}^{3+}}(\xi_{\text{guess}}) \cdot m_{\text{Cu}^{+}}(\xi_{\text{guess}})}{m_{\text{Fe}^{2+}}(\xi_{\text{guess}}) \cdot m_{\text{Cu}^{2+}}(\xi_{\text{guess}})} - K_a, \xi_{\text{guess}} \right) \quad \xi = 7.228 \cdot 10^{-9}$$

$$m_{\text{Cu}^{+}}(\xi) = 7.2 \cdot 10^{-9} \quad \text{Units are mole Cu}^{+} \text{ per kg water.}$$

Recalculate the equilibrium constant to check:

$$K_{a \text{ check}} = \frac{m_{\text{Fe}^{3+}}(\xi) \cdot m_{\text{Cu}^{+}}(\xi)}{m_{\text{Fe}^{2+}}(\xi) \cdot m_{\text{Cu}^{2+}}(\xi)} \quad K_{a \text{ check}} = 5.224 \cdot 10^{-11}$$

8.33

The molality scale Henry's Law constant was defined in Chapter 7 as

$$k_m = \lim_{m \rightarrow 0} \frac{P_2}{m}$$

If you consider the equilibrium for the reaction, $A(ao) = A(g)$, k_m is like an equilibrium constant under ideal conditions (activity/fugacity coefficients = 1) and without standard states (which are constants anyway). This is the reason why this proportionality is constant (at constant T) in the limit of dilute solution where conditions approach ideal.

The same reasoning can be used to derive the HL constant for HCl. The reaction we have to consider is then $H^{+}(ao) + Cl^{-}(ao) = HCl(g)$. The equilibrium constant for this reaction is

$$K_a = \frac{a_{\text{HCl},g}}{a_{H^{+},ao} a_{Cl^{-},ao}}$$

In the limit of ideal solution, the equilibrium constant (without standard states) is just

$$k_m = \lim_{m \rightarrow 0} \left(\frac{P}{m^2} \right)$$

since for HCl, $m = m_{H^{+},ao} = m_{Cl^{-},ao}$.

SECTION 8.3

8.35

The measured resistance can be used to calculate the conductivity (κ) using eq. 8.21. Then, if we can assume $\Lambda_0 = \Lambda$, we can calculate this value using eq. 8.27 and Table 8.6. Eq. 8.25 will then give the equivalent concentration, which is easily converted to ordinary concentration.

$$A = 7.2 \cdot \text{cm}^2 \quad l = 1.2 \cdot \text{cm} \quad R = 13 \cdot \Omega \quad \text{equiv } l$$

$$\kappa = \frac{l}{A \cdot R} \quad \kappa = 0.013 \cdot \frac{\text{siemens}}{\text{cm}}$$

$$\text{From Table 8.6} \quad \lambda_0 \text{ Ca} = 59.50 \cdot \frac{\text{cm}^2 \cdot \text{siemens}}{\text{equiv}} \quad \lambda_0 \text{ NO}_3 = 71.44 \cdot \frac{\text{cm}^2 \cdot \text{siemens}}{\text{equiv}}$$

$$\Lambda = \lambda_0 \text{ Ca} + \lambda_0 \text{ NO}_3$$

$$c_{\text{equiv}} = \frac{\kappa}{\Lambda} \quad c_{\text{equiv}} = 0.098 \cdot \frac{\text{mole}}{\text{liter}}$$

Since $\nu_i z_i = 2$ for $\text{Ca}(\text{NO}_3)_2$,

$$c = \frac{c_{\text{equiv}}}{2} \quad c = 0.049 \cdot \frac{\text{mole}}{\text{liter}}$$

8.37

We can use data in Table 8.6 and eqs 8.27 and 8.29 to calculate the equivalent conductivities and cation transference numbers, respectively.

(a) rubidium acetate

$$\lambda_0 \text{ Rb} = 77.8 \cdot \frac{\text{cm}^2 \cdot \text{siemens}}{\text{equiv}} \quad \lambda_0 \text{ acetate} = 40.9 \cdot \frac{\text{cm}^2 \cdot \text{siemens}}{\text{equiv}} \quad \text{equiv } l$$

$$\Lambda_0 = \lambda_0 \text{ Rb} + \lambda_0 \text{ acetate} \quad \Lambda_0 = 118.7 \cdot \frac{\text{cm}^2 \cdot \text{siemens}}{\text{equiv}}$$

$$t_{\text{Rb}} = \frac{\lambda_0 \text{ Rb}}{\Lambda_0} \quad t_{\text{Rb}} = 0.66$$

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(b) ammonium sulphate

$$\lambda_o \text{NH}_4 = 73.4 \cdot \frac{\text{cm}^2 \cdot \text{siemens}}{\text{equiv}} \quad \lambda_o \text{SO}_4 = 80 \cdot \frac{\text{cm}^2 \cdot \text{siemens}}{\text{equiv}}$$

$$\Lambda_o = \lambda_o \text{NH}_4 + \lambda_o \text{SO}_4 \quad \Lambda_o = 153.4 \cdot \frac{\text{cm}^2 \cdot \text{siemens}}{\text{equiv}}$$

$$t_{\text{NH}_4} = \frac{\lambda_o \text{NH}_4}{\Lambda_o} \quad t_{\text{NH}_4} = 0.48$$

(c) $\text{K}_3\text{Fe}(\text{CN})_6$

$$\lambda_o \text{K} = 73.50 \cdot \frac{\text{cm}^2 \cdot \text{siemens}}{\text{equiv}} \quad \lambda_o \text{FeCN}_6 = 99.1 \cdot \frac{\text{cm}^2 \cdot \text{siemens}}{\text{equiv}}$$

$$\Lambda_o = \lambda_o \text{K} + \lambda_o \text{FeCN}_6 \quad \Lambda_o = 172.6 \cdot \frac{\text{cm}^2 \cdot \text{siemens}}{\text{equiv}}$$

$$t_{\text{K}} = \frac{\lambda_o \text{K}}{\Lambda_o} \quad t_{\text{K}} = 0.43$$

8.39

The inverse of the resistivity is the conductivity (κ) of the solution. Eq. 8.25 can be used to then calculate the equivalent conductivity. The ionic conductivity of the hydrogen ion can then be calculated using the cation transference number and eq. 8.29.

$$\rho = 25.554 \cdot \Omega \cdot \text{cm} \quad \kappa = \frac{1}{\rho} \quad c_{\text{equiv}} = 0.1 \cdot \frac{\text{mole}}{\text{liter}} \quad t_{\text{H}} = 0.8314 \quad \text{equiv l}$$

$$\Lambda = \frac{\kappa}{c_{\text{equiv}}} \quad \Lambda = 391.328 \cdot \frac{\text{cm}^2 \cdot \text{siemens}}{\text{equiv}}$$

$$\lambda_{\text{H}} = t_{\text{H}} \cdot \Lambda \quad \lambda_{\text{H}} = 325.4 \cdot \frac{\text{cm}^2 \cdot \text{siemens}}{\text{equiv}}$$

The value given in Table 8.6 is $349.8 \text{ (cm}^2 \cdot \text{S/equiv)}$.

8.41

The data should be fit to a function of the form

$$\Lambda = \Lambda_0 + a_1 \cdot c^{0.5} + a_2 \cdot c + a_3 \cdot c^{1.5} + \dots$$

For this problem, we used a second order regression in \sqrt{c} to obtain the following fit

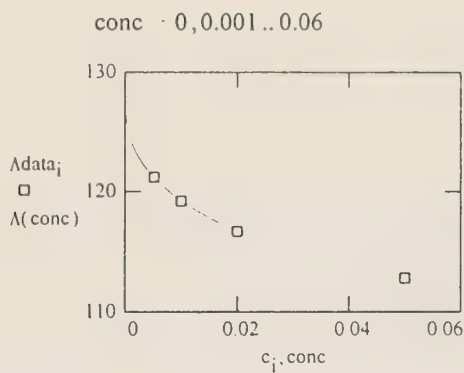
$$\Lambda(c) = 126.895 + 87.5336 \cdot c^{0.5} + 109.352 \cdot c$$

Thus, we see that $\Lambda_0 = 126.895$ (units are same as those in the problem). The standard deviation for this parameter is $\sigma = 0.025$.

It may be useful to see a graph of the data and the curve fit.

i = 0..3

c_i	Λ_{data_i}
0.005	121.25
0.01	119.24
0.02	116.7
0.05	112.79



8.43

For the reaction, $\text{PAH}(\text{ao}) = \text{PA}^-(\text{ao}) + \text{H}^+(\text{ao})$, the thermodynamic dissociation constant can be evaluated as

$$K_a = \frac{C_{\text{PA}} \cdot C_{\text{H}^+} \gamma_{\text{mean}}^2}{C_{\text{PAH}} \gamma_{\text{PAH}}}$$

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DHG will be used to evaluate the mean ionic activity coefficient. The neutral acid activity coefficient will be assumed to be one.

$$i = 0.3$$

c_i	α_i
0.001563	0.3131
0.003125	0.2408
0.00625	0.182
0.0125	0.1379

$$\alpha_{\text{DH}} = 4.58 \cdot I_i \cdot \alpha_i \cdot c_i \quad \gamma_{\text{mean}_i} = \exp \left(\frac{\alpha_{\text{DH}} \cdot \sqrt{I_i}}{1 + \sqrt{I_i}} \right)$$

The concentrations are expressed in terms of the degree dissociation, α .

$$C_{\text{PAH}_i} = c_i (1 - \alpha_i) \quad C_{\text{PA}_i} = c_i \cdot \alpha_i \quad C_{\text{H}_i} = c_i \cdot \alpha_i$$

$$K_{a_i} = \frac{C_{\text{PA}_i} \cdot C_{\text{H}_i} \cdot (\gamma_{\text{mean}_i})^2}{C_{\text{PAH}_i}}$$

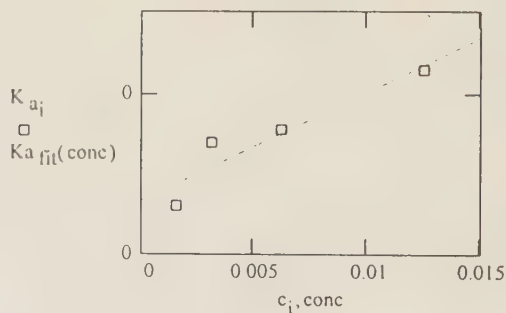
$$K_{a_i}$$

$1.83 \cdot 10^{-4}$
$1.869 \cdot 10^{-4}$
$1.877 \cdot 10^{-4}$
$1.914 \cdot 10^{-4}$

$$m = \text{slope}(c, K_{a_i}) \quad b = \text{intercept}(c, K_{a_i})$$

$$K_{a_{\text{fit}}}(\text{conc}) = b + m \cdot \text{conc}$$

$$\text{conc} = 0, 0.001 \dots 0.015$$



The extrapolated value for K_a at infinite dilution is just the intercept of the linear fit.

$$K_a = b \quad K_a = 1.83 \cdot 10^{-4}$$

SECTION 8.4

8.45

Oxidation reaction (left): $\text{H}_2(\text{g}) = 2\text{H}^+(\text{ao}) + 2\text{e}^-$ Reduction reaction (right): $2\text{AgCl}(\text{s}) + 2\text{e}^- = 2\text{Ag}(\text{s}) + 2\text{Cl}^-(\text{ao})$ Cell reaction: $2\text{AgCl}(\text{s}) + \text{H}_2(\text{g}) = 2\text{H}^+(\text{ao}) + 2\text{Cl}^-(\text{ao}) + 2\text{Ag}(\text{s})$

Table 8.7 gives the standard EMF values for the half cell reactions (given as reduction potentials).

$$\varepsilon_{\text{left}} = 0\text{-volt} \quad \varepsilon_{\text{right}} = 0.2225\text{-volt} \quad \varepsilon_{\theta} = \varepsilon_{\text{right}} - \varepsilon_{\text{left}} \quad \varepsilon_{\theta} = 0.2225\text{-volt}$$

Since we are given the EMF of the cell, and we have just determined the standard EMF, we can use eq. 8.40 to calculate the activity quotient, Q .

$$\varepsilon = \varepsilon_{\theta} - \frac{R \cdot T}{n \cdot F} \cdot \ln(Q) \quad \varepsilon = 0.20534\text{-volt} \quad T = 298.15\text{-K} \quad n = 2\text{-mole}$$

$$Q = \exp \left[\frac{(\varepsilon \cdot n \cdot F - \varepsilon_{\theta} \cdot n \cdot F)}{(R \cdot T)} \right] \quad Q = 3.803$$

$$R = 8.31451 \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad F = 96485 \frac{\text{coul}}{\text{mole}}$$

The activity quotient is also the ratio of component activities raised to their stoichiometric coefficients. We will assume that solid activities = 1. Thus, Q can be expressed as

$$Q = \frac{m_{\text{H}}^2 \cdot m_{\text{Cl}}^2 \cdot \gamma_{\text{mean}}^4}{\left(\frac{P_{\text{H}_2}}{P_{\theta}} \right)} \quad P_{\theta} = 1\text{-atm} \quad (\text{Table 8.7 uses this as the standard state})$$

$$P_{\text{H}_2} = 1\text{-atm} \quad m_{\text{H}} = 1.5346 \quad m_{\text{Cl}} = 1.5346$$

Now we can solve for the mean ionic activity coefficient.

$$\gamma_{\text{guess}} = 1$$

$$\gamma_{\text{mean}} = \text{root} \left[\frac{m_{\text{H}}^2 \cdot m_{\text{Cl}}^2 \cdot \gamma_{\text{guess}}^4}{\left(\frac{P_{\text{H}_2}}{P_{\theta}} \right)} - Q, \gamma_{\text{guess}} \right] \quad \gamma_{\text{mean}} = 0.910$$

The pH is the $-\log_{10}(a_{\text{H}^+})$

$$\text{pH} = -\log(\gamma_{\text{mean}} \cdot m_{\text{H}}) \quad \text{pH} = -0.145$$

8.47

Oxidation reaction (left): $\text{Cu (s)} = \text{Cu}^{2+} \text{ (ao)} + 2 \text{ e}^-$

Reduction reaction (right): $\text{PbSO}_4 \text{ (s)} + 2 \text{ e}^- = \text{Pb (s)} + \text{SO}_4^{2-} \text{ (ao)}$

Cell reaction: $\text{Cu (s)} + \text{PbSO}_4 \text{ (s)} = \text{Cu}^{2+} \text{ (ao)} + \text{SO}_4^{2-} \text{ (ao)} + \text{Pb (s)}$

Table 8.7 gives the standard EMF values for the half cell reactions (given as reduction potentials).

$$\varepsilon_{\text{left}} = 0.337 \cdot \text{volt} \quad \varepsilon_{\text{right}} = 0.3546 \cdot \text{volt} \quad \varepsilon_{\theta} = \varepsilon_{\text{right}} - \varepsilon_{\text{left}} \quad \varepsilon_{\theta} = -0.6916 \cdot \text{volt}$$

We still need to calculate the activity quotient, Q . The activity quotient is the ratio of component activities raised to their stoichiometric coefficients. We will assume that solid activities = 1. Thus, Q can be expressed as

$$Q = m_{\text{Cu}} \cdot m_{\text{SO}_4} \cdot \gamma_{\text{mean}}^2 \quad m_{\text{Cu}} = 0.2 \quad m_{\text{SO}_4} = 0.2 \quad \gamma_{\text{mean}} = 0.11 \quad \text{From Table 8.1}$$

$$Q = 4.84 \cdot 10^{-4}$$

Eq. 8.40 can then be used to calculate the EMF.

$$\varepsilon = \varepsilon_{\theta} + \frac{R \cdot T}{n \cdot F} \cdot \ln(Q)$$

$$\varepsilon = 0.594 \cdot \text{volt} \quad T = 298.15 \cdot \text{K} \quad n = 2 \cdot \text{mole}$$

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad F = 96485 \cdot \frac{\text{coul}}{\text{mole}}$$

8.49

Oxidation reaction (left): $\text{Pb (s)} + 2 \text{ Br}^- \text{ (ao)} = \text{PbBr}_2 \text{ (s)} + 2 \text{ e}^-$

Reduction reaction (right): $\text{Cu}^{2+} \text{ (ao)} + 2 \text{ e}^- = \text{Cu (s)}$

Cell reaction: $\text{Pb (s)} + 2 \text{ Br}^- \text{ (ao)} + \text{Cu}^{2+} \text{ (ao)} = \text{PbBr}_2 \text{ (s)} + \text{Cu (s)}$

We are given the EMF of the cell. We can also calculate the activity quotient, Q , using DHG to estimate the mean ionic activity coefficient. If we assume the solid activities are one, Q may be expressed as follows

$$m_{\text{Br}} = 0.02 \quad m_{\text{Cu}} = 0.01 \quad I = \frac{1}{2} \cdot (2^2 \cdot m_{\text{Cu}} + 1^2 \cdot m_{\text{Br}}) \quad \alpha = 1.177 \quad \gamma_{\text{mean}} = \exp\left(\frac{-\alpha \cdot 2 \cdot \sqrt{I}}{1 + \sqrt{I}}\right)$$

$$Q = \frac{1}{m_{\text{Br}}^2 \cdot m_{\text{Cu}} \cdot \gamma_{\text{mean}}^3} \quad Q = 7.091 \cdot 10^5$$

The standard EMF may now be estimated using eq. 8.40.

$$\varepsilon_{\theta} = \varepsilon + \frac{R \cdot T}{n \cdot F} \cdot \ln(Q)$$

$$\varepsilon_{\theta} = 0.615 \cdot \text{volt} \quad \varepsilon = 0.442 \cdot \text{volt} \quad T = 298.15 \cdot \text{K} \quad n = 2 \cdot \text{mole}$$

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad F = 96485 \cdot \frac{\text{coul}}{\text{mole}}$$

Oxidation reaction (left): $\text{Cu (s)} = \text{Cu}^{2+} (\text{ao}) + 2 \text{e}^-$

Reduction reaction (right): $\text{PbSO}_4 (\text{s}) + 2 \text{e}^- = \text{Pb (s)} + \text{SO}_4^{2-} (\text{ao})$

Cell reaction: $\text{Cu (s)} + \text{PbSO}_4 (\text{s}) = \text{Cu}^{2+} (\text{ao}) + \text{SO}_4^{2-} (\text{ao}) + \text{Pb (s)}$

Table 8.7 gives the standard EMF values for the half cell reactions (given as reduction potentials).

$$\varepsilon_{\text{left}} = 0.337 \cdot \text{volt} \quad \varepsilon_{\text{right}} = -0.3546 \cdot \text{volt} \quad \varepsilon_{\theta} = \varepsilon_{\text{right}} - \varepsilon_{\text{left}} \quad \varepsilon_{\theta} = -0.6916 \cdot \text{volt}$$

We still need to calculate the activity quotient, Q . The activity quotient is the ratio of component activities raised to their stoichiometric coefficients. We will assume that solid activities = 1. Thus, Q can be expressed as

$$m_{\text{Cu}} = 0.03 \quad m_{\text{SO}_4} = 0.03 \quad I = \frac{1}{2} \cdot (2^2 \cdot m_{\text{Cu}} + 2^2 \cdot m_{\text{SO}_4}) \quad \gamma_{\text{mean}} = \frac{1.177 \cdot 4 \cdot \gamma_I}{1 + \gamma_I} \quad \text{DHG equation}$$

$$Q = m_{\text{Cu}} \cdot m_{\text{SO}_4} \cdot \gamma_{\text{mean}}^2$$

$$Q = 1.321 \cdot 10^{-3}$$

Eq. 8.40 can then be used to calculate the EMF.

$$\varepsilon = \varepsilon_{\theta} - \frac{R \cdot T}{n \cdot F} \cdot \ln(Q)$$

$$\varepsilon = -0.606 \cdot \text{volt}$$

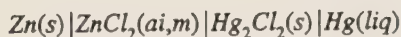
$$T = 298.15 \cdot \text{K}$$

$$n = 2 \cdot \text{mole}$$

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

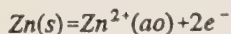
$$F = 96485 \cdot \frac{\text{coul}}{\text{mole}}$$

The following cell can be used



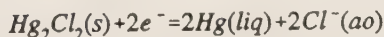
The electrode reactions are

Oxidation:



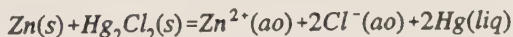
$$\mathcal{E}_{\text{left}}^{\theta} = -0.7628 \text{ volt}$$

Reduction:



$$\mathcal{E}_{\text{right}}^{\theta} = 0.2680 \text{ volt}$$

Cell Reaction:



$$\mathcal{E}^{\theta} = 1.0308 \text{ volt}$$

For this reaction, Q simplifies to

$$Q = (m)(2m)^2 \gamma_{\pm}^3 = 4m^3 \gamma_{\pm}^3$$

if we assume solid and liquid activities = 1.

The Nernst equation, eq. 8.40, can now be used to derive a formula relating measured EMFs to the mean ionic activity coefficient.

$$\mathcal{E} = 1.0308 \text{ volt} - \frac{RT}{2F} \ln(4m^3 \gamma_{\pm}^3)$$

Oxidation reaction (left): $1/2 \text{H}_2 (\text{g}) = \text{H}^+ (\text{ao}) + \text{e}^-$

Reduction reaction (right): $\text{AgCl} (\text{s}) + \text{e}^- = \text{Cl}^- (\text{ao}) + \text{Ag} (\text{s})$

Cell reaction: $1/2 \text{H}_2 (\text{g}) + \text{AgCl} (\text{s}) = \text{HCl} (\text{ai}) + \text{Ag} (\text{s})$

The Nernst equation, eq. 8.40, for this cell can be expressed as follows. Solid activities were assumed to be one, as well as the H_2 gas activity (since $P/P_\theta = 1$)

$$\varepsilon = \varepsilon_\theta - \frac{R \cdot T}{n \cdot F} \cdot \ln(m^2 \cdot \gamma_{\text{mean}}^2) \quad T = 298.15 \cdot \text{K} \quad n = 1 \cdot \text{mole} \quad F = 96485 \cdot \frac{\text{coul}}{\text{mole}} \quad R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

This can be rearranged to give

$$\varepsilon + \frac{2 \cdot R \cdot T}{n \cdot F} \cdot \ln(m) = \varepsilon_\theta - \frac{2 \cdot R \cdot T}{n \cdot F} \cdot \ln(\gamma_{\text{mean}})$$

If the quantity on the left hand side is calculated from the data points and extrapolated to $m = 0$, the right hand side will become just ε_θ , since the mean ionic activity coefficient will approach 1. The quantity on the left and right sides of the above equation is called ε' in the text, and will be referred to here as $\varepsilon_{\text{prime}}$.

i 0..4

m_i	ε_i	$\varepsilon_{\text{prime}_i} = \varepsilon_i + \frac{2 \cdot R \cdot T}{n \cdot F} \cdot \ln(m_i)$	$\varepsilon_{\text{prime}_i}$ volt
0.003215	0.52053·volt		0.225580
0.005619	0.49257·volt		0.226310
0.009138	0.46860·volt		0.227328
0.013407	0.44974·volt		0.228166
0.02563	0.41824·volt		0.229963

These $\varepsilon_{\text{prime}}$ results were fit to a polynomial in $\text{sqrt}(m)$ with the following result:

$$\varepsilon_{\text{fit}}(m) = 0.22283 + 0.0497872 \cdot m^{0.5} + 0.0324658 \cdot m$$

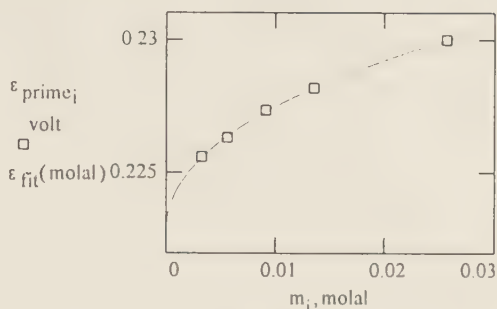
$$\varepsilon_\theta = \varepsilon_{\text{fit}}(0)$$

$$\varepsilon_\theta = 0.2228$$

The standard deviation of the leading term in the polynomial fit is $\sigma = 0.0003$.

Here is a graph of the fit and the data.

molal 0, 0.0002 .. 0.03



Another way to approach the problem is to calculate the quantity ε'' as described in the text. This uses the DHG equation to evaluate the mean ionic activity coefficient as it approaches one. The answer with this method is the same as given above, but with $\sigma = 0.00004$.

8.57

Oxidation reaction (left): $\text{Zn (s)} = \text{Zn}^{2+} \text{ (ao)} + 2 \text{ e}^-$

Reduction reaction (right): $\text{PbSO}_4 \text{ (s)} + 2 \text{ e}^- = \text{SO}_4^{2-} \text{ (ao)} + \text{Pb (Hg)}$

Cell reaction: $\text{Zn (s)} + \text{PbSO}_4 \text{ (s)} = \text{ZnSO}_4 \text{ (ai)} + \text{Pb (Hg)}$

The Nernst equation, eq. 8.40, for this cell can be expressed as follows, assuming the activities of condensed phases = 1.

$$\varepsilon = \varepsilon_\theta - \frac{R \cdot T}{n \cdot F} \cdot \ln(m^2 \cdot \gamma_{\text{mean}}^2) \quad T = 298.15 \cdot \text{K} \quad n = 2 \cdot \text{mole} \quad F = 96485 \cdot \frac{\text{coul}}{\text{mole}} \quad R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

This can be rearranged to give

$$\varepsilon + \frac{2 \cdot R \cdot T}{n \cdot F} \cdot \ln(m) = \varepsilon_\theta - \frac{2 \cdot R \cdot T}{n \cdot F} \cdot \ln(\gamma_{\text{mean}})$$

If the quantity on the left hand side is calculated from the data points and extrapolated to $m = 0$, the right hand side will become just ε_θ , since the mean ionic activity coefficient will approach 1. The quantity on the left and right sides of the above equation is called ε' in the text, and will be referred to here as $\varepsilon_{\text{prime}}$.

i 0..4

m_i
0.0005
0.001
0.002
0.005
0.01

ε_i
0.61144·volt
0.59714·volt
0.58319·volt
0.56598·volt
0.55353·volt

$$\varepsilon_{\text{prime}_i} = \varepsilon_i + \frac{2 \cdot R \cdot T}{n \cdot F} \cdot \ln(m_i)$$

$\varepsilon_{\text{prime}_i}$ volt
0.416151
0.419660
0.423519
0.429851
0.435210

These $\varepsilon_{\text{prime}}$ results were fit to a polynomial in \sqrt{m} with the following result:

$$\varepsilon_{\text{fit}}(m) = 0.407828 + 0.410941 \cdot m^{0.5} - 1.37626 \cdot m$$

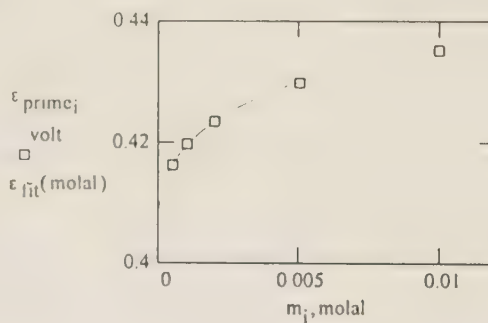
$$\varepsilon_\theta = \varepsilon_{\text{fit}}(0)$$

$$\varepsilon_\theta = 0.4078$$

The standard deviation of the leading term in the polynomial fit is $\sigma = 0.0006$.

Here is a graph of the fit and the data.

molal 0,0.0002..0.012



8.59

Cell reaction: $\text{Zn (s)} + 2 \text{MnO}_2 \text{ (s)} + \text{H}_2\text{O (liq)} = \text{Zn}^{2+} \text{ (ao)} + 2 \text{OH}^- \text{ (ao)} + \text{Mn}_2\text{O}_3 \text{ (s)}$

The maximum work obtainable from this cell is given by $(-w)_{\text{max}} = nF\varepsilon$. For a stoichiometric amount of reactants,

$$n = 2 \cdot \text{mole} \quad F = 96485 \cdot \frac{\text{coul}}{\text{mole}} \quad \varepsilon = 1.5 \cdot \text{volt}$$

$$\text{energy} = n \cdot F \cdot \varepsilon \quad \text{energy} = 289.455 \cdot \text{kJ} \quad \text{kJ} = 1000 \cdot \text{joule}$$

Now we have to determine the mass of a stoichiometric amount of reactants.

$$\text{mass Zn} = 65.39 \cdot \text{gm} \quad \text{mass MnO}_2 = 173.8736 \cdot \text{gm} \quad \text{mass H}_2\text{O} = 18.01528 \cdot \text{gm}$$

$$\text{energy specific} = \frac{\text{energy}}{\text{mass Zn} + \text{mass MnO}_2 + \text{mass H}_2\text{O}} \quad \text{energy specific} = 1.13 \cdot \frac{\text{kJ}}{\text{gm}}$$

The time this cell will last is the energy divided by the power.

$$\text{time} = \frac{(10 \cdot \text{gm}) \cdot \text{energy specific}}{5 \cdot \text{watt}} \quad \text{time} = 38 \cdot \text{min}$$

SECTION 8.5

8.61

Oxidation reaction (left): $\text{H}_2(\text{g}) = 2\text{H}^+(\text{aq}) + 2\text{e}^-$ Reduction reaction (right): $2\text{AgCl}(\text{s}) + 2\text{e}^- = 2\text{Ag}(\text{s}) + 2\text{Cl}^-(\text{aq})$ Cell reaction: $\text{H}_2(\text{g}) + 2\text{AgCl}(\text{s}) = 2\text{Ag}(\text{s}) + 2\text{HCl}(\text{aq})$ With data from Tables 6.1 and 8.3, we can calculate $\Delta_{\text{rxn}}G_\theta$ at 60 °C.

$$\begin{aligned} \Delta_{\text{fH}} \text{H}_2 &= 0 \frac{\text{kJ}}{\text{mole}} & \Delta_{\text{fH}} \text{AgCl} &= 127.068 \frac{\text{kJ}}{\text{mole}} & \Delta_{\text{fH}} \text{Ag} &= 0 \frac{\text{kJ}}{\text{mole}} & R &= 8.31451 \frac{\text{J}}{\text{mole} \cdot \text{K}} \\ \Delta_{\text{fH}} \text{H} &= 0 \frac{\text{kJ}}{\text{mole}} & \Delta_{\text{fH}} \text{Cl}^- &= -167.159 \frac{\text{kJ}}{\text{mole}} \end{aligned}$$

$$\Delta_{\text{rxn}}H_\theta = 2 \cdot \Delta_{\text{fH}} \text{Ag} + 2 \cdot \Delta_{\text{fH}} \text{H} + 2 \cdot \Delta_{\text{fH}} \text{Cl}^- - \Delta_{\text{fH}} \text{H}_2 - 2 \cdot \Delta_{\text{fH}} \text{AgCl} \quad \Delta_{\text{rxn}}H_\theta = -80.182 \frac{\text{kJ}}{\text{mole}}$$

$$S_{\text{H}_2} = 130.684 \frac{\text{J}}{\text{mole} \cdot \text{K}} \quad S_{\text{AgCl}} = 96.2 \frac{\text{J}}{\text{mole} \cdot \text{K}} \quad S_{\text{Ag}} = 42.55 \frac{\text{J}}{\text{mole} \cdot \text{K}}$$

$$S_{\text{H}} = 0 \frac{\text{J}}{\text{mole} \cdot \text{K}} \quad S_{\text{Cl}^-} = 56.5 \frac{\text{J}}{\text{mole} \cdot \text{K}}$$

$$\Delta_{\text{rxn}}S_\theta = 2 \cdot S_{\text{Ag}} + 2 \cdot S_{\text{H}} - 2 \cdot S_{\text{Cl}^-} - S_{\text{H}_2} - 2 \cdot S_{\text{AgCl}} \quad \Delta_{\text{rxn}}S_\theta = 124.984 \frac{\text{J}}{\text{mole} \cdot \text{K}}$$

$$\Delta_{\text{rxn}}G_\theta(T) = \Delta_{\text{rxn}}H_\theta - T \cdot \Delta_{\text{rxn}}S_\theta \quad \Delta_{\text{rxn}}G_\theta(333.15 \text{ K}) = -38.544 \frac{\text{kJ}}{\text{mole}}$$

Now we can use eq. 8.41 to calculate the standard EMF.

$$n = 2 \text{ mole } \text{e}^- \quad F = 96485 \frac{\text{Coul}}{\text{mole}}$$

$$\epsilon_\theta = \frac{\Delta_{\text{rxn}}G_\theta(333.15 \text{ K})}{n \cdot F} \quad \epsilon_\theta = 0.1997 \text{ volt}$$

8.63

Oxidation reaction (left): $1/2 \text{H}_2 (\text{g}) = \text{H}^+ (\text{ao}) + \text{e}^-$

Reduction reaction (right): $\text{AgBr} (\text{s}) + \text{e}^- = \text{Ag} (\text{s}) + \text{Br}^- (\text{ao})$

Cell reaction: $1/2 \text{H}_2 (\text{g}) + \text{AgBr} (\text{s}) = \text{Ag} (\text{s}) + \text{HBr} (\text{ai})$

Eq. 8.43 can be used to calculate $\Delta_{\text{rxn}}S_{\theta}$ with the given data

$$\begin{aligned} \varepsilon_{15} &:= 0.07595 \cdot \text{volt} & \varepsilon_{25} &:= 0.07131 \cdot \text{volt} & \varepsilon_{35} &:= 0.06597 \cdot \text{volt} & F &:= 96485 \cdot \frac{\text{coul}}{\text{mole}} & \text{kJ} &:= 1000 \cdot \text{joule} \\ \Delta_{\text{rxn}}S_{\theta} &:= n \cdot F \cdot \left(\frac{\varepsilon_{35} - \varepsilon_{15}}{20 \cdot \text{K}} \right) & \Delta_{\text{rxn}}S_{\theta} &= -48.146 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} & n &:= 1 \cdot \text{mole} & R &:= 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \end{aligned}$$

From Tables 6.1 and 8.3 we have the following data

$$\begin{aligned} S_{\text{Ag}} &:= 42.55 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} & S_{\text{H}} &:= 0 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} & S_{\text{H}_2} &:= 130.684 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} & S_{\text{AgBr}} &:= 107.1 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \\ S_{\text{Br}} &:= \Delta_{\text{rxn}}S_{\theta} - S_{\text{Ag}} - S_{\text{H}} + \frac{1}{2} \cdot S_{\text{H}_2} + S_{\text{AgBr}} & S_{\text{Br}} &= 81.7 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \end{aligned}$$

The value given in Table 8.3 is $82.4 \text{ J}/(\text{mole} \cdot \text{K})$.

8.65

Oxidation reaction (left): $1/2 \text{H}_2 (\text{g}) = \text{H}^+ (\text{ao}) + \text{e}^-$

Reduction reaction (right): $\text{H}_2\text{O} (\text{liq}) + \text{e}^- = 1/2 \text{H}_2 (\text{g}) + (\text{OH})^- (\text{ao})$

Cell reaction: $\text{H}_2\text{O} (\text{liq}) = \text{H}^+ (\text{ao}) + (\text{OH})^- (\text{ao})$

Table 8.7 gives

$$\varepsilon_{\text{left}} = 0 \cdot \text{volt} \quad \varepsilon_{\text{right}} = -0.82806 \cdot \text{volt} \quad \varepsilon_{\theta} = \varepsilon_{\text{right}} - \varepsilon_{\text{left}}$$

Eq. 8.45 gives the equilibrium constant (also the ion product) as

$$K_a = \exp\left(\frac{n \cdot F \cdot \varepsilon_{\theta}}{R \cdot T}\right) \quad T = 298.15 \cdot \text{K} \quad n = 1 \cdot \text{mole} \quad F = 96485 \cdot \frac{\text{coul}}{\text{mole}}$$

$$K_a = 1.007 \cdot 10^{-14} \quad R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

8.67

(a) Oxidation reaction (left): $\text{Pb} (\text{s}) + 2 \text{Cl}^- (\text{ao}) = \text{PbCl}_2 (\text{s}) + 2 \text{e}^-$

Reduction reaction (right): $\text{Hg}_2\text{Cl}_2 (\text{s}) + 2 \text{e}^- = 2 \text{Hg} (\text{liq}) + 2 \text{Cl}^- (\text{ao})$

Cell reaction: $\text{Pb} (\text{s}) + \text{Hg}_2\text{Cl}_2 (\text{s}) = \text{PbCl}_2 (\text{s}) + 2 \text{Hg} (\text{liq})$

(b) Free energies of formation from Table 6.1 can be used to calculate $\Delta_{\text{rxn}}G_{\theta}$. (Remember, the free energy of formation of elements in their most stable form at standard pressure and a given temperature is zero). Then, eq. 8.41 can be used to calculate the standard EMF.

$$\Delta_{\text{f}}G_{\text{Pb}} = 0 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta_{\text{f}}G_{\text{Hg}_2\text{Cl}_2} = 210.745 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta_{\text{f}}G_{\text{PbCl}_2} = 314.10 \cdot \frac{\text{kJ}}{\text{mole}} \quad \Delta_{\text{f}}G_{\text{Hg}} = 0 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\Delta_{\text{rxn}}G_{\theta} = \Delta_{\text{f}}G_{\text{PbCl}_2} + 2 \cdot \Delta_{\text{f}}G_{\text{Hg}} - \Delta_{\text{f}}G_{\text{Hg}_2\text{Cl}_2} - \Delta_{\text{f}}G_{\text{Pb}} \quad \Delta_{\text{rxn}}G_{\theta} = -103.355 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$\varepsilon_{\theta 25} = \frac{-\Delta_{\text{rxn}}G_{\theta}}{n \cdot F} \quad \varepsilon_{\theta 25} = 0.5356 \cdot \text{volt} \quad n = 2 \cdot \text{mole} \quad \text{kJ} = 1000 \cdot \text{joule} \quad F = 96485 \cdot \frac{\text{coul}}{\text{mole}}$$

Equation 8.40 (Nernst equation) relates the standard EMF to the actual EMF. Since we are dealing only with condensed phases, all activities are approximately one, and $\varepsilon = \varepsilon_{\theta}$.

(c) The temperature dependence of the standard EMF is given by eq. 8.43. Standard entropies can be found in Tables 3.2 and 6.1.

$$S_{\text{Pb}} = 64.81 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad S_{\text{Hg}_2\text{Cl}_2} = 192.5 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad S_{\text{PbCl}_2} = 136.0 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad S_{\text{Hg}} = 76.02 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\Delta_{\text{rxn}} S_{\theta} = S_{\text{PbCl}_2} + 2 \cdot S_{\text{Hg}} - S_{\text{Pb}} - S_{\text{Hg}_2\text{Cl}_2} \quad \Delta_{\text{rxn}} S_{\theta} = 30.73 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\frac{d\varepsilon}{dT} = \frac{\Delta_{\text{rxn}} S_{\theta}}{n \cdot F}$$

$$\varepsilon_{\theta 18} - \varepsilon_{\theta 25} = \frac{d\varepsilon}{dT} \cdot (18 - 25) \cdot \text{K} \quad \varepsilon_{\theta 18} = 0.5345 \cdot \text{volt}$$

Again, for this cell the standard EMF is the actual EMF since all activities are one.

(d) When a cell is charged reversibly, the minimum amount of heat is released. This amount is given by $(\Delta_{\text{rxn}} H_{\theta} - \Delta_{\text{rxn}} G_{\theta}) = T \Delta_{\text{rxn}} S_{\theta}$.

$$T = 298.15 \cdot \text{K}$$

$$\text{heat}_{\text{reversible}} = T \cdot \Delta_{\text{rxn}} S_{\theta} \quad \text{heat}_{\text{reversible}} = 9.16 \cdot \frac{\text{kJ}}{\text{mole}}$$

(e) If the cell were discharged totally irreversibly (as in a short circuit), the maximum amount of heat is released. This amount is given by $\Delta_{\text{rxn}} H_{\theta} = \Delta_{\text{rxn}} G_{\theta} + T \Delta_{\text{rxn}} S_{\theta}$.

$$\text{heat}_{\text{irreversible}} = \Delta_{\text{rxn}} G_{\theta} + T \cdot \Delta_{\text{rxn}} S_{\theta} \quad \text{heat}_{\text{irreversible}} = 94.19 \cdot \frac{\text{kJ}}{\text{mole}}$$

SECTION 8.6

8.69

Oxidation reaction (left): $\text{Cl}^- (\text{ao}) = 1/2 \text{Cl}_2 (\text{g}, 1 \text{ atm}) + \text{e}^-$ Reduction reaction (right): $1/2 \text{Cl}_2 (\text{g}, 0.3 \text{ atm}) + \text{e}^- = \text{Cl}^- (\text{ao})$ Cell reaction: $1/2 \text{Cl}_2 (\text{g}, 0.3 \text{ atm}) = 1/2 \text{Cl}_2 (\text{g}, 1 \text{ atm})$

Since the two half cell reactions have the same standard EMF, the overall standard EMF is zero. Thus, the Nernst equation (eq. 8.40) simplifies to

$$\varepsilon(\text{Q}) = -\frac{R \cdot T}{n \cdot F} \cdot \ln(\text{Q}) \quad T = 298.15 \cdot \text{K} \quad n = 1 \cdot \text{mole} \quad F = 96485 \cdot \frac{\text{coul}}{\text{mole}} \quad R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

All that needs to be evaluated is the activity quotient, Q. With the ideal gas approximation, the chlorine activity is P/P_0 . Since the standard pressure cancels out, Q becomes just

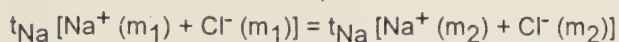
$$\text{Q} = \left(\frac{1 \cdot \text{atm}}{0.3 \cdot \text{atm}} \right)^2 \quad \varepsilon(\text{Q}) = 0.0155 \cdot \text{volt}$$

8.71

The subscript 1 refers to the NaCl compartment with $m = 0.1$. The subscript 2 refers to the NaCl compartment with $m = 0.02$.

Oxidation reaction (left): $\text{Cl}^- (m_1) = 1/2 \text{Cl}_2 (\text{g}) + \text{e}^-$ Liquid Junction (cation): $t_{\text{Na}} \text{Na}^+ (m_1) = t_{\text{Na}} \text{Na}^+ (m_2)$ Liquid Junction (anion): $t_{\text{Cl}} \text{Cl}^- (m_2) = t_{\text{Cl}} \text{Cl}^- (m_1)$ Reduction reaction (right): $1/2 \text{Cl}_2 (\text{g}) + \text{e}^- = \text{Cl}^- (m_2)$ Cell reaction: $\text{Cl}^- (m_1) + t_{\text{Na}} \text{Na}^+ (m_1) + t_{\text{Cl}} \text{Cl}^- (m_2) = \text{Cl}^- (m_2) + t_{\text{Na}} \text{Na}^+ (m_2) + t_{\text{Cl}} \text{Cl}^- (m_1)$

This cell reaction can be simplified to:



$$T = 298.15 \cdot \text{K} \quad n = 1 \cdot \text{mole}$$

The Nernst equation for this cell is expressed below (since the standard EMF is zero here).

$$m_{\text{Na1}} = 0.1 \quad m_{\text{Na2}} = 0.02 \quad m_{\text{Cl1}} = 0.1 \quad m_{\text{Cl2}} = 0.02$$

$$\gamma_{\text{mean1}} = 0.778 \quad \gamma_{\text{mean2}} = 0.875 \quad \text{From Table 8.1}$$

$$\varepsilon = \frac{R \cdot T}{n \cdot F} \cdot \ln \left[\left(\frac{m_{\text{Na2}} \cdot m_{\text{Cl2}} \cdot \gamma_{\text{mean2}}^2}{m_{\text{Na1}} \cdot m_{\text{Cl1}} \cdot \gamma_{\text{mean1}}^2} \right)^{t_{\text{Na}}} \right]$$

$$t_{\text{Na}} = \frac{0.3902 + 0.3854}{2} \quad \text{Average value from Table 8.4}$$

$$F = 96485 \cdot \frac{\text{coul}}{\text{mole}} \quad R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\varepsilon = 0.0297 \cdot \text{volt}$$

SECTION 8.7

8.73

We can use eq. 8.54 to estimate the liquid junction potential. Data can be found in Table 8.6.

$$c_1 = 0.1 \quad c_2 = 0.2 \quad T = 298.15 \cdot K \quad R = 8.31451 \frac{\text{joule}}{\text{mole} \cdot K} \quad F = 96485 \cdot \text{coul} \quad \text{equiv} \approx 1$$

$$\lambda_K = 73.50 \frac{\text{cm}^2 \cdot \text{siemens}}{\text{equiv}} \quad \lambda_{OH} = 197.6 \frac{\text{cm}^2 \cdot \text{siemens}}{\text{equiv}} \quad \lambda_{Cl} = 76.34 \frac{\text{cm}^2 \cdot \text{siemens}}{\text{equiv}}$$

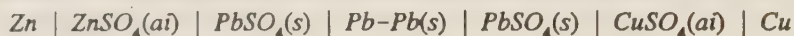
$$\Lambda_{KOH} = \lambda_K + \lambda_{OH} \quad \Lambda_{KCl} = \lambda_K + \lambda_{Cl}$$

$$\varepsilon_J = \frac{R \cdot T}{F} \left[\frac{c_1 (\lambda_K - \lambda_{OH}) - c_2 (\lambda_K - \lambda_{Cl})}{c_1 \Lambda_{KOH} - c_2 \Lambda_{KCl}} \right] \cdot \ln \left(\frac{c_1 \Lambda_{KOH}}{c_2 \Lambda_{KCl}} \right)$$

$$\varepsilon_J = 0.0107 \cdot \text{volt}$$

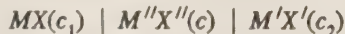
8.75

We can use the bridge to separate the cell into 2 cells in series, with neither of the resulting cells having a liquid junction. The following can be used to give the desired overall cell reaction.



8.77

The liquid junction potential of the following bridge,



can be summed from the two individual liquid junctions present. The starting point for the evaluation of either potential is eq. 8.54.

$$\varepsilon_J = \frac{RT}{F} \left[\frac{c_a(\lambda_+ - \lambda_-) - c_b(\lambda'_+ - \lambda'_-)}{c_a \Lambda - c_b \Lambda'} \right] \ln \left[\frac{c_a \Lambda}{c_b \Lambda'} \right]$$

where we have replaced the subscripts to avoid confusion with the salt bridge subscripts.

For the first junction, $c_a = c_1$ and $c_b = c$. Since $c \gg c_1$, the terms in the left brackets containing c_a are negligible compared to those containing c_b . Thus, the first junction potential is given as

$$\mathcal{E}_1 = \frac{RT}{\mathcal{F}} \left[\frac{\lambda_+'' - \lambda_-''}{\Lambda''} \right] \ln \left[\frac{c_1 \Lambda}{c \Lambda''} \right]$$

The group in the left brackets is now easily seen to be the difference between the transference numbers for the concentrated salt species.

$$\mathcal{E}_1 = \frac{RT}{\mathcal{F}} (t_+'' - t_-'') \ln \left[\frac{c_1 \Lambda}{c \Lambda''} \right]$$

For the second junction, $c_a = c$ and $c_b = c_2$. Since $c \gg c_2$, the terms in the left brackets of eq. 8.54 containing c_b are negligible to those containing c_a . Thus, the second junction potential is given as

$$\mathcal{E}_2 = \frac{RT}{\mathcal{F}} \left[\frac{\lambda_+'' - \lambda_-''}{\Lambda''} \right] \ln \left[\frac{c \Lambda''}{c_2 \Lambda'} \right]$$

$$\mathcal{E}_2 = \frac{RT}{\mathcal{F}} (t_+'' - t_-'') \ln \left[\frac{c \Lambda''}{c_2 \Lambda'} \right]$$

Combining the two junction potentials gives

$$\mathcal{E}_J = \mathcal{E}_1 + \mathcal{E}_2 = \frac{RT}{\mathcal{F}} (t_+'' - t_-'') \ln \left[\frac{c_1 \Lambda}{c_2 \Lambda'} \right]$$

Since $t_-'' = 1 - t_+''$, we have

$$\mathcal{E}_J = \frac{RT}{\mathcal{F}} (2t_+'' - 1) \ln \left[\frac{c_1 \Lambda}{c_2 \Lambda'} \right]$$

CHAPTER 9 *Transport Properties*

SECTION 9.1

9.1

We use equations (9.2), (9.9c), (9.8), and (9.3). The diameter, sigma, can be found on Table 1.7.

$$R \quad 8.31451 \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T \quad 250 \cdot \text{K} \quad P \quad 3.55 \cdot \text{torr} \quad M \quad 16.0428 \cdot 10^{-3} \frac{\text{kg}}{\text{mole}} \quad \text{nm} \quad 10^{-9} \cdot \text{m}$$

$$L \quad 6.02 \cdot 10^{23} \frac{1}{\text{mole}} \quad \sigma \quad 0.3817 \cdot \text{nm} \quad \mu\text{m} \quad 10^{-6} \cdot \text{m}$$

$$v_{\text{av}} = \frac{8 \cdot R \cdot T}{\pi \cdot M} \quad v_{\text{av}} = 574.4 \frac{\text{m}}{\text{sec}}$$

$$\lambda = \frac{R \cdot T}{2 \cdot P \cdot L \cdot \pi \cdot \sigma^2} \quad \lambda = 11.27 \cdot \mu\text{m}$$

$$n_{\text{star}} = \frac{P \cdot L}{R \cdot T}$$

$$z = 2 \cdot v_{\text{av}} \cdot \pi \cdot \sigma^2 \cdot n_{\text{star}} \quad z = 5.097 \cdot 10^7 \frac{1}{\text{sec}}$$

9.3

We use equations (9.2), (9.9c), (9.8), and (9.3). The diameters for N₂ and O₂ can be found on Table 1.7, and we weight these with their mole fractions in air to obtain an average diameter.

$$R \quad 8.31451 \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T \quad 570 \cdot \text{K} \quad P \quad 2 \cdot 10^{-6} \cdot \text{torr} \quad M \quad 29 \cdot 10^{-3} \frac{\text{kg}}{\text{mole}} \quad \text{nm} \quad 10^{-9} \cdot \text{m}$$

$$L \quad 6.02 \cdot 10^{23} \frac{1}{\text{mole}} \quad \sigma \quad (0.8) \cdot (0.3698 \cdot \text{nm}) + (0.2) \cdot (0.358 \cdot \text{nm}) \quad \mu\text{m} \quad 10^{-6} \cdot \text{m}$$

$$v_{av} = \frac{8 \cdot R \cdot T}{\pi \cdot M} \quad v_{av} = 645.1 \cdot \frac{\text{m}}{\text{sec}}$$

$$\lambda = \frac{R \cdot T}{2 \cdot P \cdot L \cdot \pi \cdot \sigma^2} \quad \lambda = 49.22 \cdot \text{m}$$

$$n_{star} = \frac{P \cdot L}{R \cdot T}$$

$$z = \frac{1}{2 \cdot v_{av} \cdot \pi \cdot \sigma^2 \cdot n_{star}} \quad z = 13.11 \cdot \frac{1}{\text{sec}}$$

9.5

We use equations (9.2), (9.9c), (9.8), and (9.3). The diameter, sigma, can be found on Table 1.7.

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T = 990 \cdot \text{K} \quad M = 83.80 \cdot 10^{-3} \cdot \frac{\text{kg}}{\text{mole}} \quad \text{nm} = 10^{-9} \cdot \text{m}$$

$$L = 6.02 \cdot 10^{23} \cdot \frac{1}{\text{mole}} \quad \sigma = 0.360 \cdot \text{nm} \quad i = 0.2 \quad \text{bar} = 10^5 \cdot \text{Pa} \quad \mu\text{m} = 10^{-6} \cdot \text{m}$$

P_i
0.01 · bar
1.00 · bar
15.0 · bar

$$v_{av} = \frac{8 \cdot R \cdot T}{\pi \cdot M} \quad v_{av} = 500.1 \cdot \frac{\text{m}}{\text{sec}}$$

$$\lambda_i = \frac{R \cdot T}{2 \cdot P_i \cdot L \cdot \pi \cdot \sigma^2} \quad \lambda = \frac{23.747}{0.237 \cdot 0.016} \cdot \mu\text{m}$$

$$\text{ratio}_i = \frac{\lambda_i}{\sigma} \quad \text{ratio} = \frac{6.596 \cdot 10^4}{659.634 \cdot 43.976}$$

$$n_{\text{star}_i} = \frac{P_i \cdot L}{R \cdot T}$$

$$z_i = \frac{2 \cdot v_{\text{av}} \cdot \pi \cdot \sigma^2 \cdot n_{\text{star}_i}}{2.1 \cdot 10^7} \quad z = \frac{2.1 \cdot 10^9}{3.2 \cdot 10^{10}} \cdot \frac{1}{\text{sec}}$$

9.7

The relative velocity is given by eq. (9.11). First, we calculate the reduced mass using eq. (9.10b).

$$R = 8.31451 \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad M_A = 16.0428 \cdot 10^{-3} \frac{\text{kg}}{\text{mole}} \quad M_B = 83.80 \cdot 10^{-3} \frac{\text{kg}}{\text{mole}} \quad T = 350 \cdot \text{K}$$

$$L\mu = \frac{M_A \cdot M_B}{M_A + M_B}$$

$$v_{AB} = \frac{8 \cdot R \cdot T}{\pi \cdot L\mu} \quad v_{AB} = 741.9 \frac{\text{m}}{\text{sec}}$$

9.9

The collision frequency is given by eq. (9.13a). First, we must calculate the reduced mass and the relative velocity. "A" denotes methane and "B" denotes krypton.

$$R = 8.31451 \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad M_A = 16.0428 \cdot 10^{-3} \frac{\text{kg}}{\text{mole}} \quad M_B = 83.80 \cdot 10^{-3} \frac{\text{kg}}{\text{mole}} \quad T = 350 \cdot \text{K}$$

$$P_A = 55 \cdot \text{torr} \quad P_B = 25 \cdot \text{torr} \quad nm = 10^{-9} \cdot m \quad \sigma_A = 0.3817 \cdot nm \quad \sigma_B = 0.360 \cdot nm$$

$$L = 6.02 \cdot 10^{23} \cdot \frac{1}{\text{mole}}$$

$$\sigma_{AB} = \frac{1}{2} \cdot \sigma_A \cdot \sigma_B \quad \text{eq. (9.12)}$$

$$L\mu = \frac{M_A \cdot M_B}{M_A + M_B} \quad \text{eq. (9.10b)}$$

$$v_{AB} = \frac{8 \cdot R \cdot T}{\pi \cdot L\mu} \quad v_{AB} = 742 \cdot \frac{\text{m}}{\text{sec}} \quad \text{eq. (9.11)}$$

$$n_{\text{star } A} = \frac{P_A \cdot L}{R \cdot T} \quad n_{\text{star } B} = \frac{P_B \cdot L}{R \cdot T}$$

In eq. (9.13a), "z_{AB}" denotes the number of collisions of A with B, or in this case, the number of times methane collides with krypton.

$$z_{AB} = \pi \cdot \sigma_{AB}^2 \cdot v_{AB} \cdot n_{\text{star } B} \quad z_{AB} = 2.21 \cdot 10^8 \cdot \frac{1}{\text{sec}}$$

$$z_{BA} = \pi \cdot \sigma_{AB}^2 \cdot v_{AB} \cdot n_{\text{star } A} \quad z_{BA} = 4.862 \cdot 10^8 \cdot \frac{1}{\text{sec}}$$

9.11

The relative velocity is given by eq. (9.11), and the number of collisions is given by eq. (9.13a). In the following calculations, the first entry in the answer vector denotes He, the second Ne, the third Ar, and the fourth Kr.

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad M_{\text{CO}_2} = 44.0098 \cdot 10^{-3} \cdot \frac{\text{kg}}{\text{mole}} \quad T = 298.15 \cdot \text{K} \quad \text{nm} = 10^{-9} \cdot \text{m}$$

$$P_{\text{CO}_2} = 5 \cdot \text{torr} \quad \sigma_{\text{CO}_2} = 0.4486 \cdot \text{nm} \quad L = 6.02 \cdot 10^{23} \cdot \frac{1}{\text{mole}} \quad i = 0..3$$

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Data for other gases:

$$P_B = 10 \text{ torr}$$

M_i	σ_i
$4.002602 \cdot 10^{-3} \frac{\text{kg}}{\text{mole}}$	0.263 nm
$20.179 \cdot 10^{-3} \frac{\text{kg}}{\text{mole}}$	0.2749 nm
$39.948 \cdot 10^{-3} \frac{\text{kg}}{\text{mole}}$	0.3403 nm
$83.80 \cdot 10^{-3} \frac{\text{kg}}{\text{mole}}$	0.360 nm

$$n_{\text{star } B} = \frac{P_B \cdot L}{R \cdot T} \quad L \mu_i = \frac{M_{\text{CO}_2} \cdot M_i}{M_{\text{CO}_2} + M_i}$$

$$\sigma_{\text{mix}_i} = \frac{1}{2} \cdot \sigma_{\text{CO}_2} + \sigma_i \quad v_{AB_i} = \frac{8 \cdot R \cdot T}{\pi \cdot L \mu_i} \quad z_{AB_i} = \pi \cdot \sigma_{\text{mix}_i}^2 \cdot v_{AB_i} \cdot n_{\text{star } B}$$

$$v_{AB} = \frac{1312}{675} \cdot \frac{\text{m}}{\text{sec}} \quad z_{AB} = \frac{1.689 \cdot 10^8}{8.991 \cdot 10^7} \cdot \frac{1}{\text{sec}}$$

$$468 \quad 7.776 \cdot 10^7$$

9.13

The collision frequency of unlike molecules is given by eq. (9.13a). The collision frequency of like molecules is given by eq. (9.8). Below, "A" denotes helium and "B" denotes argon.

R	$8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$	M _A	$4.002602 \cdot 10^{-3} \cdot \frac{\text{kg}}{\text{mole}}$	M _B	$39.948 \cdot 10^{-3} \cdot \frac{\text{kg}}{\text{mole}}$	L	$6.02 \cdot 10^{23} \cdot \frac{1}{\text{mole}}$
nm	$10^{-9} \cdot \text{m}$	σ _A	$0.263 \cdot \text{nm}$	σ _B	$0.3405 \cdot \text{nm}$	T	$350 \cdot \text{K}$
bar	$10^5 \cdot \text{Pa}$	P _A	$0.124 \cdot \text{bar}$	P _B	$0.345 \cdot \text{bar}$		

He-He collisions (z_{AA}) and Ar-Ar collisions (z_{BB}):

$$n_{\text{star A}} = \frac{P_A \cdot L}{R \cdot T} \quad v_A = \sqrt{\frac{8 \cdot R \cdot T}{\pi \cdot M_A}} \quad z_{AA} = 2 \cdot v_A \cdot \pi \cdot \sigma_A^2 \cdot n_{\text{star A}} \quad z_{AA} = 1.073 \cdot 10^9 \cdot \frac{1}{\text{sec}}$$

$$n_{\text{star B}} = \frac{P_B \cdot L}{R \cdot T} \quad v_B = \sqrt{\frac{8 \cdot R \cdot T}{\pi \cdot M_B}} \quad z_{BB} = 2 \cdot v_B \cdot \pi \cdot \sigma_B^2 \cdot n_{\text{star B}} \quad z_{BB} = 1.583 \cdot 10^9 \cdot \frac{1}{\text{sec}}$$

He-Ar collisions (z_{AB}):

$$L_{\mu} = \frac{M_A \cdot M_B}{M_A + M_B} \quad v_{AB} = \sqrt{\frac{8 \cdot R \cdot T}{\pi \cdot L_{\mu}}}$$

$$\sigma_{AB} = \frac{1}{2} \cdot (\sigma_A + \sigma_B) \quad z_{AB} = \pi \cdot \sigma_{AB}^2 \cdot v_{AB} \cdot n_{\text{star B}} \quad z_{AB} = 2.914 \cdot 10^9 \cdot \frac{1}{\text{sec}}$$

To determine the total number of collisions, we use eqs. (9.14) and (9.15):

$$Z_{AA} = \frac{z_{AA} \cdot n_{\text{star A}}}{2} \quad Z_{AA} = 1.376 \cdot 10^{33} \cdot \frac{1}{\text{m}^3 \cdot \text{sec}}$$

$$Z_{BB} = \frac{z_{BB} \cdot n_{\text{star B}}}{2} \quad Z_{BB} = 5.65 \cdot 10^{33} \cdot \frac{1}{\text{m}^3 \cdot \text{sec}}$$

$$Z_{AB} = z_{AB} \cdot n_{\text{star A}} \quad Z_{AB} = 7.474 \cdot 10^{33} \cdot \frac{1}{\text{m}^3 \cdot \text{sec}}$$

SECTION 9.2

9.15

(a) The probability is given by eq. (9.16). Since both numbers are odd, the parity factor is 1.

$$C(n, m) = \frac{n!}{m!(n-m)!} \quad P_{nm} = 1$$

$$W(n, m) = \frac{1}{2^n} \cdot C(n, m) \cdot P_{nm} \quad W(11, 5) = 0.0806$$

(b) We integrate the probability distribution function, eq. (9.19), between -6 and 6:

$$P = \int_{-6}^{+6} \frac{1}{\sqrt{2 \cdot \pi \cdot n \cdot \lambda^2}} \cdot e^{-\frac{x^2}{2 \cdot n \cdot \lambda^2}} dx \quad P = 93.0\%$$

9.17

This is similar to example 9.5. First, we use eq. (9.9c) to calculate the mean free path and eq. (9.8) to calculate the number of collisions.

$$R = 8.31451 \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T = 300 \cdot \text{K} \quad M = 39.948 \cdot 10^{-3} \frac{\text{kg}}{\text{mole}} \quad i = 0.2 \quad nm = 10^{-9} \cdot \text{m}$$

$$L = 6.02 \cdot 10^{23} \frac{1}{\text{mole}} \quad \sigma = 0.3405 \cdot \text{nm} \quad \text{bar} = 10^5 \cdot \text{Pa} \quad t = 5 \cdot \text{min} \quad P_i$$

$$v_{av} = \sqrt{\frac{8 \cdot R \cdot T}{\pi \cdot M}} \quad v_{av} = 398.8 \frac{\text{m}}{\text{sec}} \quad n_{star_i} = \frac{P_i \cdot L}{R \cdot T}$$

10·bar
1·bar
0.1·bar

$$\lambda_i = \frac{R \cdot T}{2 \cdot P_i \cdot L \cdot \pi \cdot \sigma^2} \quad \lambda = \frac{8.044}{80.438} \cdot \text{nm} = 804.382$$

$$z_i = \frac{4.957 \cdot 10^{10}}{4.957 \cdot 10^9} \cdot \frac{1}{\text{sec}} = 10$$

$$\delta x_{\text{rms}_i} = \frac{z_i \cdot t \cdot \lambda_i}{310.2} \quad \delta x_{\text{rms}} = \frac{31}{310.2} \cdot \text{mm} = 0.1$$

9.19

This is similar to example 9.5. First, we use eq. (9.9c) to calculate the mean free path and eq. (9.8) to calculate the number of collisions.

$$R = 8.31451 \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad T = 250 \cdot \text{K} \quad M = 28.0134 \cdot 10^{-3} \frac{\text{kg}}{\text{mole}} \quad \sigma = 0.3698 \cdot 10^{-9} \cdot \text{m}$$

$$L = 6.02 \cdot 10^{23} \frac{1}{\text{mole}} \quad \delta x_{\text{rms}} = 1 \cdot \text{cm} \quad P = 2.5 \cdot \text{atm}$$

$$v_{\text{av}} = \frac{8 \cdot R \cdot T}{\pi \cdot M} \quad v_{\text{av}} = 434.7 \frac{\text{m}}{\text{sec}} \quad n_{\text{star}} = \frac{P \cdot L}{R \cdot T}$$

$$\lambda = \frac{R \cdot T}{2 \cdot P \cdot L \cdot \pi \cdot \sigma^2} \quad \lambda = 2.243 \cdot 10^{-8} \cdot \text{m}$$

$$z = \frac{2 \cdot v_{\text{av}} \cdot \pi \cdot \sigma^2 \cdot n_{\text{star}}}{\lambda} \quad z = 1.938 \cdot 10^{10} \cdot \frac{1}{\text{sec}}$$

$$t = \frac{\delta x_{\text{rms}}^2}{\lambda^2 \cdot z} \quad t = 10.25 \cdot \text{sec}$$

9.21

We integrate the probability distribution function, eq. (9.23), between r_1 and r_2 .

$$W(r, t) \cdot dr = \frac{1}{2 \cdot D \cdot t} \cdot e^{-\frac{r^2}{4 \cdot D \cdot t}} \cdot r \cdot dr$$

Make the following substitution:

$$W(r, t) = \int_{r_1}^{r_2} \frac{1}{2 \cdot D \cdot t} \cdot e^{-\frac{r^2}{4 \cdot D \cdot t}} \cdot r \cdot dr$$

$$u = \frac{r^2}{4 \cdot D \cdot t} \quad du = \frac{2 \cdot r}{4 \cdot D \cdot t} \cdot dr = \frac{r}{2 \cdot D \cdot t} \cdot dr$$

$$W(r, t) = \int_{r_1}^{r_2} e^u \cdot du$$

$$W(r, t) = e^{\frac{r_2^2}{4 \cdot D \cdot t}} - e^{\frac{r_1^2}{4 \cdot D \cdot t}}$$

9.23

The rms distance for a 1-dimensional case is given by eq. (9.22). We can derive the result for a 2-dimensional system from the probability distribution. However, we can also use the fact that the 1-D result is not unique to the x-direction, but also applies to the y-direction (see example 9.9)

$$r^2 = x^2 + y^2 = 4 \cdot D \cdot t$$

$$r_{\text{rms}} = \sqrt{4 \cdot D \cdot t}$$

For this problem,

$$D = 2.2 \cdot 10^{-9} \frac{\text{m}^2}{\text{sec}} \quad r_{\text{rms}} = 15 \cdot 10^{-9} \cdot \text{m} \quad \text{ns} = 10^{-9} \cdot \text{sec} \quad t = \frac{r_{\text{rms}}^2}{4 \cdot D} = 25.6 \cdot \text{ns}$$

9.25

We can integrate the 2-dimensional probability distribution function, eq. (9.23), from 24 to infinity. However, since the probabilities must sum to one, we can also compute the probability that the sailor will not be in the water (perform the integration from 0 to 24) and subtract this probability from one. If you are working the problem on a computer, it does not make any difference, but if you are numerically evaluating the integral by hand, it is much easier to do it the second way. We substitute in eq. (9.21) for the diffusion coefficient to get the probability distribution function in terms of the number of steps and step size.

$$n = 159 \quad \lambda = 1$$

$$P = 1 - \int_0^{24} \frac{1}{n \cdot \lambda^2} \cdot e^{-2n \cdot \lambda^2 \cdot r^2} \cdot r \, dr \quad P = 0.163$$

9.27

Using the result of the previous problem, we have:

$$n = 1000 \quad \lambda = 1 \text{ cm}$$

$$r_{av} = \frac{8 \cdot n \cdot \lambda}{\pi} \quad r_{av} = 50.46 \text{ cm}$$

9.29

We integrate the 3D probability distribution function, eq. (9.24), from 0 to 1 cm.

$$D = 4.5 \cdot 10^5 \frac{\text{cm}^2}{\text{sec}} \quad t = 1 \cdot \text{hr}$$

$$W(r, t) \cdot dr = \frac{4 \cdot \pi}{(4 \cdot \pi \cdot D \cdot t)^{1.5}} \cdot e^{-\frac{r^2}{4 \cdot D \cdot t}} \cdot r^2 \cdot dr$$

$$P = \int_{0 \cdot \text{cm}}^{1 \cdot \text{cm}} \frac{r^2}{(4 \cdot \pi \cdot D \cdot t)^{1.5}} \cdot e^{-\frac{r^2}{4 \cdot D \cdot t}} \cdot 4 \cdot \pi \cdot dr \quad P = 0.6215$$

9.31

When there is no wall, we have:

$$C(n, m) = \frac{n!}{m! \cdot (n - m)!} \quad \rho_{nm} = 1$$

$$W(n, m) = \frac{1}{2^n} \cdot C(n, \frac{n + m}{2}) \cdot \rho_{nm} \quad W(10, 0) = 0.2461$$

When the reflecting wall is in place, we use eq. (9.25):

$$W_r(n, m, m_1) = W(n, m) + W(n, 2 \cdot m_1 - m)$$

$$W_r(10, 0, 3) = 0.29$$

We use eq. (9.26) to compute the probability, since there is a large number of steps:

$$n = 100 \quad l = \sqrt{2} \quad x_1 = 11$$

$$W(x, t) = \frac{1}{\sqrt{2\pi n l^2}} \exp\left[-\frac{x^2}{n l^2}\right]$$

$$P_{\text{abs}} = 2 \cdot \int_{x_1}^{\infty} W(x, n) dx \cdot 100 \quad P_{\text{abs}} = 19.2\%$$

SECTION 9.3

9.35

We use eq. (9.22). The diffusion constant can be found on Table 9.1.

$$D = 0.0059 \cdot 10^5 \frac{\text{cm}^2}{\text{sec}} \quad \text{week} \quad 7 \cdot \text{day}$$

$$t = 1 \cdot \text{week} \quad \delta x_{\text{rms}} = \sqrt{2 \cdot D \cdot t} \quad \delta x_{\text{rms}} = 0.267 \cdot \text{cm}$$

$$t = 4 \cdot \text{week} \quad \delta x_{\text{rms}} = \sqrt{2 \cdot D \cdot t} \quad \delta x_{\text{rms}} = 0.534 \cdot \text{cm}$$

9.37

We rearrange eq. (9.22) and solve for time. The diffusion coefficient can be found on Table 9.1.

$$D = 0.67 \cdot 10^5 \frac{\text{cm}^2}{\text{sec}}$$

$$\delta x_{\text{rms}} = 1 \cdot \text{mm} \quad t = \frac{\delta x_{\text{rms}}^2}{2 \cdot D} \quad t = 12.4 \cdot \text{min}$$

9.39

Equation (9.33) gives the diffusion coefficient in terms of the average velocity and the mean free path. We use equations (9.2) and (9.9c) to calculate these. The diameter, sigma, can be found on Table 1.7.

$$R = 8.31451 \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad \text{nm} = 10^{-9} \cdot \text{m} \quad P = 1 \cdot \text{atm} \quad M = 39.948 \cdot 10^{-3} \frac{\text{kg}}{\text{mole}}$$

$$L = 6.02 \cdot 10^{23} \frac{1}{\text{mole}} \quad \sigma = 0.3405 \cdot \text{nm} \quad i = 0.2$$

T_i
200·K
300·K
400·K

$$v_{av_i} = \frac{8 \cdot R \cdot T_i}{\pi \cdot M}$$

$$v_{av} = \frac{325.6}{398.8} \cdot \frac{m}{sec}$$

$$460.4$$

$$\lambda_i = \frac{R \cdot T_i}{2 \cdot P \cdot L \cdot \pi \cdot \sigma^2}$$

$$\lambda = \frac{5.292 \cdot 10^{-5}}{7.939 \cdot 10^{-5} \cdot 1.058 \cdot 10^{-4}} \cdot mm$$

$$D_i = \frac{1}{2} \cdot v_{av_i} \cdot \lambda_i$$

$$D = \frac{8.615 \cdot 10^{-6}}{1.583 \cdot 10^{-5} \cdot 2.437 \cdot 10^{-5}} \cdot \frac{m^2}{sec}$$

9.41

We use eq. (9.34). Here, the upper limit of integration is denoted "curlyQ."

$$D = 2.95 \cdot 10^{-5} \frac{cm^2}{sec} \quad x = 1 \cdot mm \quad i = 0..3 \quad t_i$$

1·min
10·min
60·min
24·hr

$$curlyQ_i = \frac{x}{4 \cdot D \cdot t_i}$$

1.188
0.376
0.153
0.031

$$c_{co_i} = \frac{1}{2} \cdot \frac{1}{\pi} \cdot \int_0^{curlyQ_i} e^{-y^2} dy$$

0.046
0.298
0.414
0.482

9.43

We rearrange eq. (9.22) and solve for time.

$$D = 10^{-12} \frac{\text{cm}^2}{\text{sec}}$$

$$\delta x_{\text{rms}} = 0.1 \cdot 10^{-6} \text{ m} \quad t = \frac{\delta x_{\text{rms}}^2}{2 \cdot D} \quad t = 50 \cdot \text{sec}$$

SECTION 9.4

9.45

We use eq. (9.37).

$$\eta = 0.01 \cdot \text{poise} \quad \Delta P = 3 \cdot \text{torr} \quad r = 0.1 \cdot \text{cm} \quad l = 5 \cdot \text{cm}$$

$$\text{flowrate} = \frac{\pi \cdot r^4 \cdot \Delta P}{8 \cdot \eta \cdot l} \quad \text{flowrate} = 188.48 \cdot \frac{\text{cm}^3}{\text{min}}$$

9.47

We use eq. (9.42). This is similar to example 9.18. The diffusion coefficient can be found on Table 9.1, and the viscosity of water can be found on Table 9.2.

$$T = 293.15 \cdot \text{K} \quad \eta = 10.05 \cdot 10^{-3} \cdot \text{poise} \quad \text{nm} = 10^{-9} \cdot \text{m}$$

$$D = 0.0059 \cdot 10^{-5} \cdot \frac{\text{cm}^2}{\text{sec}} \quad k = 1.38066 \cdot 10^{-16} \cdot \frac{\text{erg}}{\text{K}}$$

$$r = \frac{k \cdot T}{6 \cdot \pi \cdot \eta \cdot D} \quad r = 36.212 \cdot \text{nm}$$

9.49

This is similar to example 9.17. We use eq. (9.43). The diffusion coefficient given in Table 9.1 is at 20 C.

$$T_1 = 293.15 \cdot \text{K} \quad T_2 = 323.15 \cdot \text{K} \quad \eta_1 = 10.05 \cdot 10^{-3} \cdot \text{poise} \quad \eta_2 = 5.494 \cdot 10^{-3} \cdot \text{poise}$$

$$D_1 = 0.4586 \cdot 10^{-5} \cdot \frac{\text{cm}^2}{\text{sec}}$$

$$\frac{D_1 \cdot \eta_1}{T_1} = \frac{D_2 \cdot \eta_2}{T_2} \quad D_2 = D_1 \cdot \frac{\eta_1}{\eta_2} \cdot \frac{T_2}{T_1} \quad D_2 = 9.248 \cdot 10^{-6} \cdot \frac{\text{cm}^2}{\text{sec}}$$

9.51

We start with eq. (9.37). This tells us that, if the length of the tube, radius, and pressure drop remain constant, the time required is proportional to the viscosity. For an ideal gas, the viscosity is proportional to the square root of the temperature:

$$\frac{\Delta V}{\Delta t} = \frac{\pi \cdot r^4 \cdot \Delta P}{8 \cdot \eta \cdot l} \quad \eta = \frac{M \cdot \frac{8 \cdot R \cdot T}{\pi \cdot M}}{2 \cdot \sqrt{2} \cdot \pi \cdot \sigma^2 \cdot L}$$

Thus, we have:

$$T_1 = 773.15 \cdot K \quad T_2 = 293.15 \cdot K$$

$$\text{timeratio} = \frac{T_1}{T_2} \quad \text{timeratio} = 1.624 \quad \text{It will take 1.62 times as long at 500 C.}$$

9.53

Equation (9.51) relates the molecular diameter to the viscosity.

$$T = 292.05 \cdot K \quad \eta = 73.5 \cdot 10^{-6} \cdot \text{poise} \quad M = 74.1174 \cdot 10^{-3} \cdot \frac{\text{kg}}{\text{mole}} \quad R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot K}$$

$$L = 6.02 \cdot 10^{23} \cdot \frac{1}{\text{mole}} \quad \text{nm} = 10^{-9} \cdot \text{m}$$

$$\eta = \frac{M \cdot \frac{8 \cdot R \cdot T}{\pi \cdot M}}{2 \cdot \sqrt{2} \cdot \pi \cdot \sigma^2 \cdot L} \quad \sigma = \frac{M \cdot \frac{8 \cdot R \cdot T}{\pi \cdot M}}{2 \cdot \sqrt{2} \cdot \pi \cdot \eta \cdot L} \quad \sigma = 0.738 \cdot \text{nm}$$

9.55

We use eq. (9.48) to calculate the viscosity:

$$R = 8.31451 \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad M = 17.0305 \cdot 10^{-3} \frac{\text{kg}}{\text{mole}} \quad \text{nm} = 10^{-9} \cdot \text{m} \quad \mu\text{p} = 10^{-6} \cdot \text{poise}$$

$$L = 6.02 \cdot 10^{23} \frac{1}{\text{mole}} \quad k_s = 15.69 \frac{\mu\text{p}}{\text{K}} \quad S = 510 \cdot \text{K}$$

$$T = 373.15 \cdot \text{K} \quad \eta = \frac{k_s \cdot T}{L \cdot S} \quad \eta = 128.1 \cdot \mu\text{p}$$

$$T = 473.15 \cdot \text{K} \quad \eta = \frac{k_s \cdot T}{L \cdot S} \quad \eta = 164.2 \cdot \mu\text{p}$$

We can compute the diameter by solving eq. (9.49) for the diameter:

$$\sigma = \frac{\sqrt{R \cdot M}}{\pi \cdot 15 \cdot k_s \cdot L} \quad \sigma = 0.2675 \cdot \text{nm}$$

9.57

We fit the data to eq. (9.48) using a nonlinear regression program.

$$\eta = \frac{k_s \cdot T}{L \cdot S}$$

Alternatively, we can linearize the equation as follows, and use a linear regression package to find the parameters:

$$\ln \frac{\eta}{T} = \frac{S}{k_s} \cdot \frac{1}{T} - \frac{L}{k_s}$$

The parameters obtained using nonlinear regression are give below. We can compute the diameter by solving eq. (9.49) for the diameter:

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad M = 39.948 \cdot 10^{-3} \cdot \frac{\text{kg}}{\text{mole}} \quad \text{nm} = 10^{-9} \cdot \text{m} \quad \mu\text{p} = 10^{-6} \cdot \text{poise}$$

$$L = 6.02 \cdot 10^{23} \cdot \frac{\text{J}}{\text{mole}} \quad k_s = 19.09 \cdot \frac{\mu\text{p}}{\text{K}} \quad S = 137.7 \cdot \text{K}$$

$$\sigma = \frac{\sqrt{\frac{R \cdot M}{\pi^{1/2} \cdot k_s \cdot L}}}{\text{nm}} \quad \sigma = 0.3001 \cdot \text{nm}$$

9.59

Equation (9.47) gives the Enskog relation, which can be used to predict viscosities at higher pressures. First, we need the molar volume from the van der Waals equation of state:

$$P = 100 \cdot \text{atm} \quad T = 323.15 \cdot \text{K} \quad a = 0.3649 \cdot \frac{\text{Pa} \cdot \text{m}^6}{\text{mole}^2} \quad b = 42.74 \cdot 10^{-6} \cdot \frac{\text{m}^3}{\text{mole}}$$

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

As a first guess, use ifeal gas law: $V = \frac{R \cdot T}{P}$

$$V_m = \text{root } P \cdot V^3 - (R \cdot T - b \cdot P) \cdot V^2 - a \cdot V - a \cdot b, V \quad V_m = 149.351 \cdot \frac{\text{cm}^3}{\text{mole}}$$

The viscosity is then determined as follows. The value of b_0 can be found on Table 1.7.

$$\mu_p = 10^{-6} \cdot \text{poise} \quad b_0 = 113.9 \cdot \frac{\text{cm}^3}{\text{mole}} \quad \eta_0 = 163 \cdot \mu_p$$

$$\eta = \eta_0 \cdot \left(1 + 0.175 \cdot \frac{b_0}{V_m} + 0.865 \cdot \frac{b_0^2}{V_m^2} \right) \quad \eta = 266.8 \cdot \mu_p$$

9.61

The Mark-Houwink equation, eq. (9.54), can be used to obtain the intrinsic viscosity of polymeric solutions. The parameters can be found on Table 9.3:

$$K = 8.1 \cdot 10^{-2} \cdot \frac{\text{cm}^3}{\text{gm}} \quad \alpha = 0.5 \quad M = 1 \cdot 10^6 \quad \text{int}\eta = K \cdot M^\alpha \quad \text{int}\eta = 81 \cdot \frac{\text{cm}^3}{\text{gm}}$$

For a dilute solution, we can take the limit of eq. (9.51) to obtain the specific viscosity:

$$c_m = 20 \cdot \frac{\text{mg}}{\text{cm}^3} \quad \eta_{sp} = c_m \cdot \text{int}\eta \quad \eta_{sp} = 1.62$$

Finally, we use eq. (9.50) to obtain the viscosity:

$$\eta_0 = 7.5 \cdot 10^{-3} \cdot \text{poise} \quad \mu_p = 10^{-3} \cdot \text{poise}$$

$$\eta = \eta_0 \cdot (1 + \eta_{sp}) \quad \eta = 19.65 \cdot \mu_p$$

9.63

We can rearrange the Mark-Houwink equation as follows:

$$\text{int}\eta = K \cdot M_v^\alpha \quad M_v = \left(\frac{\text{int}\eta}{K} \right)^{\frac{1}{\alpha}}$$

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The intrinsic viscosity can be written as follows, using eqs. (9.50) and (9.51)

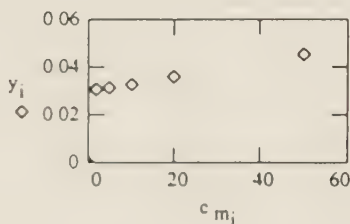
$$\text{intr}\eta = \lim_{c_m \rightarrow 0} \frac{\eta_{sp}}{c_m} \quad \eta_{sp} = \frac{\eta - \eta_0}{\eta_0} \quad \text{intr}\eta = \lim_{c_m \rightarrow 0} \frac{\eta - \eta_0}{c_m}$$

So, to find the intrinsic viscosity, we regress $(\eta/\eta_0 - 1)/c_m$ versus c_m , and find the limit as c_m goes to zero.

i = 0..5

$$y_i = \frac{\eta_i}{c_{m_i}} - \frac{6.04}{c_{m_i}}$$

c_{m_i}	η_i
0	6.04
2	6.41
5	6.98
10	8.02
20	10.38
50	19.69



The intrinsic viscosity seems to be about 0.003. We plug this result into the Mark-Houwink equation to find M_v .

$$\text{intr}\eta = 0.03 \cdot \frac{\text{cm}^3}{\text{mg}} \quad K = 0.95 \cdot 10^{-2} \cdot \frac{\text{cm}^3}{\text{gm}} \quad \alpha = 0.74$$

$$M_v = \frac{\text{intr}\eta^\alpha}{K} \quad M_v = 5.357 \cdot 10^4$$

We can use eq. (9.56) to find M_n :

$$\frac{M_v}{M_n} = ((1 - \alpha) \cdot \Gamma(1 - \alpha))^\alpha$$

$$M_n = \frac{M_v}{((1 - \alpha) \cdot \Gamma(1 - \alpha))^\alpha} \quad M_n = 2.85 \cdot 10^4$$

SECTION 9.5

9.65

We use eq. (9.57):

$$\omega = 2\pi \cdot \frac{\text{rev}}{\text{min}} \quad x = 6 \cdot \text{cm} \quad \Delta x = 5.1 \cdot \text{mm} \quad \Delta t = 3 \cdot \text{hr}$$

$$s = \frac{\Delta x}{\omega^2 \cdot x} \quad s = 1.994 \cdot 10^{13} \cdot \text{sec}$$

9.67

(a) We use eq. (9.58):

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad D = 0.4586 \cdot 10^{-5} \cdot \frac{\text{cm}^2}{\text{sec}} \quad \rho_0 = 0.9982 \cdot \frac{\text{gm}}{\text{cm}^3} \quad v_s = 0.630 \cdot \frac{\text{cm}^3}{\text{gm}}$$

$$T = 293.15 \cdot \text{K} \quad M = 342.2407 \cdot \frac{\text{gm}}{\text{mole}}$$

$$s = \frac{M \cdot D}{R \cdot T} \cdot \frac{1}{\rho_0 \cdot v_s} \quad s = 2.39 \cdot 10^{14} \cdot \text{sec}$$

(b) We use eq. (9.57):

$$\omega = 2\pi \cdot \frac{\text{rev}}{\text{min}} \quad x = 5 \cdot \text{cm} \quad \Delta x = 1 \cdot \text{mm} \quad \Delta t = 1 \cdot \text{hr}$$

$$\omega = \frac{\Delta x}{\Delta t} \cdot \frac{1}{s \cdot x} \quad \omega = 1.456 \cdot 10^5 \cdot \frac{\text{rev}}{\text{min}}$$

9.69

We use eq. (9.59) and solve for the molecular weight.

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad \text{rev} = 2 \cdot \pi \cdot \text{rad} \quad \omega = 80000 \cdot \frac{\text{rev}}{\text{min}} \quad \rho_0 = 0.9951 \cdot \frac{\text{gm}}{\text{cm}^3} \quad v_s = 0.75 \cdot \frac{\text{cm}^3}{\text{gm}}$$

$$T = 296.15 \cdot \text{K} \quad x_1 = 0.7 \cdot \text{cm} \quad x_2 = 1 \cdot \text{cm} \quad c2_c1 = 4.2$$

$$M = \frac{\ln(c2_c1)}{x_2^2 - x_1^2} \cdot \frac{2 \cdot R \cdot T}{(1 - \rho_0 \cdot v_s) \cdot \omega^2}$$

$$M = 7.783 \cdot 10^3 \cdot \frac{\text{gm}}{\text{mole}}$$

CHAPTER 10 *Chemical Kinetics*

SECTION 10.2

10.1

For a 3/2 order reaction, the rate law will be something like:

$$\frac{dc_a}{dt} = k \cdot c_a^{1.5} \quad \text{with the units:} \quad \frac{\text{mole}}{\text{liter} \cdot \text{sec}} = k \cdot \frac{\text{mole}^{1.5}}{\text{liter}^{1.5}}$$

Thus, k must have units of:

$$\frac{1}{\sqrt{\text{mole}}} \cdot \frac{\sqrt{\text{liter}}}{\text{sec}}$$

10.3

This is similar to example 10.1. We use eq. (10.4):

$\ln(v) = \ln(k) + n \cdot \ln(C)$ The slope of this plot will give the order of the reaction.

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$$i = 0..14$$

$$n = 0..13$$

t_i	C_i
0·min	1
2·min	0.9602
3·min	0.9427
5·min	0.9084
6·min	0.8911
8·min	0.8576
9·min	0.8412
11·min	0.8089
12·min	0.7957
14·min	0.7666
15·min	0.7530
17·min	0.7256
18·min	0.7107
20·min	0.6873
21·min	0.6735

$$v_n = \frac{C_n - C_{n-1}}{t_n - t_{n-1}} \cdot \text{min} \quad C_{av_n} = \frac{C_n + C_{n-1}}{2}$$

$$y_n = \ln v_n \quad x_n = \ln C_{av_n}$$

$$\text{order} = \text{slope}(x, y)$$

$$\text{order} = 1.073$$

10.5

We use the method of initial velocities to analyze this problem. First, we try to determine the rate law. From the first two data points, it appears that when we double $[\text{OCI-}]$, we double the rate. From the first and third data points, the conclusion is that when we double $[\text{I-}]$, we double the rate. Finally, from the first and fourth data points, we can see that when we decrease $[\text{OH-}]$ by a factor of two, we double the rate. This suggests that the rate law is first order in $[\text{OCI-}]$ and $[\text{I-}]$, and is inversely proportional to $[\text{OH-}]$:

$$v = k [\text{OCI-}] [\text{I-}] / [\text{OH-}]$$

Now, we can use any of the data points to estimate k .

$$v = 1.75 \cdot 10^{-4} \frac{\text{mole}}{\text{liter} \cdot \text{sec}} \quad [\text{OH-}] = 1 \frac{\text{mole}}{\text{liter}} \quad [\text{I-}] = 0.0017 \frac{\text{mole}}{\text{liter}} \quad [\text{OCI-}] = 0.0017 \frac{\text{mole}}{\text{liter}}$$

$$k = \frac{v \cdot [\text{OH-}]}{[\text{OCI-}] [\text{I-}]}$$

$$k = 60.554 \cdot \frac{1}{\text{sec}}$$

10.7

Since we do not have the partial pressures of the individual species, we must first derive them from the data given. Let us write the reaction as $A = 2B + C$, and define an extent of reaction, x . Then, the partial pressures of the species at any time will be:

$$P_A = P_0 - x$$

$$P_B = 2 \cdot x$$

$$P_C = x$$

and the total pressure will be:

$$P = P_A + P_B + P_C + P_{N_2} = P_0 - x + 2 \cdot x + x + 4.2 \text{ torr}$$

$$P = P_0 + 2 \cdot x + 4.2 \text{ torr}$$

$$x = \frac{P - 4.2 \text{ torr} - P_0}{2}$$

Now, for a first order reaction:

$$\frac{dP_A}{dt} = -k \cdot P_A \quad P_A = P_0 - x$$

$$\frac{dx}{dt} = k \cdot P_0 - x$$

$$\ln \frac{P_0 - x}{P_0} = -k \cdot t$$

So, a plot of the left-hand side vs. t should be linear with a slope of $-k$.

$$i = 0..14$$

$$t_i = P_i$$

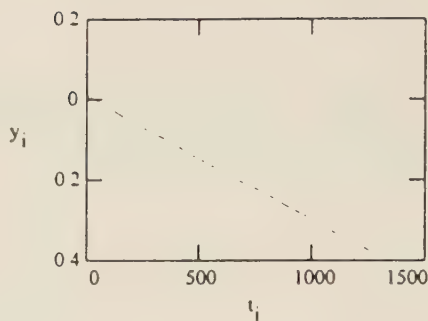
0 min	173.5 torr
2 min	187.3 torr
3 min	193.4 torr
5 min	205.3 torr
6 min	211.3 torr
8 min	222.9 torr
9 min	228.6 torr
11 min	239.8 torr
12 min	244.4 torr
14 min	254.4 torr
15 min	259.2 torr
17 min	268.7 torr
18 min	273.9 torr
20 min	282.0 torr
21 min	286.8 torr

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$$x_i = \frac{P_i - 4.2 \text{ torr}}{2} \quad y_i = \ln \frac{P_0 - x_i}{P_0}$$

$$k = \text{slope}(t, y)$$

$$k = 0.0185 \cdot \frac{1}{\text{min}}$$



10.9

We use eq. (10.6). This shows that a graph of $\ln(I - I_{\text{inf}})$ vs. t will be linear with a slope of $-k$.

$$I - I_{\text{inf}} = I_0 - I_{\text{inf}} \cdot \exp(-k \cdot t)$$

$$I_0 = 0.14 \quad I_{\text{inf}} = 4.95$$

t_i	I_i
1-sec	3.65
2-sec	2.87
3-sec	2.03
4-sec	0.992
5-sec	0.517
6-sec	0.274
8-sec	1.22
10-sec	1.99
12-sec	2.77
14-sec	3.17
16-sec	3.46
20-sec	3.91
24-sec	4.41
30-sec	4.76
35-sec	4.79

$$y_i = \ln \frac{I_i - I_{\text{inf}}}{I_0 - I_{\text{inf}}}$$

$$k = \text{slope}(t, y)$$

$$k = 0.122 \cdot \frac{1}{\text{sec}}$$

The relaxation time is defined as $1/k$.

$$\tau_R = \frac{1}{k}$$

$$\tau_R = 8.201 \cdot \text{sec}$$

10.11

We can use the information given to calculate the rate constant. Since the reaction is first-order, we know that it follows an exponential decay. When the reaction is 20% complete, 80% of the reactant remains.

$$\text{conc} = e^{-k \cdot t} \quad t_{0.8} = 20 \cdot \text{min} \quad \text{conc} = 0.80$$

$$k = \frac{\ln(\text{conc})}{t_{0.8}} \quad k = 1.86 \cdot 10^{-4} \cdot \frac{1}{\text{sec}}$$

When the reaction is 90% complete, the concentration of the reactant will be 10% of the original concentration.

$$\text{conc} = 0.1 \quad t = \frac{\ln(\text{conc})}{k} \quad t = 206.4 \cdot \text{min}$$

10.13

Since we are only given total pressure, we must relate this to the partial pressure of ethylene oxide and the extent of reaction. Let x be the extent of reaction. Then the partial pressures of the species will be:

$$P_{\text{EO}} = P_0 - x$$

$$P_{\text{CH}_4} = x$$

$$P_{\text{CO}} = x$$

The total pressure is given by:

$$P = P_{\text{EO}} + P_{\text{CH}_4} + P_{\text{CO}} = P_0 - x + 2 \cdot x$$

$$P = P_0 + x$$

$$x = P - P_0 \quad P_{\text{EO}} = P_0 - x = P_0 - (P - P_0) = 2 \cdot P_0 - P$$

$$i = 0..9$$

$$t_i \quad P_i$$

0 min	115.30 torr
6 min	122.91 torr
7 min	124.51 torr
8 min	126.18 torr
9 min	127.53 torr
10 min	129.10 torr
11 min	130.57 torr
12 min	132.02 torr
13 min	133.49 torr
18 min	140.16 torr

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 Since the reaction is first-order, we have:

$$\frac{dP_{EO}}{dt} = -k \cdot P_{EO}$$

$$\frac{d(2 \cdot P_0 - P)}{dt} = -k(2 \cdot P_0 - P)$$

$$\ln \frac{2 \cdot P_0 - P}{2 \cdot P_0 - P_0} = -k \cdot t \quad \text{A plot of the left-hand side vs. } t \text{ should yield a linear plot with a slope of } -k.$$

$$y_i = \ln \frac{2 \cdot P_0 - P_i}{2 \cdot P_0 - P_0} \quad k = \text{slope}(t, y) \quad k = 1.371 \cdot 10^{-2} \cdot \frac{1}{\text{min}}$$

We can repeat this calculation without the zero point:

$$i = 0..8$$

t_i	P_{r_i}
6 min	122.91 torr
7 min	124.51 torr
8 min	126.18 torr
9 min	127.53 torr
10 min	129.10 torr
11 min	130.57 torr
12 min	132.02 torr
13 min	133.49 torr
18 min	140.16 torr

$$y_i = \ln \frac{2 \cdot P_0 - P_{r_i}}{2 \cdot P_0 - P_0} \quad k = \text{slope}(t, y) \quad k = 1.451 \cdot 10^{-2} \cdot \frac{1}{\text{min}}$$

10.15

The concentration will be proportional to the volume of titer. Since the reaction is pseudo-first order, we can plot $\ln(\text{titer})$ vs. time to obtain the rate constant.

$$\text{ml} = 10^{-3} \cdot \text{liter}$$

$$i = 0..5$$

t_i	Titer _i
0 min	24.5 ml
15 min	18.1 ml
30 min	13.2 ml
45 min	9.7 ml
60 min	7.1 ml
75 min	5.2 ml

$$y_i = \ln \frac{\text{Titer}_i}{\text{mL}}$$

$$k = \text{slope}(t, y)$$

$$k = 2.07 \cdot 10^{-2} \cdot \frac{1}{\text{min}}$$

10.17

Since a and b are equal, we can use eq. (10.8), and solve for the time. When the reaction is 90% complete, the concentrations of the reactants will be 10% of the original value.

$$C_o = 0.365 \frac{\text{mole}}{\text{liter}} \quad k = 1.23 \frac{\text{liter}}{\text{mole} \cdot \text{sec}} \quad C_{\text{final}} = 0.1 \cdot C_o$$

$$\frac{1}{C_{\text{final}}} - \frac{1}{C_o} = k \cdot t \quad t = \frac{\frac{1}{C_{\text{final}}} - \frac{1}{C_o}}{k} \quad t = 20.75 \cdot \text{sec}$$

10.19

Since the reaction is second-order, we can use eq. (10.10):

$$\frac{1}{L} - \frac{1}{L_{\text{inf}}} = \frac{1}{L_o} - \frac{1}{L_{\text{inf}}} - \frac{C_o \cdot k \cdot t}{L_o \cdot L_{\text{inf}}} \quad t_{\text{inf}} = 0.560$$

$$i = 0.8$$

$$t_i = L_i$$

$$L_{\text{inf}} = 0.560 \quad C_o = 0.01 \frac{\text{mole}}{\text{liter}}$$

0-min	1.560
5-min	1.315
7-min	1.247
9-min	1.193
15-min	1.064
18-min	1.020
20-min	0.994
25-min	0.945
27-min	0.923

$$y_i = \frac{1}{L_i} - \frac{1}{L_{\text{inf}}}$$

$$\text{intercept}(t, y) = 1.003$$

$$k = \frac{\text{slope}(t, y)}{C_o \cdot \text{intercept}(t, y)}$$

$$k = 6.448 \frac{\text{liter}}{\text{mole} \cdot \text{min}}$$

10.21

We use eq. (10.11b):

$$k \cdot t = \frac{1}{(b-a)} \cdot \ln \frac{a \cdot (b-x)}{b \cdot (a-x)}$$

$$a = 2.508 \cdot 10^{-3} \frac{\text{mole}}{\text{liter}} \quad b = 3.230 \cdot 10^{-3} \frac{\text{mole}}{\text{liter}} \quad \text{mmol} = 10^{-3} \cdot \text{mole}$$

$$i = 0..6$$

t_i	BrO_i
0·min	0·mmol liter
3.65·min	0.560·mmol liter
7.65·min	0.953·mmol liter
15.05·min	1.420·mmol liter
26.00·min	1.800·mmol liter
47.60·min	2.117·mmol liter
90.60·min	2.367·mmol liter

$$x_i = \text{BrO}_i$$

$$y_i = \frac{1}{(b-a)} \cdot \ln \frac{a \cdot b - x_i}{b \cdot a - x_i}$$

$$k = \text{slope}(t, y)$$

$$k = 0.396 \cdot \frac{\text{liter}}{\text{mole} \cdot \text{sec}}$$

10.23

A second-order reaction will have a rate law of the form:

$$\frac{dC}{dt} = k \cdot C^2$$

$$C = p \cdot \lambda - \lambda_{\text{inf}}$$

$$\frac{d(p \cdot \lambda - \lambda_{\text{inf}})}{dt} = k \cdot (p \cdot \lambda - \lambda_{\text{inf}})^2$$

$$p \cdot \frac{d\lambda_{\text{inf}}}{dt} = k \cdot p^2 \cdot \lambda_{\text{inf}}^2$$

$$\frac{d\lambda_{\text{inf}}}{dt} = k \cdot p \cdot \lambda_{\text{inf}}^2$$

$$\int_{\lambda_0}^{\lambda_{\text{inf}}} \frac{1}{\lambda \cdot \lambda_{\text{inf}}^2} d\lambda_{\text{inf}} = \int_0^t k \cdot p dt$$

$$\frac{1}{\lambda_{\text{inf}}} - \frac{1}{\lambda_0} = k \cdot p \cdot t$$

$$\frac{1}{\lambda_{\text{inf}}} - \frac{1}{\lambda_0} = k \cdot p \cdot t$$

We can find the value of the proportionality constant by using the initial concentration:

$$C_0 = p \cdot \lambda_0 \cdot \lambda_{\text{inf}} \quad p = \frac{C_0}{\lambda_0 \cdot \lambda_{\text{inf}}}$$

$$\frac{1}{\lambda_{\text{inf}}} - \frac{1}{\lambda_0} = \frac{k \cdot C_0 \cdot t}{\lambda_0 \cdot \lambda_{\text{inf}}}$$

10.25

Let x be the extent of reaction. Then, the concentrations of A and P at any time will be:

$$A = a - x \quad P = p - x$$

We can substitute these into the rate law to obtain:

$$\frac{d(a - x)}{dt} = k(a - x) \cdot (p - x)$$

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Since a is a constant:

$$\frac{d(a - x)}{dt} = -\frac{dx}{dt}$$

$$\frac{dx}{dt} = k \cdot (a - x) \cdot (p - x)$$

$$\int_0^{x_t} \frac{1}{k \cdot (a - x) \cdot (p - x)} dx = \int_0^t 1 dt$$

$$t = \frac{\ln(a - x_t) - \ln(p - x_t) - \ln(a) + \ln(p)}{(p - a) \cdot k}$$

$$t = \frac{\ln \frac{p - x_t}{a - x_t} - \ln \frac{a}{p}}{k \cdot (p - a)}$$

$$t = \frac{\ln \frac{a \cdot p - x_t}{p \cdot a - x_t} - \ln \frac{a}{p}}{k \cdot (p - a)}$$

SECTION 10.3

10.27

The dependence of the rate constant on temperature is given by eq. (10.18):

$$\frac{d \ln(k)}{dT} = -\frac{E_a}{R \cdot T^2}$$

The rate will increase faster for the reaction with the larger activation energy. Even if you don't remember eq. (10.18), you should be able to tell this from the definition of an activation energy.

10.29

If both rate constants follow an Arrhenius dependence on temperature, and the pre-exponential factors are independent of temperature, we can compute the activation energy:

$$\frac{k_1}{k_2} = \frac{A \cdot e^{\frac{E_a}{R T_1}}}{A \cdot e^{\frac{E_a}{R T_2}}} = \exp \left(\frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right)$$

$$E_a = \frac{R \cdot \ln \frac{k_1}{k_2}}{\frac{1}{T_2} - \frac{1}{T_1}}$$

$$R = 8.31451 \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad \text{kJ} = 1000 \cdot \text{joule} \quad k_{\text{ratio}} = \frac{1}{2} \quad T_1 = 298.15 \cdot \text{K} \quad T_2 = 308.15 \cdot \text{K}$$

$$E_a = \frac{R \cdot \ln k_{\text{ratio}}}{\frac{1}{T_2} - \frac{1}{T_1}} = 53 \cdot \text{kJ}$$

We can use eq. (10.18):

$$\ln(k) = \ln(A) - \frac{E_a}{R \cdot T}$$

$$i = 0..9$$

$$T_i =$$

$$k_i =$$

$$kJ = 1000 \cdot \text{joule}$$

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot K}$$

273.1 · K	7.97 · 10 ⁷ · $\frac{1}{\text{sec}}$
288.1 · K	
293.1 · K	1.04 · 10 ⁵ · $\frac{1}{\text{sec}}$
298.1 · K	
308.1 · K	1.76 · 10 ⁵ · $\frac{1}{\text{sec}}$
313.1 · K	
318.1 · K	3.38 · 10 ⁵ · $\frac{1}{\text{sec}}$
323.1 · K	
328.1 · K	1.35 · 10 ⁴ · $\frac{1}{\text{sec}}$
338.1 · K	
	2.47 · 10 ⁴ · $\frac{1}{\text{sec}}$
	4.98 · 10 ⁴ · $\frac{1}{\text{sec}}$
	7.59 · 10 ⁴ · $\frac{1}{\text{sec}}$
	1.50 · 10 ³ · $\frac{1}{\text{sec}}$
	4.87 · 10 ³ · $\frac{1}{\text{sec}}$

$$y_i = \ln k_i \cdot \text{sec}$$

$$x_i = \frac{1}{T_i}$$

$$E_a = R \cdot \text{slope}(x, y)$$

$$E_a = 101.401 \cdot \frac{kJ}{\text{mole}}$$

$$A = \exp(\text{intercept}(x, y))$$

$$A = 2.105 \cdot 10^{13}$$

10.33

$$k = \frac{k_1 \sqrt{k_2}}{k_3} = \frac{A_1 e^{-E_{a1}/RT} \sqrt{A_2 e^{-E_{a2}/RT}}}{A_3 e^{-E_{a3}/RT}}$$

$$\ln(k) = -\frac{E_{a\text{overall}}}{RT} + \ln(A) = -\frac{E_{a1}}{RT} - \frac{1}{2} \frac{E_{a2}}{RT} + \frac{E_{a3}}{RT} + \ln\left(\frac{A_1 \sqrt{A_2}}{A_3}\right)$$

We combine all the terms which are divided by RT to obtain the activation energy:

$$E_{a\text{overall}} = E_{a1} + \frac{1}{2} E_{a2} - E_{a3}$$

SECTION 10.4

10.35

We use eq. (10.23):

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad M_A = 15.0348 \cdot \frac{\text{gm}}{\text{mole}} \quad M_B = M_A \quad L\mu = \frac{M_A \cdot M_B}{M_A - M_B}$$

$$p = 1 \quad \sigma = 4 \cdot 10^{-8} \cdot \text{cm} \quad S_{AB} = \pi \cdot \sigma^2 \quad T = 500 \cdot \text{K}$$

$$L = 6.022137 \cdot 10^{23} \cdot \frac{1}{\text{mole}} \quad E_{\min} = 0 \cdot \frac{\text{joule}}{\text{mole}}$$

$$k = p \cdot L \cdot S_{AB} \cdot \frac{8 \cdot R \cdot T}{\pi \cdot L \mu} \cdot \exp \left(\frac{E_{\min}}{R \cdot T} \right) \quad k = 3.592 \cdot 10^{14} \cdot \frac{\text{cm}^3}{\text{mole} \cdot \text{sec}}$$

10.37

We use eq. (10.23):

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad M_A = 31.9988 \cdot \frac{\text{gm}}{\text{mole}} \quad M_B = 2.0159 \cdot \frac{\text{gm}}{\text{mole}} \quad L\mu = \frac{M_A \cdot M_B}{M_A - M_B}$$

$$p = 1 \quad \sigma_A = 0.358 \cdot 10^{-9} \cdot \text{m} \quad \sigma_B = 0.287 \cdot 10^{-9} \cdot \text{m} \quad \sigma_{AB} = \frac{1}{2} \cdot \sigma_A + \sigma_B$$

$$L = 6.022137 \cdot 10^{23} \cdot \frac{1}{\text{mole}} \quad E_{\min} = 0 \cdot \frac{\text{joule}}{\text{mole}} \quad T = 1500 \cdot \text{K} \quad S_{AB} = \pi \cdot \sigma_{AB}^2$$

$$k = p \cdot L \cdot S_{AB} \cdot \frac{8 \cdot R \cdot T}{\pi \cdot L \mu} \cdot \exp \left(\frac{E_{\min}}{R \cdot T} \right) \quad k = 8.052 \cdot 10^{14} \cdot \frac{\text{cm}^3}{\text{mole} \cdot \text{sec}}$$

10.39

We use the formulas for a bimolecular reaction, eq. (10.28).

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad h = 6.62607 \cdot 10^{-34} \cdot \text{joule} \cdot \text{sec} \quad k_B = 1.38066 \cdot 10^{-23} \cdot \frac{\text{joule}}{\text{K}} \quad \text{kJ} = 1000 \cdot \text{joule}$$

$$E_a = 42 \cdot \frac{\text{kJ}}{\text{mole}} \quad A = 8 \cdot 10^{13} \cdot \frac{\text{cm}^3}{\text{mole} \cdot \text{sec}} \quad T = 300 \cdot \text{K} \quad C = 1 \cdot \frac{\text{mole}}{\text{cm}^3}$$

$$\Delta S = R \cdot \ln \frac{A \cdot h \cdot C}{e^2 \cdot k_B \cdot T} \quad \Delta S = 4.6 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\Delta H = E_a - 2 \cdot R \cdot T \quad \Delta H = 37 \cdot \frac{\text{kJ}}{\text{mole}}$$

10.41

This is similar to example 10.9. We can write:

$$\ln \frac{k_i \cdot h}{k_B \cdot T_i} = \frac{\Delta S}{R} - \frac{\Delta H}{R \cdot T_i}$$

i = 0..8

T_i

k_i

556·K
575·K
625·K
647·K
666·K
683·K
700·K
716·K
781·K

$3.25 \cdot 10^{-7}$
$1.22 \cdot 10^{-6}$
$3.02 \cdot 10^{-5}$
$8.59 \cdot 10^{-5}$
$2.19 \cdot 10^{-4}$
$5.12 \cdot 10^{-4}$
$1.16 \cdot 10^{-3}$
$2.50 \cdot 10^{-3}$
$3.95 \cdot 10^{-2}$

$$R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}} \quad h = 6.62607 \cdot 10^{-34} \cdot \text{joule} \cdot \text{sec} \quad \text{kJ} = 1000 \cdot \text{joule}$$

$$k_B = 1.38066 \cdot 10^{-23} \cdot \frac{\text{joule}}{\text{K}}$$

$$y_i = \ln \frac{k_i \cdot h}{k_B \cdot T_i \cdot \text{sec}} \quad x_i = \frac{1}{T_i}$$

$$\Delta S = R \cdot \text{intercept}(x, y) \quad \Delta S = 49.749 \cdot \frac{\text{joule}}{\text{mole} \cdot \text{K}}$$

$$\Delta H = R \cdot \text{slope}(x, y) \quad \Delta H = 180.561 \cdot \frac{\text{kJ}}{\text{mole}}$$

SECTION 10.5

10.43

We use L'Hopital's rule, taking derivatives with respect to k_2 , and taking the limit as $k_2 \rightarrow k_1$.

$$[B] = \frac{k_1 a (e^{-k_1 t} - e^{-k_2 t})}{k_2 - k_1}$$

$$[B] = \lim (k_2 \rightarrow k_1) \left[\frac{k_1 a (t e^{-k_2 t})}{1} \right]$$

$$[B] = k_1 a t e^{-k_1 t}$$

10.45

We use L'Hopital's rule, taking derivatives with respect to k_2 of eq. (10.34b), and taking the limit as $k_2 \rightarrow k_1$.

$$[B] = \frac{k_1 a (e^{-k_1 t} - e^{-k_2 t})}{k_2 - k_1}$$

$$[B] = \lim (k_2 \rightarrow k_1) \left[\frac{k_1 a (t e^{-k_2 t})}{1} \right]$$

$$[B] = k_1 a t e^{-k_1 t}$$

SECTION 10.6

10.47

We must rearrange eq. (10.41):

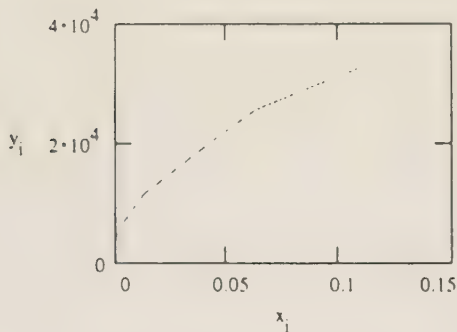
$$k_{\text{uni}} = \frac{k_1 \cdot k_3 \cdot M}{k_3 + k_2 \cdot M}$$

$$\frac{1}{k_{\text{uni}}} = \frac{1}{k_1 \cdot M} + \frac{k_2}{k_1 \cdot k_3} \quad M = \frac{N}{V} = \frac{P}{RT}$$

$$\frac{1}{k_{\text{uni}}} = \frac{R \cdot T}{k_1 \cdot P} + \frac{k_2}{k_1 \cdot k_3}$$

So, a plot of $1/k_{\text{uni}}$ vs. $1/P$ should be linear if the Lindeman mechanism holds.

$$y_i = \frac{1}{k_i} \quad x_i = \frac{1}{P_i}$$



The graph deviates from linearity, indicating that the Lindeman mechanism does not explain this data very well.

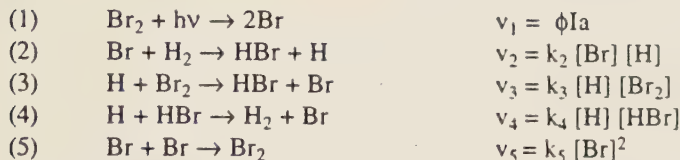
 $i = 0..9$ $P_i =$ $k_i =$

84.1·torr	$2.98 \cdot 10^{-4} \cdot \frac{1}{\text{sec}}$
34.0·torr	
11.0·torr	$2.82 \cdot 10^{-4} \cdot \frac{1}{\text{sec}}$
6.07·torr	
2.89·torr	$2.23 \cdot 10^{-4} \cdot \frac{1}{\text{sec}}$
1.37·torr	
0.569·torr	$2.00 \cdot 10^{-4} \cdot \frac{1}{\text{sec}}$
0.170·torr	
0.120·torr	$1.54 \cdot 10^{-4} \cdot \frac{1}{\text{sec}}$
0.067·torr	
	$1.30 \cdot 10^{-4} \cdot \frac{1}{\text{sec}}$
	$0.875 \cdot 10^{-4} \cdot \frac{1}{\text{sec}}$
	$0.486 \cdot 10^{-4} \cdot \frac{1}{\text{sec}}$
	$0.392 \cdot 10^{-4} \cdot \frac{1}{\text{sec}}$
	$0.303 \cdot 10^{-4} \cdot \frac{1}{\text{sec}}$

SECTION 10.7

10.49

Example (10.16) shows the velocity for a photo-initiated reaction. The elementary steps and velocities are:



The overall rate can be written in terms of the disappearance of Br_2 :

$$-d[\text{Br}_2]/dt = v_1 + v_3 - v_5$$

Now, we use the steady-state approximation on the radical species:

$$\begin{aligned}
 0 = d[\text{H}]/dt &= v_2 - v_3 - v_4 & 0 = d[\text{Br}]/dt &= 2v_1 - v_2 + v_3 + v_4 - 2v_5 \\
 v_2 - v_3 &= v_4 & 2v_1 &= 2v_5 \\
 & & v_1 &= v_5 \\
 & & \phi I_a &= k_5 [\text{Br}]^2 \\
 & & [\text{Br}] &= [\phi I_a / k_5]^{1/2}
 \end{aligned}$$

Now that we have an expression for the concentration of Br, we can use the equation for $d[\text{H}]/dt$ to find $[\text{H}]$:

$$v_2 - v_3 = v_4$$

$$k_2 [\text{Br}] [\text{H}_2] - k_3 [\text{H}] [\text{Br}_2] = k_4 [\text{H}] [\text{HBr}]$$

$$k_2 [\phi I_a / k_5]^{1/2} [\text{H}_2] - k_3 [\text{H}] [\text{Br}_2] = k_4 [\text{H}] [\text{HBr}]$$

$$k_2 [\text{H}_2] [\phi I_a / k_5]^{1/2} = [\text{H}] (k_4 [\text{HBr}] + k_3 [\text{Br}_2])$$

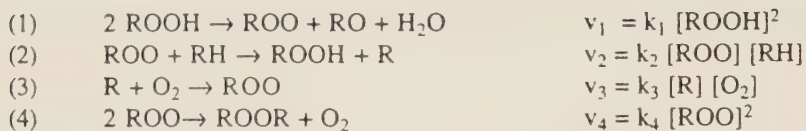
$$[\text{H}] = \frac{k_2 [\text{H}_2] \sqrt{\phi I_a}}{\sqrt{k_5} (k_4 [\text{HBr}] + k_3 [\text{Br}_2])}$$

Now, since $v_1 = v_5$, the overall rate is given by v_3 :

$$v = v_3 = k_3 [\text{H}] [\text{Br}_2] = \frac{k_2 k_3 [\text{H}_2] [\text{Br}_2] \sqrt{\phi I_a}}{\sqrt{k_5} (k_4 [\text{HBr}] + k_3 [\text{Br}_2])}$$

10.51

The elementary steps and velocities are:



The overall rate can be written in terms of the disappearance of O_2 :

$$-d[\text{O}_2]/dt = v_3 - v_4$$

Now, we use the steady-state approximation on the radical species:

$0 = d[\text{R}]/dt = v_3 - v_4$	$0 = d[\text{ROO}]/dt = v_1 - v_2 + v_3 - 2v_4$
$k_2 [\text{ROO}] [\text{RH}] = k_3 [\text{R}] [\text{O}_2]$	$v_1 = 2v_4$
$[\text{R}] = k_2 [\text{ROO}] [\text{RH}] / k_3 [\text{O}_2]$	$k_1 [\text{ROOH}]^2 = 2k_4 [\text{ROO}]^2$
	$[\text{ROO}] = [\text{ROOH}] [k_1 / 2k_4]^{1/2}$

We can solve for the concentration of $[\text{R}]$ now:

$$[\text{R}] = k_2 [\text{ROO}] [\text{RH}] / k_3 [\text{O}_2]$$

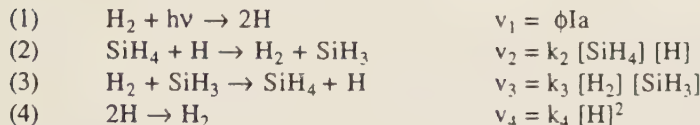
$$[\text{R}] = \left[\frac{k_1 k_2^2}{2k_3^2 k_4} \right]^{1/2} \frac{[\text{ROOH}] [\text{RH}]}{[\text{O}_2]}$$

Now, we know that the overall rate is given by $v_3 - v_4$. If we make the long-chain approximation, then the rate of propagation is much larger than the rate of termination, and so we assume that the overall rate is given by v_3 .

$$v = v_3 = k_3 [\text{O}_2] [\text{R}] = \left[\frac{k_1 k_2^2}{2k_4} \right]^{1/2} [\text{ROOH}] [\text{RH}]$$

10.53

Example (10.16) shows the velocity for a photo-initiated reaction. The elementary steps and velocities are:



We use the steady-state approximation on the radical species:

$$\begin{aligned}
 0 &= d[\text{SiH}_3]/dt = v_2 - v_3 & 0 &= d[\text{H}]/dt = 2v_1 - v_2 + v_3 - 2v_4 \\
 k_2 [\text{SiH}_4] [\text{H}] &= k_3 [\text{H}_2] [\text{SiH}_3] & 2v_1 &= 2v_4 \\
 & & v_1 &= v_4 \\
 & & \phi I_a &= k_4 [\text{H}]^2 \\
 & & [\text{H}] &= [\phi I_a / k_4]^{1/2}
 \end{aligned}$$

Now we can solve for $[\text{SiH}_3]$:

$$k_2 [\text{SiH}_4] [\text{H}] = k_3 [\text{H}_2] [\text{SiH}_3]$$

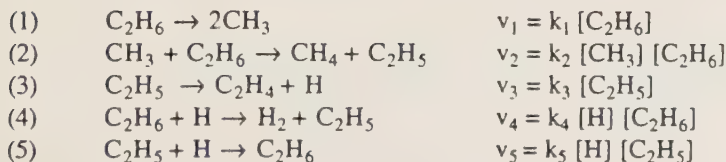
$$k_2 [\text{SiH}_4] \sqrt{\frac{I_a \phi}{k_4}} = k_3 [\text{H}_2] [\text{SiH}_3]$$

$$[\text{SiH}_3] = \frac{k_2 [\text{SiH}_4]}{k_3 [\text{H}_2]} \sqrt{\frac{I_a \phi}{k_4}}$$

$[\text{SiH}_3]$ is inversely proportional to $[\text{H}_2]$. If the goal is to maximize $[\text{SiH}_3]$, then the concentration of hydrogen should be small.

10.55

The elementary steps and velocities are:



The overall velocity can be written in terms of the appearance of ethylene:

$$v = d[\text{C}_2\text{H}_4]/dt = v_3 = k_3 [\text{C}_2\text{H}_5]$$

We use the steady-state approximation on the radical species:

$$0 = d[\text{CH}_3]/dt = 2v_1 - v_2$$

$$0 = d[\text{H}]/dt = v_3 - v_4 - v_5$$

$$0 = d[\text{C}_2\text{H}_5]/dt = v_2 - v_3 + v_4 - v_5$$

We can add the last two equations and substitute $2v_1 = v_2$. This gives us an expression for the concentration of H:

$$2v_1 = 2v_5$$

$$k_1 [\text{C}_2\text{H}_6] = k_5 [\text{H}] [\text{C}_2\text{H}_5]$$

$$[\text{H}] = k_1 [\text{C}_2\text{H}_6] / k_5 [\text{C}_2\text{H}_5]$$

Now, we use the equation from the steady-state assumption on [H] to solve for the concentration of the ethyl radical.

$$0 = v_3 - v_4 - v_5$$

We use the long chain approximation (the rate of propagation is much faster than termination), so $v_4 \gg v_5$, and we have:

$$v_3 = v_4 \quad k_3 [\text{C}_2\text{H}_5] = k_4 [\text{H}] [\text{C}_2\text{H}_6]$$

$$k_3 [\text{C}_2\text{H}_5] = \frac{k_1 k_4 [\text{C}_2\text{H}_6]^2}{k_5 [\text{C}_2\text{H}_5]}$$

$$k_3 k_5 [\text{C}_2\text{H}_5]^2 = k_1 k_4 [\text{C}_2\text{H}_6]^2$$

$$[\text{C}_2\text{H}_5] = \sqrt{\frac{k_1 k_4}{k_3 k_5}} [\text{C}_2\text{H}_6]$$

Thus, the overall rate is given by:

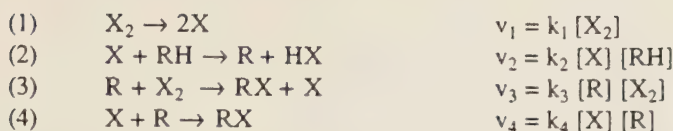
$$v = k_3 [\text{C}_2\text{H}_5] = k_3 \sqrt{\frac{k_1 k_4}{k_3 k_5}} [\text{C}_2\text{H}_6] = k_{\text{eff}} [\text{C}_2\text{H}_6] \quad \text{where} \quad k_{\text{eff}} = \sqrt{\frac{k_1 k_3 k_4}{k_5}}$$

With this effective rate constant, the activation energy of the overall reaction will be:

$$E_{a_{\text{eff}}} = \frac{1}{2} (E_{a_1} + E_{a_3} + E_{a_4} - E_{a_5})$$

10.57

The elementary steps and velocities are:



The overall velocity can be written in terms of the appearance of HX:

$$v = d[HX]/dt = v_2 = k_2 [X] [RH]$$

We use the steady-state approximation on the radical species:

$$0 = d[R]/dt = v_2 - v_3 - v_4$$

$$0 = d[X]/dt = 2v_1 - v_2 + v_3 - v_4$$

We can add the last two equations to obtain an expression for [R]:

$$2v_1 = 2v_4$$

$$k_1 [X_2] = k_4 [X] [R]$$

$$[R] = k_1 [X_2] / k_4 [X]$$

Now, we use the equation from the steady-state assumption on [R] to solve for [X]:

$$0 = v_2 - v_3 - v_4$$

We use the long chain approximation (the rate of propagation is much faster than termination), so $v_3 \gg v_4$, and we have:

$$v_2 = v_3 \quad k_2 [X] [RH] = k_3 [R] [X_2]$$

$$k_2 [X] [RH] = \frac{k_1 k_3 [X_2]^2}{k_4 [X]}$$

$$k_2 k_4 [X]^2 [RH] = k_1 k_3 [X_2]^2$$

$$[X] = \sqrt{\frac{k_1 k_3}{k_2 k_4}} \frac{[X_2]}{[RH]^{1/2}}$$

Thus, the overall rate is given by:

$$v = k_2 [X] [RH] = k_2 \sqrt{\frac{k_1 k_3}{k_2 k_4}} \frac{[X_2]}{[RH]^{1/2}} [RH] = k_{\text{eff}} [X_2] [RH]^{1/2} \quad \text{where} \quad k_{\text{eff}} = \sqrt{\frac{k_1 k_2 k_3}{k_4}}$$

SECTION 10.8

10.59

The rate of propagation for these types of reactions is given by eq. (10.49):

$$v_p = k_p [M] [R_x \cdot]$$

To obtain $[R_x \cdot]$, we set the rate of initiation equal to the rate of termination:

$$I_a \phi = k_t [R_x \cdot]^2$$

$$[R_x \cdot] = \sqrt{\frac{I_a \phi}{k_t}}$$

$$v_p = k_p [M] [R_x \cdot] = \frac{k_p \sqrt{I_a \phi}}{k_t^{1/2}} [M]$$

The kinetic chain length can now be computed using eq. (10.44):

$$\bar{v} = \frac{v_p}{v_i} = \frac{k_p \sqrt{I_a \phi}}{k_t^{1/2} I_a \phi} [M] = \frac{k_p [M]}{\sqrt{k_t I_a \phi}}$$

10.61

We use eq. (10.51) to compute the rate of polymerization:

$$k_p = 2.3 \cdot 10^3 \cdot \frac{\text{liter}}{\text{mole} \cdot \text{sec}}$$

$$k_t = 2.9 \cdot 10^2 \cdot \frac{\text{liter}}{\text{mole} \cdot \text{sec}}$$

$$k_i = 1.07 \cdot 10^{-5} \cdot \text{sec}$$

$$kJ = 1000 \cdot \text{joule}$$

$$f = 1$$

$$M = 1 \cdot \frac{\text{mole}}{\text{liter}}$$

$$I_n = 0.001 \cdot \frac{\text{mole}}{\text{liter}}$$

$$v_p = k_p \cdot \sqrt{\frac{k_i \cdot f}{k_t}} \cdot M \cdot I_n^{0.5}$$

$$v_p = 0.014 \cdot \frac{\text{mole}}{\text{liter}}$$

To calculate the activation energy, we define an effective rate constant:

$$k_{\text{eff}} = k_p \cdot \sqrt{\frac{k_i}{k_t}} \quad E_{a_p} = 26 \cdot \frac{\text{kJ}}{\text{mole}} \quad E_{a_t} = 13 \cdot \frac{\text{kJ}}{\text{mole}} \quad E_{a_i} = 130 \cdot \frac{\text{kJ}}{\text{mole}}$$

$$E_{a_{\text{eff}}} = E_{a_p} + \frac{1}{2} \cdot E_{a_i} - \frac{1}{2} \cdot E_{a_t} \quad E_{a_{\text{eff}}} = 84.5 \cdot \frac{\text{kJ}}{\text{mole}}$$

Since the activation energy is positive, the rate will increase with temperature. To look at the behavior of the kinetic chain length, we use eq. (10.52) and define an effective rate constant again:

$$v = \frac{k_p \cdot M}{\sqrt{f \cdot k_i \cdot k_t} \cdot \ln} \quad k_v = \frac{k_p}{\sqrt{k_i \cdot k_t}} \quad E_{a_v} = E_{a_p} - \frac{1}{2} \cdot E_{a_i} - \frac{1}{2} \cdot E_{a_t}$$

$$E_{a_v} = -45.5 \cdot \frac{\text{kJ}}{\text{mole}}$$

Since the effective activation energy is zero, the kinetic chain length will decrease with temperature.

SECTION 10.9

10.63

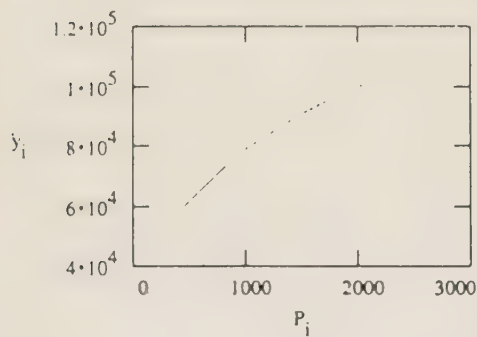
We use eq. (10.56):

$$\frac{P}{V_{\text{ads}}} = \frac{1}{b \cdot V_{\text{max}}} + \frac{1}{V_{\text{max}}} \cdot P \quad \text{Plot } P/V_{\text{ads}} \text{ vs. } P.$$

$$y_i = \frac{P_i}{V_{\text{ads}_i}}$$

$$V_{\text{max}} = \frac{1}{\text{slope}(P, y)} \quad V_{\text{max}} = 39.072 \cdot \frac{\text{cm}^3}{\text{gm}}$$

$$b = \frac{1}{V_{\text{max}} \cdot \text{intercept}(P, y)} \quad b = 0.069 \cdot \frac{1}{\text{torr}}$$



$$i = 0..7$$

$$V_{\text{ads}_i} = \quad P_i =$$

$5.89 \cdot \frac{\text{cm}^3}{\text{gm}}$	$2.45 \cdot \text{torr}$
$7.76 \cdot \frac{\text{cm}^3}{\text{gm}}$	$3.5 \cdot \text{torr}$
$10.10 \cdot \frac{\text{cm}^3}{\text{gm}}$	$5.2 \cdot \text{torr}$
$12.35 \cdot \frac{\text{cm}^3}{\text{gm}}$	$7.2 \cdot \text{torr}$
$16.45 \cdot \frac{\text{cm}^3}{\text{gm}}$	$11.2 \cdot \text{torr}$
$18.05 \cdot \frac{\text{cm}^3}{\text{gm}}$	$12.8 \cdot \text{torr}$
$19.72 \cdot \frac{\text{cm}^3}{\text{gm}}$	$14.6 \cdot \text{torr}$
$21.10 \cdot \frac{\text{cm}^3}{\text{gm}}$	$16.1 \cdot \text{torr}$

10.65

Use eq. (10.56):

$$\frac{P}{V_{\text{ads}}} = \frac{1}{b \cdot V_{\text{max}}} + \frac{1}{V_{\text{max}}} \cdot P \quad \text{Plot } P/V_{\text{ads}} \text{ vs. } P.$$

$$i = 0..4$$

$$P_i = \quad V_i =$$

35.9 · torr	3.70 · cm ³
64.5 · torr	5.09 · cm ³
120 · torr	6.70 · cm ³
232 · torr	8.48 · cm ³
357 · torr	9.92 · cm ³

$$y_i = \frac{P_i}{V_i}$$

$$V_{\text{max}} = \frac{1}{\text{slope}(P, y)} \quad V_{\text{max}} = 12.2 \cdot \text{cm}^3$$

$$b = \frac{1}{V_{\text{max}} \cdot \text{intercept}(P, y)} \quad b = 0.011 \cdot \frac{1}{\text{torr}}$$

10.67

The most general expression for a Langmuir-type adsorption would be:

$$v = \frac{k S_0 b_{\text{NO}} P_{\text{NO}}}{1 + b_{\text{NO}} P_{\text{NO}} + b_{\text{N}_2} P_{\text{N}_2} + b_{\text{O}_2} P_{\text{O}_2}}$$

If the following are true:

$$b_{\text{O}_2} P_{\text{O}_2} \gg 1$$

$$b_{\text{O}_2} P_{\text{O}_2} \gg b_{\text{N}_2} P_{\text{N}_2}$$

$$b_{\text{O}_2} P_{\text{O}_2} \gg b_{\text{NO}} P_{\text{NO}}$$

then we will have a rate law of the form:

$$v = \frac{k_{\text{eff}} P_{\text{NO}}}{P_{\text{O}_2}}$$

10.69

If dissociation occurs upon adsorption, we have:



where S is a site and H_s is hydrogen on the surface.

At equilibrium, the rates of adsorption and desorption are equal:

$$k_a P_{\text{H}_2} (1 - \theta)^2 = k_d \theta^2$$

$$\sqrt{\frac{k_a}{k_d}} P_{\text{H}_2}^{1/2} (1 - \theta) = \theta$$

$$\sqrt{\frac{k_a}{k_d}} P_{\text{H}_2}^{1/2} - \theta \sqrt{\frac{k_a}{k_d}} P_{\text{H}_2}^{1/2} = \theta$$

$$\sqrt{\frac{k_a}{k_d}} P_{\text{H}_2}^{1/2} = \theta \left(1 + \sqrt{\frac{k_a}{k_d}} P_{\text{H}_2}^{1/2} \right)$$

$$\theta = \frac{\sqrt{\frac{k_a}{k_d}} P_{\text{H}_2}^{1/2}}{\left(1 + \sqrt{\frac{k_a}{k_d}} P_{\text{H}_2}^{1/2} \right)}$$

$$\theta = \frac{b P_{\text{H}_2}^{1/2}}{(1 + b P_{\text{H}_2}^{1/2})} \quad \text{where } b = \sqrt{\frac{k_a}{k_d}}$$

SECTION 10.10

10.71

A material balance on the enzyme gives:

$$E_0 = [E] + [ES] + [ESI]$$

At equilibrium, from eq. (10.61), we have:

$$K'_i = \frac{[ES][I]}{[ESI]} \quad \text{and} \quad K_m = \frac{[E][S]}{[ES]} \quad \Rightarrow \quad [ES] = \frac{[E][S]}{K_m}$$

$$[ESI] = \frac{[ES][I]}{K'_i} = \frac{[E][S][I]}{K'_i K_m}$$

We can plug these into the enzyme balance:

$$E_0 = [E] + [ES] + [ESI] = [E] + \frac{[E][S]}{K_m} + \frac{[E][S][I]}{K'_i K_m} = [E] \left(1 + \frac{[S]}{K_m} + \frac{[S][I]}{K'_i K_m} \right)$$

$$[E] = \frac{E_0}{\left(1 + \frac{[S]}{K_m} + \frac{[S][I]}{K'_i K_m} \right)}$$

The rate is given by:

$$v = k_2 [ES] = \frac{k_2 [E][S]}{K_m} = \frac{k_2 [S] E_0}{K_m \left(1 + \frac{[S]}{K_m} + \frac{[S][I]}{K'_i K_m} \right)}$$

$$v = \frac{v_{\max} [S]}{K_m + [S] + \frac{[S][I]}{K'_i}} = \frac{v_{\max} [S]}{K_m + [S] \left(1 + \frac{[I]}{K'_i} \right)}$$

To find the slope and intercept of the graphical method described in the problem:

$$\frac{1}{v} = \frac{K_m + [S] \left(1 + \frac{[I]}{K'_i} \right)}{v_{\max} [S]}$$

$$\frac{1}{v} = \frac{K_m}{v_{\max}} \frac{1}{[S]} + \frac{\left(1 + \frac{[I]}{K'_i} \right)}{v_{\max}}$$

$$\text{slope} = \frac{K_m}{v_{\max}} \quad \text{intercept} = \frac{1}{v_{\max}} \left(1 + \frac{[I]}{K'_i} \right)$$

10.73

This is similar to example 10.18. We use a Lineweaver-Burk plot, which is a plot of $1/v$ vs. $1/[S]$.

$$i = 0..8$$

$$S_i = \quad v_i =$$

0.03	0.14
0.04	0.165
0.05	0.18
0.0863	0.26
0.129	0.305
0.216	0.345
0.431	0.40
0.647	0.435
1.078	0.445

$$\frac{1}{v} = \frac{1}{v_{\max}} + \frac{K_m}{v_{\max}} \cdot \frac{1}{S}$$

$$y_i = \frac{1}{v_i} \quad x_i = \frac{1}{S_i}$$

$$v_{\max} = \frac{1}{\text{intercept}(x, y)} \quad v_{\max} = 0.47$$

$$K_m = v_{\max} \cdot \text{slope}(x, y) \quad K_m = 0.073$$

1e

10.75

This is similar to example 10.18. We use a Lineweaver-Burk plot, which is a plot of $1/v$ vs. $1/[S]$.

$$i = 0..3$$

$$S_i =$$

$$v_i =$$

$$\frac{1}{v} = \frac{1}{v_{\max}} + \frac{K_m}{v_{\max}} \cdot \frac{1}{S}$$

$2.5 \cdot 10^{-4} \cdot \frac{\text{mole}}{\text{liter}}$	$2.2 \cdot 10^{-6} \cdot \frac{\text{mole}}{\text{liter} \cdot \text{min}}$
$5.0 \cdot 10^{-4} \cdot \frac{\text{mole}}{\text{liter}}$	$3.8 \cdot 10^{-6} \cdot \frac{\text{mole}}{\text{liter} \cdot \text{min}}$
$1.0 \cdot 10^{-3} \cdot \frac{\text{mole}}{\text{liter}}$	$5.9 \cdot 10^{-6} \cdot \frac{\text{mole}}{\text{liter} \cdot \text{min}}$
$1.5 \cdot 10^{-3} \cdot \frac{\text{mole}}{\text{liter}}$	$7.1 \cdot 10^{-6} \cdot \frac{\text{mole}}{\text{liter} \cdot \text{min}}$

$$y_i = \frac{1}{v_i} \quad x_i = \frac{1}{S_i}$$

$$v_{\max} = \frac{1}{\text{intercept}(x, y)}$$

$$v_{\max} = 1.32 \cdot 10^{-5} \cdot \frac{\text{mole}}{\text{liter} \cdot \text{min}}$$

$$K_m = v_{\max} \cdot \text{slope}(x, y)$$

$$K_m = 1.24 \cdot 10^{-3} \cdot \frac{1}{\text{liter}}$$

10.77

A material balance on the enzyme gives:

$$E_0 = [E] + [ES] + [EI] + [ESI]$$

At equilibrium, from eq. (10.61), we have:

$$K_m = \frac{[E][S]}{[ES]} \Rightarrow [ES] = \frac{[E][S]}{K_m}$$

$$\text{and} \quad K_i = \frac{[E][I]}{[EI]} \Rightarrow [EI] = \frac{[E][I]}{K_i}$$

$$K_i = \frac{[ES][I]}{[ESI]} \Rightarrow [ESI] = \frac{[ES][I]}{K_i} = \frac{[E][S][I]}{K_i K_m}$$

We can plug these into the enzyme balance:

$$E_0 = [E] + [ES] + [EI] + [ESI] = [E] + \frac{[E][S]}{K_m} + \frac{[E][I]}{K_i} + \frac{[E][S][I]}{K_i K_m} = [E] \left(1 + \frac{[S]}{K_m} + \frac{[I]}{K_i} + \frac{[S][I]}{K_i K_m} \right)$$

$$[E] = \frac{E_0}{\left(1 + \frac{[S]}{K_m} + \frac{[I]}{K_i} + \frac{[S][I]}{K_i K_m} \right)}$$

The rate is given by:

$$v = k_2 [ES] = \frac{k_2 [E][S]}{K_m} = \frac{k_2 [S] E_0}{K_m \left(1 + \frac{[S]}{K_m} + \frac{[I]}{K_i} + \frac{[S][I]}{K_i K_m} \right)}$$

$$v = \frac{v_{\max} [S]}{K_m + [S] + \frac{[I] K_m}{K_i} + \frac{[S][I]}{K_i}}$$

SECTION 10.11

10.79

For two molecules of equal size, eq. (10.67) reduces to:

$$k = \left(\frac{2 \cdot R \cdot T}{3 \cdot \eta} \right) \cdot \left[\frac{(r_A + r_B)^2}{r_A \cdot r_B} \right] = \frac{8 \cdot R \cdot T}{3 \cdot \eta}$$

We can get the viscosity from Table 9.2:

$$T = 313.15 \cdot K \quad \eta = 3.41 \cdot 10^{-3} \cdot \frac{\text{gm}}{\text{cm} \cdot \text{sec}} \quad R = 8.31451 \cdot \frac{\text{joule}}{\text{mole} \cdot K}$$

$$k = \frac{8 \cdot R \cdot T}{3 \cdot \eta} \quad k = 2 \cdot 10^{10} \cdot \frac{\text{liter}}{\text{mole} \cdot \text{sec}}$$

10.81

Equation (10.67) is:

$$k = \left(\frac{2 \cdot R \cdot T}{3 \cdot \eta} \right) \cdot \left[\frac{(r_A + r_B)^2}{r_A \cdot r_B} \right]$$

All other things being equal, at two different temperatures, the relative rates would be:

$$k_1 = \left(\frac{2 \cdot R \cdot T_1}{3 \cdot \eta_1} \right) \cdot \left[\frac{(r_A + r_B)^2}{r_A \cdot r_B} \right] \quad k_2 = \left(\frac{2 \cdot R \cdot T_2}{3 \cdot \eta_2} \right) \cdot \left[\frac{(r_A + r_B)^2}{r_A \cdot r_B} \right] \quad \frac{k_{50}}{k_{20}} = \frac{T_{50} \cdot \eta_{20}}{T_{20} \cdot \eta_{50}}$$

Using data from Table 9.2,

$$T_{50} = 323.15 \cdot K \quad T_{20} = 293.15 \cdot K \quad \text{mp} = 10^{-3} \cdot \text{poise} \quad \eta_{50} = 5.494 \cdot \text{mp} \quad \eta_{20} = 10.05 \cdot \text{mp}$$

$$k_{\text{ratio}} = \frac{T_{50} \cdot \eta_{20}}{T_{20} \cdot \eta_{50}} \quad k_{\text{ratio}} = 2.016$$

10.83

We can rearrange eq. (10.71) to solve for k_1 :

$$\tau = \frac{1}{k_1 - k_2 \cdot (A_{eq} + B_{eq})} \quad k_1 = \frac{1}{\tau \cdot \left[1 + \frac{k_2}{k_1} \cdot (A_{eq} + B_{eq}) \right]}$$

We know the ratio of k_1 to k_2 from the equilibrium:

$$\frac{k_2}{k_1} = K_{eq} = \frac{H_2O}{H \cdot OH} \quad k_{ratio} = \frac{55.6 \cdot \frac{\text{mole}}{\text{liter}}}{\left(10^{-7} \cdot \frac{\text{mole}}{\text{liter}} \right)^2} \quad k_{ratio} = 5.56 \cdot 10^{15} \cdot \frac{\text{liter}}{\text{mole}}$$

$$\mu s = 10^{-6} \cdot \text{sec} \quad A_{eq} = 10^{-7} \cdot \frac{\text{mole}}{\text{liter}} \quad B_{eq} = 10^{-7} \cdot \frac{\text{mole}}{\text{liter}} \quad \tau = 36 \cdot \mu s$$

$$k_1 = \frac{1}{\tau \cdot \left[1 + k_{ratio} \cdot (A_{eq} + B_{eq}) \right]} \quad k_1 = 2.5 \cdot 10^{-5} \cdot \frac{1}{\text{sec}}$$

$$k_2 = k_{ratio} \cdot k_1 \quad k_2 = 1.4 \cdot 10^{11} \cdot \frac{\text{liter}}{\text{mole} \cdot \text{sec}}$$

10.85

First we write the rate of appearance of A:

$$\frac{d[A]}{dt} = -k_1[A] + k_{-1}[B]$$

We can relate [A] and [B] to the equilibrium concentrations and an extent of reaction, x:

$$[A] = [A]_{eq} - x \quad \text{and} \quad [B] = [B]_{eq} + x$$

$$\frac{dx}{dt} = k_1([A]_{eq} - x) - k_{-1}([B]_{eq} + x)$$

$$\frac{dx}{dt} = -(k_1 + k_{-1})x + (k_1[A]_{eq} - k_{-1}[B]_{eq})$$

Because of the equilibrium condition, the second term is zero.

$$\frac{dx}{dt} = -(k_1 + k_{-1})x$$

The definition of the relaxation time is:

$$\tau = -\frac{x}{dx/dt} = \frac{1}{(k_1 + k_{-1})}$$

CHAPTER 11 *Quantum Theory*

SECTION 11.1

11.1

$$p = mv = \frac{h\nu}{c} = \frac{h}{\lambda} \Rightarrow v = \frac{h}{m\lambda}$$

$$h = 6.626 \times 10^{-34} \text{ J s} \quad \text{and} \quad \lambda = 400 \text{ nm}$$

a) $m = 9.11 \times 10^{-31} \text{ kg}$

$$v = \frac{6.626 \times 10^{-34}}{(400 \times 10^{-9}) (9.11 \times 10^{-31})} = 1.82 \times 10^3 \text{ m/s}$$

b) $m = \frac{4.003 \times 10^{-3} \text{ kg/mol}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 6.647 \times 10^{-27} \text{ kg}$

$$v = 0.2492 \text{ m/s}$$

c) $m = 1 \text{ g}$

$$v = 1.657 \times 10^{-24} \text{ m/s}$$

11.3

$$E = h\nu = \frac{hc}{\lambda} = \frac{1}{2}mv^2 = \frac{M}{2L} \left(\sqrt{\frac{3RT}{M}} \right)^2 = \frac{3RT}{2L} \Rightarrow \lambda = \frac{2hcL}{3RT}$$

$$T = 300 \text{ K}$$

$$\lambda = 3.197 \times 10^{-5} \text{ m} = 31.97 \text{ } \mu\text{m}$$

11.5

$$1 \text{ g H}_2\text{O} \times 1^\circ\text{C} \times 4.184 \text{ J / g }^\circ\text{C} = 4.184 \text{ J}$$

$$\lambda = 750 \text{ nm}$$

$$E_{750} = \frac{hc}{\lambda} = 2.649 \times 10^{-19} \text{ J}$$

$$\# \text{ photons} = \frac{4.184 \text{ J}}{E_{750}} = 1.580 \times 10^{19} \text{ photons}$$

11.7

$$\theta = 90^\circ$$

$$\lambda_i = 300 \text{ pm} = 300 \times 10^{-12} \text{ m}$$

$$\lambda_f = \lambda_i + \Delta\lambda = 302.4 \text{ pm, where } \Delta\lambda \text{ is defined in the problem}$$

$$-\Delta E = \frac{hc}{\lambda_i} - \frac{hc}{\lambda_f} = \frac{1}{2} m_e v^2$$

$$\Rightarrow v^2 = \frac{2hc}{m_e} \left(\frac{1}{\lambda_i} - \frac{1}{\lambda_f} \right)$$

$$\Rightarrow v = \sqrt{\frac{2hc}{m_e} \left(\frac{1}{\lambda_i} - \frac{1}{\lambda_f} \right)} = 3.40 \times 10^6 \text{ m/s}$$

SECTION 11.2

11.9

$$1 \text{ cm} \times \frac{1 \text{ bohr}}{5.2918 \times 10^{-9} \text{ cm}} \times \frac{1 \text{ GB}}{10^9 \text{ bohr}} = 0.189 \text{ GB}$$

$$1 \text{ inch} \times \frac{2.54 \text{ cm}}{\text{inch}} \times \frac{0.189 \text{ GB}}{\text{cm}} = 0.480 \text{ GB}$$

$$1 \text{ g} \times \frac{1 m_e}{9.1094 \times 10^{-28} \text{ g}} \times \frac{1 \text{ MU}}{10^{27} \text{ m}} = 1.098 \text{ MU}$$

$$1 \text{ J} = 1 \text{ kg m}^2 / \text{s}^2 \times \left(\frac{100 \text{ cm}}{\text{m}} \right)^2 \times \left(\frac{0.189 \text{ GB}}{\text{cm}} \right)^2 \times \left(\frac{1000 \text{ g}}{\text{kg}} \right) \times \left(\frac{1.098 \text{ MU}}{\text{g}} \right) = 3.92 \times 10^5 \text{ MU GB}^2 / \text{s}^2 = 0.3$$

$$(4.184 \text{ J / g K}) \times (1 \text{ g}) \times (1 \text{ K}) \times (0.392 \text{ MEU / J}) = 1.64 \text{ MEU}$$

11.11

$$E_h = 1 \text{ hartree}$$

For Helium, $Z = 2$ and $N = 1$

$$IP = -E = \frac{1}{2} \frac{Z^2}{N^2} E_h = \frac{1}{2} \frac{2^2}{1^2} \text{ hartree} \times \frac{27.2114 \text{ eV}}{\text{hartree}} = 54.4228 \text{ eV}$$

11.13

$$\mathfrak{R} = 109,737 \text{ cm}^{-1}$$

$$\mathfrak{R}_{\text{He}} = Z^2 \mathfrak{R} = 4\mathfrak{R} = 438,948 \text{ cm}^{-1}$$

$$\tilde{\nu} = \mathfrak{R}_{\text{He}} \left(\frac{1}{N_1^2} - \frac{1}{N_2^2} \right)$$

$\underline{N_1}$	$\underline{N_2}$	$\tilde{\nu} / \text{cm}^{-1}$
3	4	21,338
3	∞	48,772
4	5	9876
4	∞	27,434
5	6	5365
5	∞	17,558

11.15

$$N\hbar = m_e v r \text{ (de Broglie Hypothesis) and } r = \frac{N^2 a_0}{Z}$$

$$\Rightarrow v = \frac{N\hbar}{m_e r} = \frac{Z\hbar}{m_e N a_0}$$

$$\Rightarrow \frac{v}{c} = \frac{Z\hbar}{m_e c N a_0}$$

$$\text{let } N = 1$$

$$\text{H (Z=1):} \quad v/c = 0.0073$$

$$\text{Hg}^{79+} \text{ (Z=80)} \quad v/c = 0.584$$

$$\text{U}^{91+} \text{ (Z=92)} \quad v/c = 0.671$$

$$\frac{v}{c} = \frac{Z\hbar}{m_e c N a_0} = 1 \Rightarrow Z = \frac{m_e c a_0}{\hbar} = 137.05$$

This implies $v/c > 1$ when $Z \geq 138$

11.17

$$r = \frac{N^2 a_0}{Z} \Rightarrow N = \sqrt{\frac{Zr}{a_0}}$$

$$\text{let } Z = 1, r = 1 \text{ cm}$$

$$\text{then } N = 13746.7 \cong 13747$$

11.19

let $\lambda = 100 \text{ pm}$, $m = m_e$

$$\lambda = \frac{h}{mv} \Rightarrow v = \frac{h}{m\lambda}$$

$$T \text{ (kinetic energy)} = \frac{1}{2} mv^2 = \frac{h^2}{2m_e \lambda^2} = 150.4 \text{ eV}$$

SECTION 11.3

11.21

$$\hat{O} \exp[i\theta] = \frac{d}{d\theta} \sin\theta \frac{d}{d\theta} \exp[i\theta] = \frac{d}{d\theta} \left(\frac{\exp[i\theta] - \exp[-i\theta]}{2i} \right) i \exp[i\theta] = \frac{d}{d\theta} \left(\frac{\exp[2i\theta] - 1}{2} \right) = i \exp[2i\theta]$$

Therefore, $e^{i\theta}$ is not an eigenfunction of this operator11.23

$$\left[\frac{d}{dr}, \frac{1}{r} \right] f(r) = \frac{d}{dr} \left(\frac{f}{r} \right) - \frac{1}{r} \frac{df}{dr} = \frac{1}{r} \frac{df}{dr} - \frac{1}{r^2} f - \frac{1}{r} \frac{df}{dr} = -\frac{1}{r^2} f$$

$$\Rightarrow \left[\frac{d}{dr}, \frac{1}{r} \right] = -\frac{1}{r^2}$$

11.25

$$\hat{O} 3\exp[i\phi] = i \frac{d}{d\phi} 3\exp[i\phi] = -3\exp[i\phi]$$

Therefore, $3e^{i\phi}$ is an eigenfunction of this operator with eigenvalue = -1

11.27

$$\left(\frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} + \frac{2}{r} \right) A \exp[-br] = \frac{1}{r^2} \frac{d}{dr} (-Abr^2 \exp[-br]) + \frac{2A \exp[-br]}{r}$$

$$= \frac{1}{r^2} (-Abr^2 (-b \exp[-br]) - 2Abr \exp[-br]) + \frac{2A \exp[-br]}{r}$$

$$= Ab^2 \exp[-br] + (2A - 2Ab) \frac{\exp[-br]}{r}$$

$$\Rightarrow 2A - 2Ab = 0 \Rightarrow b = 1 \text{ and } A \neq 0$$

$$\text{eigenvalue} = b^2 = 1$$

11.29

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$\nabla^2 (x^2 + y^2 + z^2) = \frac{\partial^2}{\partial x^2} x^2 + \frac{\partial^2}{\partial y^2} y^2 + \frac{\partial^2}{\partial z^2} z^2 = 2 + 2 + 2 = 6 \quad \text{not an eigenfunction}$$

$$\nabla^2 = \left(\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \right) + \left(\frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right) + \left(\frac{1}{r^2 \sin \theta} \frac{\partial^2}{\partial \phi^2} \right)$$

$$(x^2 + y^2 + z^2) = r^2$$

$$\nabla^2 r^2 = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} r^2 = \frac{1}{r^2} \frac{\partial}{\partial r} 2r^3 = \frac{1}{r^2} (6r^2) = 6$$

SECTION 11.4

11.31

$$p_x \psi = \frac{\hbar}{i} \frac{\partial}{\partial x} A \exp[ikx] = \frac{\hbar}{i} A ik \exp[ikx] = \hbar k A \exp[ikx] = \hbar k \psi$$

eigenvalue is $\hbar k$

11.33

$$1 = A^2 \int_0^1 \cos^2(n\pi x) dx = A^2 \left(\frac{2n\pi + \sin 2n\pi}{4n\pi} \right) = \frac{A^2}{2} \quad \text{since } \sin 2n\pi = 0 \text{ for integer } n$$

$$\Rightarrow A^2 = 2 \Rightarrow A = \sqrt{2}$$

$$2 \int_0^1 \cos(n\pi x) \cos(m\pi x) dx = 2 \left(\frac{(m+n)\sin(m-n)\pi + (m-n)\sin(m+n)\pi}{(m^2 - n^2)\pi} \right) = 0 \text{ if } m \neq n$$

$$\Rightarrow \sqrt{2} \cos(n\pi x) \text{ are orthonormal}$$

SECTION 11.5

11.35

$$\psi = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$$

$$\text{probability} = \int_0^{a/4} \psi^2 dx = \int_0^{a/4} \frac{2}{a} \sin^2 \frac{n\pi x}{a} dx \quad \text{let } u = \frac{n\pi x}{a}$$

$$\Rightarrow \langle x \rangle = \frac{2}{(n\pi)} \int_0^{n\pi/4} \sin^2 u \, du = \frac{2}{(n\pi)} \left(\frac{(n\pi)}{8} - \frac{1}{4} \sin \frac{n\pi}{2} \right) = \frac{1}{4} - \frac{1}{2n\pi} \sin \frac{n\pi}{2}$$

$$\lim_{n \rightarrow \infty} \left(\frac{1}{4} - \frac{1}{2n\pi} \sin \frac{n\pi}{2} \right) = \frac{1}{4}$$

11.37

$$\psi = A \sin \frac{n\pi x}{a}$$

$$1 = \int_0^a \psi^2 dx = \int_0^a A^2 \sin^2 \frac{n\pi x}{a} dx \quad \text{let } u = \frac{n\pi x}{a}$$

$$\Rightarrow 1 = A^2 \frac{a}{(n\pi)} \int_0^{n\pi} \sin^2 u \, du = A^2 \frac{a}{(n\pi)} \left(\frac{u}{2} - \frac{1}{4} \sin 2u \right)_0^{n\pi} =$$

$$\Rightarrow 1 = A^2 \frac{a}{(n\pi)} \left(\frac{n\pi}{2} \right) = A^2 \frac{a}{2} \Rightarrow A = \sqrt{\frac{2}{a}}$$

11.39

$$E = (n_x^2 + n_y^2) \frac{h^2}{8ma^2}$$

(n_x, n_y)	E (multiples of $h^2/8ma^2$)	degeneracy
1,1	2	1
2,1	5	2
2,2	8	1
3,1	10	2
2,3	13	2
4,1	17	2
3,3	18	1
4,2	20	2
4,3	25	2
5,1	26	2

17 total states, highest energy is 26

11.41

$$E_0 = \frac{3h^2}{8ma^2}$$

a) $m = (2.016 \times 10^{-3} / \text{L}) \text{ kg}$
 $a = 1 \times 10^{-3} \text{ m}$

$$E_0 = 4.92 \times 10^{-35} \text{ J}$$

b) $m = m_e$
 $a = 1 \times 10^{-10} \text{ m}$

$$E_0 = 1.81 \times 10^{-17} \text{ J}$$

11.43

$$\psi = A_x \sin \frac{n_x \pi x}{a} A_y \sin \frac{n_y \pi y}{b} A_z \sin \frac{n_z \pi z}{c}$$

$$H\psi = -\frac{\hbar^2}{2m} \nabla^2 \psi = -\frac{\hbar^2}{2m} \left(-\frac{n_x^2 \pi^2}{a^2} - \frac{n_y^2 \pi^2}{b^2} - \frac{n_z^2 \pi^2}{c^2} \right) A_x \sin \frac{n_x \pi x}{a} A_y \sin \frac{n_y \pi y}{b} A_z \sin \frac{n_z \pi z}{c} = E\psi$$

$$\Rightarrow E = -\frac{\hbar^2}{2m} \left(-\frac{n_x^2 \pi^2}{a^2} - \frac{n_y^2 \pi^2}{b^2} - \frac{n_z^2 \pi^2}{c^2} \right) = \frac{\hbar^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

SECTION 11.6

11.45

$$\begin{aligned}
 1 &= \int_{-\infty}^{\infty} |\psi|^2 dx = A_1^2 \int_{-\infty}^{\infty} (2y)^2 \exp[-y^2] dx \quad \text{let } x = \alpha y \\
 &= 4\alpha A_1^2 \int_{-\infty}^{\infty} y^2 \exp[-y^2] dy = 4\alpha A_1^2 \left(\frac{\sqrt{\pi}}{2} \right) \\
 \Rightarrow A_1^2 &= \frac{1}{2\alpha \sqrt{\pi}} \Rightarrow A_1 = \frac{1}{(2\alpha)^{1/2} (\pi)^{1/4}}
 \end{aligned}$$

11.47

$$\begin{aligned}
 \int_{-\infty}^{\infty} \psi_0^* \psi_1 dx &= k_0 k_1 \int_{-\infty}^{\infty} \exp[-y^2/2] y \exp[-y^2/2] dy \\
 &= C \int_{-\infty}^{\infty} y \exp[-y^2] dy = 0 \quad \text{since the integrand is odd}
 \end{aligned}$$

$$\begin{aligned}
 \int_{-\infty}^{\infty} \psi_0^* \psi_2 dx &= k_0 k_2 \int_{-\infty}^{\infty} \exp[-y^2/2] (4y^2 - 2) \exp[-y^2/2] dy \\
 &= C \int_{-\infty}^{\infty} (4y^2 - 2) \exp[-y^2] dy \\
 &= C \left(4 \frac{\sqrt{\pi}}{2} - 2\sqrt{\pi} \right) = 0
 \end{aligned}$$

11.51

$$\langle p \rangle = \int_{-\infty}^{\infty} \psi_1^* p \psi_1 dx = \frac{A_1^2 \int_{-\infty}^{\infty} 2y \exp[-y^2/2] \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) 2y \exp[-y^2/2] dx}{A_1^2 \int_{-\infty}^{\infty} 4y^2 \exp[-y^2] dy} \quad \text{let } x = \alpha y$$

$$= \frac{\frac{\hbar}{i} \frac{1}{\alpha} \int_{-\infty}^{\infty} y \exp[-y^2/2] \left[x \frac{-x}{\alpha^2} + 1 \right] \exp[-y^2/2] dx}{\int_{-\infty}^{\infty} \alpha y^2 \exp[-y^2] dy}$$

$$= \frac{\frac{\hbar}{i} \int_{-\infty}^{\infty} y(1-y^2) \exp[-y^2] dy}{\int_{-\infty}^{\infty} \alpha y^2 \exp[-y^2] dy} = 0 \quad \text{since the integrand in the numerator is odd}$$

$$\langle p^2 \rangle = \frac{A_1^2 \int_{-\infty}^{\infty} 2y \exp[-y^2/2] \left(-\hbar^2 \frac{\partial^2}{\partial x^2} \right) 2y \exp[-y^2/2] dx}{A_1^2 \int_{-\infty}^{\infty} 4y^2 \exp[-y^2] dx} \quad \text{let } x = \alpha y$$

$$= \frac{-\hbar^2 \frac{1}{\alpha} \int_{-\infty}^{\infty} y \exp[-y^2/2] \left[\frac{x^3}{\alpha^4} - \frac{3x}{\alpha^2} \right] \exp[-y^2/2] dx}{\int_{-\infty}^{\infty} \alpha y^2 \exp[-y^2] dy}$$

$$= \frac{\frac{-\hbar^2}{\alpha^2} \int_{-\infty}^{\infty} (y^4 - 3y^2) \exp[-y^2] dy}{\int_{-\infty}^{\infty} y^2 \exp[-y^2] dy} = \frac{-\hbar^2}{\alpha^2} \frac{\left(\frac{3}{4} \sqrt{\pi} - \frac{3}{2} \sqrt{\pi} \right)}{\frac{1}{2} \sqrt{\pi}} = \frac{3}{2} \frac{\hbar^2}{\alpha^2}$$

$$\Delta x \Delta p = \sqrt{\langle x^2 \rangle \langle p^2 \rangle} = \sqrt{\frac{3}{2} \alpha^2 \frac{3}{2} \frac{\hbar^2}{\alpha^2}} = \frac{3}{2} \hbar \geq \frac{\hbar}{2}$$

11.53

a)

$$\hat{A} = y - \frac{d}{dy}$$

$$\hat{B} = y + \frac{d}{dy}$$

$$[\hat{A}\hat{B}]f = \left(y - \frac{d}{dy}\right)\left(yf + \frac{df}{dy}\right) = y^2f + y\frac{df}{dy} - y\frac{df}{dy} - 1f - \frac{d^2f}{dy^2} = \left(y^2 - \frac{d^2}{dy^2} - 1\right)f = (\hat{h} - 1)f$$

$$[\hat{B}\hat{A}]f = \left(y + \frac{d}{dy}\right)\left(yf - \frac{df}{dy}\right) = y^2f - y\frac{df}{dy} + y\frac{df}{dy} + 1f - \frac{d^2f}{dy^2} = \left(y^2 - \frac{d^2}{dy^2} + 1\right)f = (\hat{h} + 1)f$$

b)

$$\hat{h}\psi = (\hat{A}\hat{B} + 1)\psi = \hat{A}\hat{B}\psi + 1\psi = \hat{A}0 + 1\psi = 1\psi$$

11.55

This solution uses the answers to problems 11.53 and 11.54

a)

$$[\hat{A}, \hat{B}]f = (\hat{A}\hat{B} - \hat{B}\hat{A})f = (\hat{h} - 1)f - (\hat{h} + 1)f = -2f \Rightarrow [\hat{A}, \hat{B}] = -2$$

b)

$$\hat{A}\hat{B}\psi_n = 2n\psi_n \quad \text{from 11.54}$$

$$\hat{A}\hat{B}\psi_n = \hat{A}(\hat{B}\psi_n) = \hat{A}(\text{const } \psi_{n-1}) = \text{const } (\hat{A}\psi_{n-1}) = \text{const } \psi_n \Rightarrow \text{const} = 2n$$

11.57

$$\nu = 8.963 \times 10^{13} \text{ Hz}$$

$$M_H = 1.008 \times 10^{-3} \text{ kg/mol}$$

$$M_{Cl} = 34.969 \times 10^{-3} \text{ kg/mol}$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \Rightarrow k = 4\pi^2 \mu \nu^2 = 4\pi^2 \frac{m_1 m_2}{m_1 + m_2} \nu^2 = \frac{4\pi^2}{L} \frac{M_H M_{Cl}}{M_H + M_{Cl}} \nu^2 = 5.16 \times 10^2 \text{ kg/s}^2$$

$$x = 1 \text{ cm}$$

$$g = 9.81 \text{ m/s}^2$$

$$F_{\text{spring}} = F_{\text{gravity}}$$

SECTION 11.7

11.59

m_{H} = mass of hydrogen atom

r_{CH} = 0.11 nm

$\phi = 180^\circ - \theta_{\text{T}} = 70.53^\circ$

$R = r_{\text{CH}} \sin \phi = 0.104 \text{ nm}$

$I = 3 m_{\text{H}} R^2 = 5.4 \times 10^{-47} \text{ kg m}^2$

$$kT = \frac{m^2 h^2}{8\pi^2 I} \Rightarrow m^2 = \frac{kT 8\pi^2 I}{h^2} = 40 \cong 36$$

$$\Rightarrow m = 6$$

11.61

$$T = 300 \text{ K}$$

$$m_{\text{H}} = \text{mass of hydrogen atom}$$

$$r_{\text{OH}} = 95.8 \text{ pm}$$

$$\phi = 180^\circ - 120^\circ = 60^\circ$$

$$R = r_{\text{OH}} \sin \phi = 83.0 \text{ pm}$$

$$I = m_{\text{H}} R^2 = 1.15 \times 10^{-47} \text{ kg m}^2$$

$$\frac{E_m}{kT} = \frac{m^2 h^2}{8\pi^2 I kT}$$

m	E
0	0
1	0.117
2	0.467
3	1.051
4	1.869
5	2.920
6	4.205

11.63

$$\begin{aligned}
 L_- &= L_x - iL_y = i \left(\sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) - i \left(-i \left(\cos \phi \frac{\partial}{\partial \theta} - \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right) \right) \\
 &= -(\cos \phi - i \sin \phi) \frac{\partial}{\partial \theta} + i \cot \theta (\cos \phi - i \sin \phi) \frac{\partial}{\partial \phi} \\
 &= -\exp[-i\phi] \frac{\partial}{\partial \theta} + i \cot \theta \exp[-i\phi] \frac{\partial}{\partial \phi}
 \end{aligned}$$

$$L_- \cos \theta = -\exp[-i\phi] \frac{\partial}{\partial \theta} \cos \theta + i \cot \theta \exp[-i\phi] \frac{\partial}{\partial \phi} \cos \theta = \exp[-i\phi] \sin \theta$$

$$\begin{aligned}
 L_+ L_- \cos \theta &= L_+ (\exp[-i\phi] \sin \theta) = \exp[i\phi] \frac{\partial}{\partial \theta} (\exp[-i\phi] \sin \theta) + i \cot \theta \exp[i\phi] \frac{\partial}{\partial \phi} (\exp[-i\phi] \sin \theta) \\
 &= \cos \theta + i \cot \theta (\sin \theta) \exp[i\phi] (-i \exp[-i\phi]) = 2 \cos \theta
 \end{aligned}$$

11.65

$$L_z \sin \theta \exp[i\phi] = -i \frac{\partial}{\partial \phi} \sin \theta \exp[i\phi] = -i \sin \theta (i \exp[i\phi]) = \sin \theta \exp[i\phi]$$

$$\text{eigenvalue} = m = 1$$

$$L_z \sin \theta \exp[-i\phi] = -i \frac{\partial}{\partial \phi} \sin \theta \exp[-i\phi] = -i \sin \theta (-i \exp[-i\phi]) = -\sin \theta \exp[-i\phi]$$

$$\text{eigenvalue} = m = -1$$

$$L_z \cos \theta = -i \frac{\partial}{\partial \phi} \cos \theta = 0$$

$$\text{eigenvalue} = m = 0$$

11.67

$$\begin{aligned} L_- L_+ \Psi_{l,m} &= C^2 \Psi_{l,m} = (L^2 - L_z^2 - L_z) \Psi_{l,m} = [l(l+1) - m^2 - m] \Psi_{l,m} \\ &= [l(l+1) - m(m+1)] \Psi_{l,m} \end{aligned}$$

$$\Rightarrow C^2 = [l(l+1) - m(m+1)]^{1/2}$$

$$C = 0 \text{ if } m = l$$

11.69

$$I = \frac{9}{2}$$

$$m_l = \frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}, \frac{-1}{2}, \frac{-3}{2}, \frac{-5}{2}, \frac{-7}{2}, \frac{-9}{2}$$

10 Orientations

$$\cos \theta = \frac{m_l}{|I|} = \frac{m_l}{\sqrt{I(I+1)}} = \frac{\frac{9}{2}}{\sqrt{\frac{9}{2} \left(\frac{11}{2} \right)}} = \frac{9}{\sqrt{99}} \Rightarrow \theta = \arccos \left(\frac{9}{\sqrt{99}} \right) = 25.24^\circ$$

11.71

$$I = \frac{9}{2}$$

$$m_l = \frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}, \frac{-1}{2}, \frac{-3}{2}, \frac{-5}{2}, \frac{-7}{2}, \frac{-9}{2}$$

10 Orientations

$$\cos\theta = \frac{m_l}{|l|} = \frac{m_l}{\sqrt{l(l+1)}} = \frac{\frac{9}{2}}{\sqrt{\frac{9}{2}\left(\frac{11}{2}\right)}} = \frac{9}{\sqrt{99}} \Rightarrow \theta = \arccos\left(\frac{9}{\sqrt{99}}\right) = 25.24^\circ$$

11.73

$$I = 1.448 \times 10^{-46} \text{ kg}\cdot\text{m}^2$$

$$T = 300 \text{ K}$$

$$E = kT = \frac{J(J+1)h^2}{8\pi^2 I} \Rightarrow J(J+1) = \frac{8\pi^2 I kT}{h^2} = 108 \cong 110 \Rightarrow J = 10$$

11.75

$$I = 2.644 \times 10^{-46} \text{ kg}\cdot\text{m}^2$$

$$T = 300 \text{ K}$$

$$\frac{E}{kT} = \frac{J(J+1)h^2}{8\pi^2IkT} = J(J+1)(0.05077)$$

<u>J</u>	<u>E/kT</u>
0	0
5	1.523
10	5.585
15	12.18
20	21.32

SECTION 11.8

11.77

$$I = 2.644 \times 10^{-46} \text{ kg}\cdot\text{m}^2$$

$$J_i = 1$$

$$J_f = 2$$

$$\Delta E = h\nu = \frac{hc}{\lambda} = \frac{h^2}{8\pi^2I} [J_f(J_f + 1) - J_i(J_i + 1)]$$

$$\Rightarrow \lambda = \frac{8\pi^2Ic}{h} [J_f(J_f + 1) - J_i(J_i + 1)]^{-1} = 0.2362 \text{ nm}$$

11.79

$$m = m_e$$

$$a = 10 \text{ bohr}$$

$$E = (n_x^2 + n_y^2 + n_z^2) \frac{h^2}{8ma^2}$$

$$\Delta E = E_{211} - E_{111}$$

$$\Rightarrow \bar{\nu} = \frac{\Delta E}{hc} = \frac{(2^2 - 1^2)h}{8ma^2c} = 3.249 \times 10^4 \text{ cm}^{-1}$$

11.81

$$m = m_e$$

$$a = 0.424 \text{ nm}$$

$$E = n^2 \frac{h^2}{8ma^2}$$

$$\Delta E = E_3 - E_2$$

$$\Rightarrow \bar{\nu} = \frac{\Delta E}{hc} = \frac{(3^2 - 2^2)h}{8ma^2c} = 84,352 \text{ cm}^{-1} = 10.46 \text{ eV}$$

11.83

$$I_{12}^2 \equiv \left[\int_0^a x \sin \frac{\pi x}{a} \sin \frac{2\pi x}{a} dx \right]^2 = \left(\frac{8a}{9\pi} \right)^2 = \frac{64a^2}{81\pi^2} \quad \text{This should then be scaled to 1}$$

$$I_{13}^2 \equiv \left[\int_0^a x \sin \frac{\pi x}{a} \sin \frac{3\pi x}{a} dx \right]^2 = 0$$

$$I_{14}^2 \equiv \frac{\left[\int_0^a x \sin \frac{\pi x}{a} \sin \frac{2\pi x}{a} dx \right]^2}{I_{12}^2} = 0.0064$$

11.85

$$\begin{aligned} I_x &\equiv \iint (\sin \theta \cos \phi) \cos \theta (3 \cos^2 \theta - 1) \sin \theta d\theta d\phi = \int_0^{2\pi} \cos \phi d\phi \int_0^\pi \cos \theta (3 \cos^2 \theta - 1) \sin^2 \theta d\theta \\ &= 0 \left(\int \dots d\theta \right) = 0 \end{aligned}$$

$$\begin{aligned} I_y &\equiv \iint (\sin \theta \sin \phi) \cos \theta (3 \cos^2 \theta - 1) \sin \theta d\theta d\phi = \int_0^{2\pi} \sin \phi d\phi \int_0^\pi \cos \theta (3 \cos^2 \theta - 1) \sin^2 \theta d\theta \\ &= 0 \left(\int \dots d\theta \right) = 0 \end{aligned}$$

$$\begin{aligned} I_z &\equiv \int_0^{2\pi} d\phi \int_0^\pi R \cos \theta \cos \theta (3 \cos^2 \theta - 1) \sin \theta d\theta = 2\pi R \int_0^\pi (3 \cos^4 \theta - \cos^2 \theta) \sin \theta d\theta \\ &= 2\pi R \int_{-1}^1 3u^4 - u^2 du \quad \text{if } u = \cos \theta \\ &= 2\pi R \left(\frac{3}{5} - \frac{1}{3} + \frac{3}{5} - \frac{1}{3} \right) = \frac{16\pi R}{15} \Rightarrow I_z^2 = \frac{256\pi^2 R^2}{225} \end{aligned}$$

SECTION 11.8

11.87

$$\nu_{\text{tunnel}} = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h}$$

V_0	ν_{tunnel}
50	$3.14 \times 10^{16} \text{ Hz}$
100	$1.24 \times 10^{16} \text{ Hz}$
500	$2.63 \times 10^{14} \text{ Hz}$

11.89

$$V(x) = 4 V_0 x (1-x)$$

$$E_1^1 = E_1^0 + \int_0^1 \psi_1^* V(x) \psi_1 dx = \frac{\pi^2}{2} + 4 V_0 (2) \int_0^1 \sin^2 (\pi x) x (1-x) dx$$

$$= 4.93 + 0.869 V_0$$

$$E_2^1 = E_2^0 + \int_0^1 \psi_2^* V(x) \psi_2 dx = 2\pi^2 + 8 V_0 \int_0^1 \sin^2 (2\pi x) x (1-x) dx$$

$$= 19.74 + 0.717 V_0$$

$$V(x) = V_0 \sin^2(\pi x)$$

$$\begin{aligned} E_1^1 &= E_1^0 + \int_0^1 \psi_1^* V(x) \psi_1 dx = \frac{\pi^2}{2} + 2 V_0 \int_0^1 \sin^4(\pi x) dx \\ &= \frac{\pi^2}{2} + \frac{3}{4} V_0 \end{aligned}$$

$$\begin{aligned} E_2^1 &= E_2^0 + \int_0^1 \psi_2^* V(x) \psi_2 dx = 2\pi^2 + 2 V_0 \int_0^1 \sin^2(2\pi x) \sin^2(\pi x) dx \\ &= 2\pi^2 + \frac{1}{2} V_0 \end{aligned}$$

CHAPTER 12 Atoms

SECTION 12.1

12.1

$$r = \sigma a_0$$

$$1 = \int |\psi|^2 d\tau = \iiint_{\text{all space}} A^2 \sigma^2 \exp[-\sigma] \cos^2 \theta (r^2) \sin \theta d\phi d\theta dr$$

$$= 2\pi A^2 \int_0^\pi \cos^2 \theta \sin \theta d\theta \int_0^\infty \sigma^2 \exp[-\sigma] r^2 dr = 2\pi A^2 \left(\frac{2}{3}\right) (24a_0^3) \text{ (using u - substitution to evaluate each integral)}$$

$$\Rightarrow A^2 = \frac{1}{32\pi a_0^3} \Rightarrow A = \frac{1}{\sqrt{32\pi a_0^3}}$$

12.3

$$R = (2 - \sigma) \exp\left[-\frac{\sigma}{2}\right]$$

$$\frac{-1}{2} \frac{1}{\sigma^2} \frac{\partial}{\partial \sigma} \sigma^2 \frac{\partial}{\partial \sigma} (2 - \sigma) \exp\left[-\frac{\sigma}{2}\right] - \frac{1}{\sigma} (2 - \sigma) \exp\left[-\frac{\sigma}{2}\right] + \frac{0(0+1)}{2\sigma^2} (2 - \sigma) \exp\left[-\frac{\sigma}{2}\right]$$

$$= \frac{-1}{2} \frac{1}{\sigma^2} \frac{\partial}{\partial \sigma} \sigma^2 \left[(2 - \sigma) \left(\frac{-1}{2} \right) - 1 \right] \exp\left[-\frac{\sigma}{2}\right] - \frac{1}{\sigma} (2 - \sigma) \exp\left[-\frac{\sigma}{2}\right]$$

$$= \frac{-1}{2} \frac{1}{\sigma^2} \left[\left(\frac{\sigma^3}{2} - 2\sigma^2 \right) \left(\frac{-1}{2} \right) + \left(\frac{3\sigma^3}{2} - 4\sigma \right) \right] \exp\left[-\frac{\sigma}{2}\right] - \frac{1}{\sigma} (2 - \sigma) \exp\left[-\frac{\sigma}{2}\right]$$

$$= \left(\frac{-1}{4} + \frac{1}{8} \sigma \right) \exp\left[-\frac{\sigma}{2}\right] = \frac{-1}{8} (2 - \sigma) \exp\left[-\frac{\sigma}{2}\right] = \frac{-1}{8} R$$

$$\epsilon = \frac{-1}{8}$$

12.5

$$R = A \exp[-3\sigma]$$

$r = \sigma a_0$ (use in u -substitution to evaluate integrals)

$$\text{probability} = \frac{A^2 \int_0^{a_0} \exp[-6\sigma] r^2 dr}{A^2 \int_0^{\infty} \exp[-6\sigma] r^2 dr} = \frac{a_0^3 \int_0^1 \exp[-6\sigma] \sigma^2 d\sigma}{a_0^3 \int_0^{\infty} \exp[-6\sigma] \sigma^2 d\sigma} = 0.938031$$

evaluate integrals by tables or numerically

12.7

$$R = 2A\sigma \exp[-\sigma]$$

$r = \sigma a_0$ (use in u - substitution to evaluate integrals)

$$\langle r \rangle = \frac{\int r R^2 r^2 dr}{\int R^2 r^2 dr} = \frac{4A^2 \int_0^\infty \sigma^2 \exp[-2\sigma] r^3 dr}{4A^2 \int_0^\infty \sigma^2 \exp[-2\sigma] r^2 dr} = \frac{a_0^4 \frac{5!}{2^6}}{a_0^3 \frac{4!}{2^5}} = \frac{5}{2} a_0$$

12.9

$$R = A(2 - Z\sigma) \exp\left[-\frac{Z\sigma}{2}\right] = 0$$

$$\Rightarrow 2 - Z\sigma = 0 \Rightarrow \sigma = \frac{2}{Z} \Rightarrow r_{\text{node}} = a_0 \sigma = \frac{2a_0}{Z}$$

$r = \sigma a_0$ (use in u - substitution to evaluate integrals)

$w = Z\sigma$ (use in u - substitution to evaluate integrals)

$$\begin{aligned} \text{probability(inside)} &= \frac{\int_0^{r_{\text{node}}} R^2 r^2 dr \int r}{\int_0^\infty R^2 r^2 dr} = \frac{A^2 \int_0^{\frac{2a_0}{Z}} (2 - Z\sigma)^2 \exp[-Z\sigma] r^2 dr}{A^2 \int_0^\infty (2 - Z\sigma)^2 \exp[-Z\sigma] r^2 dr} = \frac{a_0^3 \int_0^{\frac{2}{Z}} (2 - Z\sigma)^2 \exp[-Z\sigma] \sigma^2 d\sigma}{a_0^3 \int_0^\infty (2 - Z\sigma)^2 \exp[-Z\sigma] \sigma^2 d\sigma} \\ &= \frac{\frac{1}{Z^3} \int_0^2 (2 - w)^2 \exp[-w] w^2 dw}{\frac{1}{Z^3} \int_0^\infty (2 - w)^2 \exp[-w] w^2 dw} = 0.052653 \end{aligned}$$

$$\text{Probability (outside)} = 1 - \text{probability (inside)} = 0.947347$$

12.11

For 2s and 2p, $n = 2$ Energy is a function of n only. Therefore $E_{2s} = E_{2p}$. They are degenerate

12.13

$$R = A \exp[-3\sigma]$$

 $r = \sigma a_0$ (use in u -substitution to evaluate integrals)

$$\langle r^2 \rangle = \frac{\int_0^\infty r^2 R^2 r^2 dr}{\int_0^\infty R^2 r^2 dr} = \frac{A^2 \int_0^\infty \exp[-6\sigma] r^4 dr}{A^2 \int_0^\infty \exp[-6\sigma] r^2 dr} = \frac{a_0^5 \frac{4!}{6^5}}{a_0^3 \frac{2!}{6^3}} = \frac{1}{3} a_0^2$$

12.15

$$\begin{aligned} d_1 + d_{-1} &= R(r) \sin \theta \cos \theta \exp[i\phi] + R(r) \sin \theta \cos \theta \exp[-i\phi] \\ &= R(r) \sin \theta \cos \theta (2 \cos \phi) = 2R(r) \cos \theta (\sin \theta \cos \phi) = 2R(r) \left(\frac{z}{r} \right) \left(\frac{x}{r} \right) \\ &= xzF(r) = d_{xz} \end{aligned}$$

$$\begin{aligned} d_2 - d_{-2} &= R(r) \sin^2 \theta \exp[2i\phi] - R(r) \sin^2 \theta \exp[-2i\phi] \\ &= R(r) \sin^2 \theta (2i \sin 2\phi) = 4iR(r) \sin \theta \sin \theta (\sin \phi \cos \phi) = 4iR(r) \sin \theta \cos \phi (\sin \theta \sin \phi) \\ &= 4iR(r) \left(\frac{x}{r} \right) \left(\frac{y}{r} \right) = xyF(r) = d_{xy} \end{aligned}$$

Note: $R(r)$ and $F(r)$ are not the same in different cases

12.17

$$\begin{aligned}
 f_2 - f_{-2} &= R(r) \sin^2 \theta \cos \theta \exp[2i\phi] - R(r) \sin^2 \theta \cos \theta \exp[-2i\phi] \\
 &= R(r) \sin^2 \theta \cos \theta (2i \sin 2\phi) = 4iR(r) \sin \theta \sin \theta \cos \theta (\sin \phi \cos \phi) = 4iR(r) \sin \theta \cos \phi (\sin \theta \sin \phi) (\cos \theta) \\
 &= 4iR(r) \left(\frac{x}{r} \right) \left(\frac{y}{r} \right) \left(\frac{z}{r} \right) = xyzF(r) = F_{xyz}
 \end{aligned}$$

12.19

$$\begin{aligned}
 \psi^* \psi &\propto \mathbf{p}_1^* \mathbf{p}_1 + \mathbf{p}_0^* \mathbf{p}_0 + \mathbf{p}_{-1}^* \mathbf{p}_{-1} \propto \left| \frac{1}{\sqrt{2}} \sin \theta \exp[i\phi] \right|^2 + |\cos \theta|^2 + \left| \frac{1}{\sqrt{2}} \sin \theta \exp[-i\phi] \right|^2 \\
 &= \frac{1}{2} \sin^2 \theta + \cos^2 \theta + \frac{1}{2} \sin^2 \theta = 1
 \end{aligned}$$

SECTION 12.2

12.21

$$S_y = \frac{1}{2i} (S_+ - S_-)$$

$$S_y \alpha = \frac{1}{2i} (0 - \beta) = -\frac{i}{2} \beta$$

$$S_y \beta = \frac{1}{2i} (\alpha - 0) = \frac{i}{2} \alpha$$

12.23

$$S_x S_y \beta = S_x \left(-\frac{i}{2} \alpha \right) = -\frac{i}{2} \frac{1}{2} \beta = -\frac{i}{4} \beta$$

12.25

$$\text{let } \chi = \alpha + i\beta$$

$$S_y \chi = S_y (\alpha + i\beta) = \frac{i}{2} \beta + i \frac{-i}{2} \alpha = \frac{1}{2} (\alpha + i\beta) = \frac{1}{2} \chi$$

$$\text{let } \xi = \alpha - i\beta$$

$$S_y \xi = S_y (\alpha - i\beta) = \frac{i}{2} \beta - i \frac{i}{2} \alpha = -\frac{1}{2} (\alpha - i\beta) = -\frac{1}{2} \xi$$

SECTION 12.3

12.27

$$Z = 3$$

$$E_h = 27.2 \text{ eV}$$



$$E_{\text{vac}} = -\left(Z - \frac{5}{16}\right)^2 E_h = -7.223 E_h$$

$$\text{IP} = -\frac{Z^2}{2} E_h - E_{\text{vac}} = 2.723 E_h = 74.1 \text{ eV}$$



$$\text{IP} = \frac{Z^2}{2} E_h = 122.4 \text{ eV} \quad (\text{Hydrogen-like ion})$$

SECTION 12.4

12.29

$$\begin{aligned}\int |\chi_s|^2 d\tau_1 d\tau_2 &= \frac{1}{2} \int (\alpha_1 \beta_2 + \alpha_2 \beta_1)^2 d\tau_1 d\tau_2 = \frac{1}{2} \int \alpha_1^2 \beta_2^2 + 2\alpha_1 \beta_2 \alpha_2 \beta_1 + \alpha_2^2 \beta_1^2 d\tau_1 d\tau_2 \\ &= \frac{1}{2} [1(1) + 2(0)(0) + 1(1)] = \frac{1}{2} (2) = 1\end{aligned}$$

$$\begin{aligned}\int |\chi_a|^2 d\tau_1 d\tau_2 &= \frac{1}{2} \int (\alpha_1 \beta_2 - \alpha_2 \beta_1)^2 d\tau_1 d\tau_2 = \frac{1}{2} \int \alpha_1^2 \beta_2^2 - 2\alpha_1 \beta_2 \alpha_2 \beta_1 + \alpha_2^2 \beta_1^2 d\tau_1 d\tau_2 \\ &= \frac{1}{2} [1(1) - 2(0)(0) + 1(1)] = \frac{1}{2} (2) = 1\end{aligned}$$

$$\begin{aligned}\int \chi_s \chi_a d\tau_1 d\tau_2 &= \frac{1}{2} \int (\alpha_1 \beta_2 + \alpha_2 \beta_1)(\alpha_1 \beta_2 - \alpha_2 \beta_1) d\tau_1 d\tau_2 = \frac{1}{2} \int \alpha_1^2 \beta_2^2 + \alpha_1 \beta_2 \alpha_2 \beta_1 - \alpha_1 \beta_2 \alpha_2 \beta_1 - \alpha_2^2 \beta_1^2 d\tau_1 d\tau_2 \\ &= \frac{1}{2} [1(1) - 0 - 1(1)] = \frac{1}{2} (0) = 0\end{aligned}$$

12.31

$$S_{x1} S_{x2} \alpha_1 \alpha_2 = S_{x1} \alpha_1 \left(\frac{1}{2} \beta_2 \right) = \left(\frac{1}{2} \beta_1 \right) \left(\frac{1}{2} \beta_2 \right) = \frac{1}{4} \beta_1 \beta_2$$

not an eigenvalue equation

12.33

$$X_s = \frac{\alpha_1\beta_2 + \alpha_2\beta_1}{\sqrt{2}}$$

$$X_a = \frac{\alpha_1\beta_2 - \alpha_2\beta_1}{\sqrt{2}}$$

$$\begin{aligned} S_T^2 \frac{\alpha_1\beta_2}{\sqrt{2}} &= \left\{ S_1^2 + S_2^2 + 2(S_{1x}S_{2x} + S_{1y}S_{2y} + S_{1z}S_{2z}) \right\} \frac{\alpha_1\beta_2}{\sqrt{2}} \\ &= \frac{1}{\sqrt{2}} \left(\frac{3}{4}\alpha_1\beta_2 + \frac{3}{4}\alpha_1\beta_2 + 2\left(\frac{1}{4}\beta_1\alpha_2 - \frac{1}{4}\beta_1\alpha_2 - \frac{1}{4}\alpha_1\beta_2 \right) \right) = \frac{1}{\sqrt{2}} (\alpha_1\beta_2 + \beta_1\alpha_2) = X_s \end{aligned}$$

$$S_T^2 \frac{\alpha_2\beta_1}{\sqrt{2}} = \frac{1}{\sqrt{2}} (\alpha_1\beta_2 + \beta_1\alpha_2) = X_s$$

$$S_T^2 X_s = 2X_s = s_T(s_T + 1)X_s$$

$$\Rightarrow s_T = 1$$

$$S_T^2 X_a = X_s - X_s = 0$$

$$\Rightarrow s_T = 0$$

12.35

$$\lambda_1 = 58.44 \text{ nm}$$

$$\lambda_2 = 2058.2 \text{ nm}$$

$$\Delta E = \frac{1}{\lambda_1} - \frac{1}{\lambda_2} = 166.3 \times 10^3 \text{ cm}^{-1}$$

SECTION 12.6

12.37

$$j_1 = 3/2$$

$$j_2 = 5/2$$

$$J = (j_1 + j_2), (j_1 + j_2 - 1), \dots, |j_1 - j_2| = 4, 3, 2, 1$$

degeneracy = $2J + 1$	4	$2(4)+1 = 9$
	3	7
	2	5
	1	3

$$\text{Total} = 9 + 7 + 5 + 3 = 24$$

12.39

$$j_1 = 1$$

$$j_2 = 1/2$$

$$j_3 = 1/2$$

$$J_{12} = (j_1 + j_2), (j_1 + j_2 - 1), \dots, |j_1 - j_2| = 3/2, 1/2$$

$$J_{123} = (J_{12} + j_3), (J_{12} + j_3 - 1), \dots, |J_{12} - j_3| = 2, 1 \text{ and } 1, 0$$

$$\text{degeneracy} = \sum 2J + 1 = 5 + 2(3) + 1(1) = 12$$

12.41

a)

$$\begin{array}{lll} {}^4\text{S} & \begin{array}{l} L = 0 \\ S = 3/2 \end{array} & \begin{array}{l} g_L = 2L + 1 = 1 \\ g_S = 2S + 1 = 4 \end{array} \\ & & g = g_L (g_S) = 1(4) = 4 \end{array}$$

b)

$$\begin{array}{lll} {}^4\text{G} & \begin{array}{l} L = 4 \\ S = 3/2 \end{array} & \begin{array}{l} g_L = 2L + 1 = 9 \\ g_S = 2S + 1 = 4 \end{array} \\ & & g = g_L (g_S) = 9(4) = 36 \end{array}$$

c)

$$\begin{array}{lll} {}^3\text{P} & \begin{array}{l} L = 1 \\ S = 1 \end{array} & \begin{array}{l} g_L = 2L + 1 = 3 \\ g_S = 2S + 1 = 3 \end{array} \\ & & g = g_L (g_S) = 3(3) = 9 \end{array}$$

d)

$$\begin{array}{lll} {}^2\text{D} & \begin{array}{l} L = 2 \\ S = 1/2 \end{array} & \begin{array}{l} g_L = 2L + 1 = 5 \\ g_S = 2S + 1 = 2 \end{array} \\ & & g = g_L (g_S) = 5(2) = 10 \end{array}$$

SECTION 12.7

12.43

d orbital - The maximum number of electrons in the d orbitals is 10.

The number of configurations for 5 electrons in a d orbital is:

$$\frac{10!}{(10-5)!5!} = \frac{10(9)(8)(7)(6)}{5(4)(3)(2)(1)} = 252$$

$$\begin{array}{lcl} \text{ground state:} & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\ & \underline{\quad} & \underline{\quad} & \underline{\quad} & \underline{\quad} & \underline{\quad} \\ \text{l:} & 2 & 1 & 0 & -1 & -2 \end{array}$$

For this configuration, $L = 0$ and $S = 5/2$

$$\begin{array}{lll} {}^6\text{S} & L = 0 & g_L = 2L + 1 = 1 \\ & S = 5/2 & g_S = 2S + 1 = 6 \\ & & g = g_L (g_S) = 1(6) = 6 \end{array}$$

12.45

p orbital - The maximum number of electrons in the p orbitals is 6

The number of configurations for 3 electrons in a p orbital is:

$$\frac{6!}{(6-3)!3!} = \frac{6(5)(4)}{3(2)(1)} = 20$$

p_1	p_0	p_{-1}	M_L	M_S	4S	2D	2P
$\uparrow\downarrow$	\uparrow		2	1/2		x	
$\uparrow\downarrow$	\downarrow		2	-1/2		x	
$\uparrow\downarrow$		\uparrow	1	1/2		x	
$\uparrow\downarrow$		\downarrow	1	-1/2		x	
\uparrow	$\uparrow\downarrow$		1	1/2			x
\downarrow	$\uparrow\downarrow$		1	-1/2			x
	$\uparrow\downarrow$	\uparrow	-1	1/2		x	
	$\uparrow\downarrow$	\downarrow	-1	-1/2		x	
\uparrow		$\uparrow\downarrow$	-1	1/2			x
\downarrow		$\uparrow\downarrow$	-1	-1/2			x
	\uparrow	$\uparrow\downarrow$	-2	1/2		x	
	\downarrow	$\uparrow\downarrow$	-2	-1/2		x	
\uparrow	\uparrow	\uparrow	0	3/2	x		
\uparrow	\uparrow	\downarrow	0	1/2	x		
\uparrow	\downarrow	\uparrow	0	1/2			x
\downarrow	\uparrow	\uparrow	0	1/2		x	
\downarrow	\downarrow	\uparrow	0	-1/2	x		
\downarrow	\uparrow	\downarrow	0	-1/2		x	
\uparrow	\downarrow	\downarrow	0	-1/2			x
\downarrow	\downarrow	\downarrow	0	-3/2		x	

Student's Solutions Manual

12.47

$$d^2 \quad S = 1, L = 3 \quad {}^3F$$

$$f^9 = f^5 \quad S = 5/2, L = 5 \quad {}^6H$$

$$f^{14} = f^0 \quad S = 0, L = 0 \quad {}^1S$$

$$s^1 d^5 \quad S = 1/2 + 5/2 = 3, L = 0 \quad {}^7S$$

$$f^3 \quad S = 3/2, L = 6 \quad {}^4I$$

$$g^2 \quad S = 1, L = 7 \quad {}^3K$$

12.49

$${}^6H \quad S = 5/2, L = 5 \quad g = 6(11) = 66$$

$$J = L + S, L + S - 1, \dots, |L - S| = 15/2, 13/2, 11/2, 9/2, 7/2, 5/2$$

$$g_J = \sum 2J + 1 = 16 + 14 + 12 + 10 + 8 + 6 = 66$$

12.51

$$E_2 = 0 \text{ cm}^{-1}$$

$$E_1 = 158.265 \text{ cm}^{-1}$$

$$E_0 = 226.997 \text{ cm}^{-1}$$

$$\frac{E_J - E_{J-1}}{hc} = \frac{1}{2} A(J(J+1) - L(L+1) - S(S+1)) - \frac{1}{2} A((J-1)J - L(L+1) - S(S+1)) = \frac{A}{2} [J^2 + J - (J^2 - J)] =$$

$$\Rightarrow A = \frac{E_J - E_{J-1}}{hcJ}$$

$$J = 2: \quad A = \frac{E_2 - E_1}{2hc} = -79.13 \text{ cm}^{-1}$$

$$J = 1: \quad A = \frac{E_1 - E_0}{hc} = -68.73 \text{ cm}^{-1}$$

12.53

$$E_4 = 0 \text{ cm}^{-1}$$

$$E_3 = 415.932 \text{ cm}^{-1}$$

$$E_2 = 704.003 \text{ cm}^{-1}$$

$$E_1 = 888.132 \text{ cm}^{-1}$$

$$E_0 = 978.076 \text{ cm}^{-1}$$

$$\frac{E_J - E_{J-1}}{hc} = \frac{1}{2} A(J(J+1) - L(L+1) - S(S+1)) - \frac{1}{2} A((J-1)J - L(L+1) - S(S+1)) = \frac{A}{2} [J^2 + J - (J^2 - J)] =$$

$$\Rightarrow A = \frac{E_J - E_{J-1}}{hcJ}$$

$$J = 4: \quad A = \frac{E_4 - E_3}{4hc} = -103.98 \text{ cm}^{-1}$$

$$J = 3: \quad A = \frac{E_3 - E_2}{3hc} = -96.02 \text{ cm}^{-1}$$

$$J = 2: \quad A = \frac{E_2 - E_1}{2hc} = -92.06 \text{ cm}^{-1}$$

$$J = 1: \quad A = \frac{E_1 - E_0}{hc} = -89.94 \text{ cm}^{-1}$$

SECTION 12.8

12.55

The ground state electronic configuration for K is $[\text{Ar}]4s^1$. This gives a term symbol of 4^2S . The selection rules for allowed transitions are $\Delta S = 0$ and $\Delta L = \pm 1$. This implies the excited state is 4^2P , which is separated by spin-orbit coupling into $4^2P_{3/2}$ and $4^2P_{1/2}$.

$$\nu_{3/2} = 393.366 \text{ nm}$$

$$\nu_{1/2} = 396.847 \text{ nm}$$

$$\frac{E_J - E_{J-1}}{hc} = \frac{1}{2} A (J(J+1) - L(L+1) - S(S+1)) - \frac{1}{2} A ((J-1)J - L(L+1) - S(S+1)) = \frac{A}{2} [J^2 + J - (J^2 - J)] = AJ$$

$$\Rightarrow A = \frac{E_J - E_{J-1}}{hcJ} = \frac{\frac{1}{\nu_J} - \frac{1}{\nu_{J-1}}}{J}$$

$$J = 3/2: \quad A = \frac{\frac{1}{\nu_{3/2}} - \frac{1}{\nu_{1/2}}}{\frac{3}{2}} = 148.7 \text{ cm}^{-1}$$

The ground state has energy levels $3^2P_{1/2}$ (1) and $3^2P_{3/2}$ (2)

The first excited state has energy level $4^2S_{1/2}$ (3)

The second excited state has energy levels $3^2D_{3/2}$ (4) and $3^2D_{5/2}$ (5)

line	transition
ν_1	(1) to (3)
ν_2	(2) to (3)
ν_3	(1) to (4)
ν_4	(2) to (4)
ν_5	(2) to (5)

$$\Delta E(^2P) = \nu_2 - \nu_1 = 112.1 \text{ cm}^{-1} = A \left(\frac{3}{2} \right) \Rightarrow A = 74.7 \text{ cm}^{-1}$$

SECTION 12.9

12.59

$$g_L = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

$${}^4S_{3/2} \quad J = 3/2, S = 3/2, L = 0 \quad g_L = 1 + \frac{\frac{3}{2}(\frac{3}{2}+1) + \frac{3}{2}(\frac{3}{2}+1) - 0(0+1)}{2 \cdot \frac{3}{2}(\frac{3}{2}+1)} = 1 + \frac{2(\frac{15}{4})}{\frac{15}{2}} = 1 + 1 = 2$$

$${}^4P_{5/2} \quad J = 5/2, S = 3/2, L = 1 \quad g_L = 1 + 6/10 = 1.6$$

$${}^4P_{3/2} \quad J = 3/2, S = 3/2, L = 1 \quad g_L = 1 + 22/30 = 1.733$$

$${}^4P_{1/2} \quad J = 1/2, S = 3/2, L = 1 \quad g_L = 1 + 5/3 = 2.667$$

12.61

3P_2 splits into 5 lines ($M_j = -2$ to 2); 3S_1 splits into 3 lines ($M_j = -1$ to 1)

Parallel - $\Delta M_j = \pm 1$ 6 lines

Perpendicular - $\Delta M_j = \pm 1, 0$ 9 lines

12.63

$$g_L = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

$$^3\text{H}_4 \quad J = 4, S = 1, L = 5 \quad g_L = 1 - 1/5 = 0.8$$

$$|\mu_J| = g_L \sqrt{J(J+1)} \mu_B = 3.58 \mu_B$$

The lower bound for the magnetic moment would be the spin-only moment

$$|\mu_S| = 2\sqrt{S(S+1)} \mu_B = 2.83 \mu_B$$

Therefore, the range of values would be $2.83 \mu_B$ to $3.58 \mu_B$

12.65

$$g = 2$$

$$B_o = 1.4 \text{ Tesla}$$

$$\nu = \frac{g\mu_B B_o}{h} = 39.2 \times 10^9 \text{ Hz}$$

12.67

In the absence of an electric field, there will be a single line for the transition.

In the presence of the field, the 1P_1 line will be split into two levels, one for $M_J = 0$ and one for $M_J = \pm 1$, since $(\pm 1)^2 = 1$. This will lead to two lines in the transition

12.69

$$g_N = 5.585486$$

$$\mu_N = 5.0508 \times 10^{-27} \text{ J / Tesla}$$

$$\nu = 500 \times 10^6 \text{ Hz}$$

$$\nu = \frac{g_N \mu_N B_o}{h} \Rightarrow B_o = \frac{h\nu}{g_N \mu_N} = 11.74 \text{ Tesla}$$

SECTION 12.10

12.71

$$\frac{I(P_{3/2})}{I(P_{1/2})} = \frac{g_{3/2}}{g_{1/2}} \frac{\exp\left[\frac{-E_{3/2}}{kT}\right]}{\exp\left[\frac{-E_{1/2}}{kT}\right]} = \frac{g_{3/2}}{g_{1/2}} \exp\left[\frac{\Delta E}{kT}\right]$$

$$g_l = 2J + 1$$

The relative intensity will be less for the 4d and 4f lines because the energy difference is less, meaning the exponential is closer to 1, and the ratio of degeneracies is also closer to 1 for larger J.

The high energy peak is due to $4d_{3/2}$ and the low energy peak is due to $4d_{5/2}$.

SECTION 12.11

12.73

$$^{23}\text{Na} = [\text{Ne}] 3s^1 \quad L = 0, \quad S = 1/2$$

$$I = 3/2$$

$$T = I + S, \dots, |I-S| = 2, 1$$

12.75

$$H\psi = \{-g\mu_B B_o S_z + Ah I_z S_z\} \psi = (-g\mu_B B_o m_s + Ah m_l m_s) \psi = E\psi$$

$$\Rightarrow E = -g\mu_B B_o m_s + Ah m_l m_s$$

There will be two transitions, $m_s = \pm 1/2$ when $m_l = 1/2$ and $m_s = \pm 1/2$ when $m_l = -1/2$.

$$\nu_1 = \frac{\frac{1}{2} g\mu_B B_o + \frac{1}{4} Ah - \left(-\frac{1}{2} g\mu_B B_o - \frac{1}{4} Ah\right)}{h} = \frac{g\mu_B B_o}{h} + \frac{1}{2} A$$

$$\nu_2 = \frac{\frac{1}{2} g\mu_B B_o - \frac{1}{4} Ah - \left(-\frac{1}{2} g\mu_B B_o + \frac{1}{4} Ah\right)}{h} = \frac{g\mu_B B_o}{h} - \frac{1}{2} A$$

$$\Delta\nu = \nu_1 - \nu_2 = A$$

CHAPTER 13 *Diatomic Molecules*

SECTION 13.2

13.1

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\mu^{35-35} = 2.903359 \times 10^{-23} \text{ g}$$

$$\mu^{35-37} = 2.983962 \times 10^{-23} \text{ g}$$

$$\mu^{35-35} = 3.069168 \times 10^{-23} \text{ g}$$

$$\omega_e^{35-35} = 564.9 \text{ cm}^{-1}$$

$$\omega_e^{35-37} = \omega_e^{35-35} \sqrt{\frac{\mu^{35-35}}{\mu^{35-37}}} = 557.2 \text{ cm}^{-1}$$

$$\omega_e^{37-37} = \omega_e^{35-35} \sqrt{\frac{\mu^{35-35}}{\mu^{37-37}}} = 549.4 \text{ cm}^{-1}$$

13.3

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$k_e = (2\pi c \omega_e)^2 \mu = (2\pi c \omega_e)^2 \frac{m_C m_O}{m_C + m_O} = 1902.5 \text{ kg / s}^2$$

$$m = 1 \text{ lb} = 0.4536 \text{ kg}$$

$$mg = k_e x \Rightarrow x = \frac{mg}{k_e} = 0.234 \text{ cm}$$

13.5

$$\Delta_f H_0 = \frac{1}{2} D_0(\text{Cl}_2) + \frac{1}{2} D_0(\text{H}_2) - D_0(\text{HCl}) = -0.9599 \text{ eV} = -92.61 \text{ kJ / mol}$$

13.7

Note: All unprimed variables refer to H₂; All primed variables refer to D₂; All double-primed variables refer to HD.

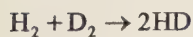
$$\omega_e' = \omega_e \sqrt{\frac{\mu}{\mu'}} = 3109.1 \text{ cm}^{-1}$$

$$\omega_e'' = \omega_e \sqrt{\frac{\mu}{\mu''}} = 3806.8 \text{ cm}^{-1}$$

$$D_e = D_0 + \frac{1}{2} \omega_e = 38309.4 \text{ cm}^{-1}$$

$$D_0' = D_e - \frac{1}{2} \omega_e' = 36754.9 \text{ cm}^{-1} = 4.5570 \text{ eV}$$

$$D_0'' = D_e - \frac{1}{2} \omega_e'' = 36406.0 \text{ cm}^{-1} = 4.5138 \text{ eV}$$



$$\Delta H_0 = D_0 + D_0' - 2D_0'' = 6.7 \times 10^{-3} \text{ eV} = 647 \text{ J / mol}$$

13.9

$$D_e = D_o + \frac{1}{2} \omega_e - \frac{1}{4} \omega_e \chi_e = 90674 \text{ cm}^{-1} = 11.242 \text{ eV}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$k = (2\pi c \omega_e)^2 \mu \Rightarrow \sqrt{k} = 2\pi c \omega_e \sqrt{\mu} = 2\pi c \omega_e \sqrt{\frac{m_C m_O}{m_C + m_O}} = 1379.34 \sqrt{g/s}$$

$$\beta = \sqrt{\frac{k}{2D_e}} = 22.9816 \text{ nm}^{-1}$$

$$R_e = 0.1128 \text{ nm}$$

$$E = D_e \left(1 - \exp \left[-\beta (R - R_e) \right] \right)^2$$

R (nm)	E (eV)
0.06	62.88 eV
0.11	0.0497
0.2	8.42
0.3	10.94
5	11.24

13.11

$$n_{\max} = \frac{\omega_e}{2\omega_e \chi_e} = 81.61 \approx 81$$

$$D_e = \frac{\omega_e^2}{4\omega_e \chi_e} = 96288.04 \text{ cm}^{-1} = 11.94 \text{ eV}$$

13.13

$$\tilde{\nu}_0 = \frac{E_1 - E_0}{hc} = \omega_e - 2\omega_e x_e = 3958.38 \text{ cm}^{-1} \text{ (fundamental)}$$

$$\tilde{\nu}_1 = \frac{E_2 - E_0}{hc} = 2\omega_e - 6\omega_e x_e = 7736.63 \text{ cm}^{-1} \text{ (first overtone)}$$

$$\tilde{\nu}_2 = \frac{E_2 - E_1}{hc} = \omega_e - 4\omega_e x_e = 3778.24 \text{ cm}^{-1} \text{ (hot band)}$$

13.15

$$\tilde{\nu}_0 = \frac{E_1 - E_0}{hc} = \omega_e - 2\omega_e x_e = 381.25 \text{ cm}^{-1} \text{ (fundamental)}$$

$$\tilde{\nu}_2 = \frac{E_2 - E_1}{hc} = \omega_e - 4\omega_e x_e = 378.32 \text{ cm}^{-1} \text{ (hot band)}$$

$$T = 300 \text{ K}$$

$$\text{Relative Intensity} \equiv \frac{N_1}{N_0} = \exp\left[-\frac{hc\omega_e}{kT}\right] = 0.158$$

13.17

$$\omega_e = 159.12 \text{ cm}^{-1}$$

$$\omega_e \chi_e = 0.725 \text{ cm}^{-1}$$

$$\omega_e \gamma_e = 0.0011 \text{ cm}^{-1}$$

$$E_n = \omega_e \left(n + \frac{1}{2}\right) - \omega_e \chi_e \left(n + \frac{1}{2}\right)^2 - \omega_e \gamma_e \left(n + \frac{1}{2}\right)^3$$

$$E_n = E_{n-1} \Rightarrow \omega_e \left(n + \frac{1}{2}\right) - \omega_e \chi_e \left(n + \frac{1}{2}\right)^2 - \omega_e \gamma_e \left(n + \frac{1}{2}\right)^3 = \omega_e \left(n - \frac{1}{2}\right) - \omega_e \chi_e \left(n - \frac{1}{2}\right)^2 - \omega_e \gamma_e \left(n - \frac{1}{2}\right)^3$$

$$\Rightarrow \left(\frac{1}{4}\omega_e \gamma_e - \omega_e\right) + 2\omega_e \chi_e n + 3\omega_e \gamma_e n^2 = 0$$

Use the quadratic equation to solve for n .

$$n = 90.9 \cong 90$$

$$\Rightarrow D_0 = E_{90} - E_0 = 7567.7 \text{ cm}^{-1} = .9383 \text{ eV}$$

SECTION 13.3

13.19

$$\Delta E_J^n = E_{J+1}^n - E_J^n = (J+1)(J+2)B_n - (J+1)^2(J+2)^2D_c - \left\{ (J)(J+1)B_n - (J)^2(J+1)^2D_c \right\}$$

$$\Delta E_J^n = 2(J+1)B_n - 4(J+1)^3D_c$$

$$\omega_e = 1405.65 \text{ cm}^{-1}$$

$$\tilde{B}_e = 7.5131 \text{ cm}^{-1}$$

$$\alpha_e = 0.2132 \text{ cm}^{-1}$$

$$D_e = \frac{4\tilde{B}_e^3}{\omega_e^2} = 8.58545 \times 10^{-4} \text{ cm}^{-1}$$

$$B_0 = \tilde{B}_e - \frac{1}{2}\alpha_e = 7.4065 \text{ cm}^{-1}$$

$$\Delta E_J^0 = 2(J+1)B_0 - 4(J+1)^3D_c$$

J	ΔE_J^0 (GHz)
0	443.98
1	887.33
2	1329.5
3	1769.7

13.21

$$\Delta E_J^n = E_{J+1}^n - E_J^n = (J+1)(J+2)B_n - (J+1)^2(J+2)^2D_c - \left\{ (J)(J+1)B_n - (J)^2(J+1)^2D_c \right\}$$

$$\Delta E_J^n = 2(J+1)B_n - 4(J+1)^3D_c$$

$$\Delta E_1^0 = 4B_0 - 32D_c = 230.53797 \text{ GHz}$$

$$\Delta E_3^0 = 8B_0 - 256D_c = 461.0468 \text{ GHz}$$

$$8\Delta E_1^0 - \Delta E_3^0 = 24B_0 = 1383.2567 \text{ GHz} \Rightarrow B_0 = 57.6357 \text{ GHz}$$

$$2\Delta E_1^0 - \Delta E_3^0 = 192D_c = 0.02914 \text{ GHz} \Rightarrow D_c = 151.8 \text{ MHz}$$

13.23

$$T = 300 \text{ K}$$

$$\mu = 1.656 \times 10^{-24} \text{ g}$$

$$R_e = 1.414 \times 10^{-8} \text{ cm}$$

$$I = \mu R_e^2$$

$$\frac{N'}{N_0} = (2J' + 1) \exp \left[- \frac{J'(J' + 1)}{kT} \frac{h^2}{8\pi^2 \mu R_e^2} \right]$$

J'	N'/N_0
0	1
4	4.0
10	0.24
20	1.6×10^{-6}

13.25

Note: The unprimed variables refer to the 35 isotope of chlorine; the primed variables refer to the 37 isotope of chlorine

$$B_e = 15.58369 \text{ GHz}$$

$$B'_e = 15.18922 \text{ GHz}$$

$$\mu = 2.044172 \times 10^{-23} \text{ g}$$

$$\mu' = 2.083803 \times 10^{-23} \text{ g}$$

$$I = \mu R_e^2$$

$$B_e = \frac{h}{8\pi^2 I} = \frac{h}{8\pi^2 \mu R_e^2} \Rightarrow R_e = \left(\frac{h}{8\pi^2 \mu B_e} \right)^{1/2} = 0.1623078 \text{ nm}$$

$$B'_e = \frac{h}{8\pi^2 I'} = \frac{h}{8\pi^2 \mu' R_e'^2} \Rightarrow R'_e = \left(\frac{h}{8\pi^2 \mu' B'_e} \right)^{1/2} = 0.1628311 \text{ nm}$$

13.27

$$\omega_e = 384.18 \text{ cm}^{-1}$$

$$\omega_e \chi_e = 1.465 \text{ cm}^{-1}$$

$$B_e = 0.1142 \text{ cm}^{-1}$$

$$\alpha_e = 0.00053 \text{ cm}^{-1}$$

$$D_e \cong 0 \text{ cm}^{-1}$$

$$E_J^n = \omega_e \left(n + \frac{1}{2}\right) - \omega_e \chi_e \left(n + \frac{1}{2}\right)^2 + (J)(J+1) \left(B_e - \left(n + \frac{1}{2}\right) \alpha_e \right) - (J)^2 (J+1)^2 D_e$$

$$R0 = E_1^1 - E_0^0 = \frac{3}{2} \omega_e - \frac{9}{4} \omega_e \chi_e + 2B_e - 3\alpha_e - 4D_e - \left(\frac{1}{2} \omega_e - \frac{1}{4} \omega_e \chi_e \right) = \omega_e - 2\omega_e \chi_e + 2B_e - 3\alpha_e = 381.48 \text{ cm}^{-1}$$

$$P1 = E_0^1 - E_1^0 = \frac{3}{2} \omega_e - \frac{9}{4} \omega_e \chi_e - \left(\frac{1}{2} \omega_e - \frac{1}{4} \omega_e \chi_e + 2B_e - \alpha_e - 4D_e \right) = \omega_e - 2\omega_e \chi_e - 2B_e + \alpha_e = 381.02 \text{ cm}^{-1}$$

13.31

$$J_{\max} = 8$$

$$B_e \cong B_o = 1.9227 \text{ cm}^{-1}$$

J_{\max} is found by maximizing the expression for the relative population in the J th rotational energy level, as given by Boltzmann's Law.

$$J_{\max} = \frac{1}{2} \left(\left(\frac{2kT}{B_e h} \right)^{1/2} - 1 \right)$$

$$\Rightarrow \frac{2kT}{B_e h} = (2J_{\max} + 1)^2 \Rightarrow T = \frac{B_e h}{2k} (2J_{\max} + 1)^2 \cong 400 \text{ K}$$

13.33

$$\omega_e = 2170.21 \text{ cm}^{-1}$$

$$\omega_e x_e = 13.461 \text{ cm}^{-1}$$

$$B_e = 1.9314 \text{ cm}^{-1}$$

$$\alpha_e = 0.01748 \text{ cm}^{-1}$$

$$E_J^n = \omega_e \left(n + \frac{1}{2}\right) - \omega_e x_e \left(n + \frac{1}{2}\right)^2 + (J)(J+1) \left(B_e - \left(n + \frac{1}{2}\right) \alpha_e\right)$$

$$E_0^1 = E_J^0 \Rightarrow \frac{3}{2} \omega_e - \frac{9}{4} \omega_e x_e = \left(\frac{1}{2} \omega_e - \frac{1}{4} \omega_e x_e + J(J+1) B_e - \frac{1}{2} J(J+1) \alpha_e \right) \Rightarrow J(J+1) = \frac{\omega_e - 2 \omega_e x_e}{B_e - \alpha_e} = 1114.75$$

$$\Rightarrow J = 33$$

13.35

$$\omega_e = 498.8 \text{ cm}^{-1}$$

$$\frac{I}{I_o} = C_1 \exp\left[-\frac{n\omega_e hc}{kT}\right] \Rightarrow \ln\left(\frac{I}{I_o}\right) = \ln(C_1) - \frac{n\omega_e hc}{kT}$$

Plot $\ln\left(\frac{I}{I_o}\right)$ vs. n and do linear regression; slope = $-\frac{\omega_e hc}{kT}$

n	I/I_o (mm) - from figure	$\ln(I/I_o)$
0	27.6	3.32
1	15.2	2.72
2	9.4	2.24
3	6.1	1.81
4	4.9	1.59
5	3.0	1.10

$$\text{slope} = -0.4263$$

$$T = 1686 \text{ K} \cong 1700 \pm 100 \text{ K (within standard error)}$$

SECTION 13.4

13.37

$(2s\sigma_g)^1(2s\sigma_u^*)^1$	$\Lambda = 0 \quad S = 0 \text{ or } 1$	$^1\Sigma_u^+ \text{ or } ^3\Sigma_u^+$
$(2p\sigma_g)^2(2p\pi_u)^2$	first term gives $\Lambda = 0 \quad S = 0$ second term gives $\Lambda = 0 \quad S = 0 \text{ or } 1$ $\Lambda = \pm 2 \quad S = 0$	or
	Total symbols are	$^1\Sigma_g^+ \text{ or } ^3\Sigma_g^- \text{ or } ^1\Delta_g$
$(2p\sigma_g)^1(2p\pi_u)^3$	$\Lambda = \pm 2 \quad S = 0 \text{ or } 1$	$^1\Pi_u \text{ or } ^3\Pi_u$
$(2p\sigma_g)^1(2p\pi_u)^1(2p\pi_g^*)^1$	$\Lambda = \pm 2 \quad S = 0 \text{ or } 1$ $\Lambda = 0 \quad S = 0 \text{ or } 1$	or
	Total symbols are	$^1\Sigma_u^{+/-} \text{ or } ^3\Sigma_u^{+/-} \text{ or } ^1\Delta_u \text{ or } ^3\Delta_u$

SECTION 13.5

13.39

$$(1s\sigma_g)^2 \rightarrow (1s\sigma_g)^1(2p\pi_u)^1 \quad \Lambda = \pm 1 \quad S = 0 \text{ or } 1$$

term symbols are $^1\Pi_u$ or $^3\Pi_u$

13.41

$^1\Sigma^+$:	$1 \times 1 = 1$	$^1\Sigma^-$:	$1 \times 1 = 1$
$^2\Pi$:	$2 \times 2 = 4$	$^2\Delta$:	$2 \times 2 = 4$
$^3\Sigma_g$:	$3 \times 1 = 3$	$^3\Sigma_u$:	$3 \times 1 = 3$

13.43

O_2^+	$(1s\sigma_g)^2(1s\sigma_u^*)^2(2s\sigma_g)^2(2s\sigma_u^*)^2(2p\pi_u)^4(2p\sigma_g)^2(2p\pi_g^*)^1$	bond order = 5/2
O_2	$(1s\sigma_g)^2(1s\sigma_u^*)^2(2s\sigma_g)^2(2s\sigma_u^*)^2(2p\pi_u)^4(2p\sigma_g)^2(2p\pi_g^*)^2$	bond order = 2
O_2^-	$(1s\sigma_g)^2(1s\sigma_u^*)^2(2s\sigma_g)^2(2s\sigma_u^*)^2(2p\pi_u)^4(2p\sigma_g)^2(2p\pi_g^*)^3$	bond order = 3/2

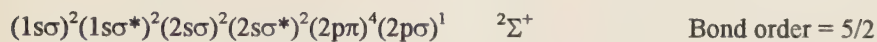
As the bond order decreases, the strength of the bond also decreases. This is consistent with the fact that the bond length increases as the bond strength decreases (as shown by the data in the problem).

13.45

$X^1\Sigma_g$	$(1s\sigma_g)^2(1s\sigma_u^*)^2(2s\sigma_g)^2(2s\sigma_u^*)^2(2p\pi_u)^4$
$^3\Pi_u$	$(1s\sigma_g)^2(1s\sigma_u^*)^2(2s\sigma_g)^2(2s\sigma_u^*)^2(2p\pi_u)^3(2p\sigma_g)^1$
$^3\Sigma_g$	$(1s\sigma_g)^2(1s\sigma_u^*)^2(2s\sigma_g)^2(2s\sigma_u^*)^2(2p\pi_u)^2(2p\sigma_g)^2$

13.47

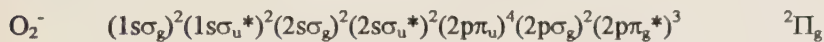
BO is a near-homonuclear molecule with 13 electrons



13.49



13.51



13.53

The selection rules are: $\Delta\Lambda = 0, \pm 1$
 $\Delta S = 0$
 + does not go to -

The allowed transitions are: $X^3\Sigma^- \leftrightarrow A^3\Pi$
 $b^1\Sigma^+ \leftrightarrow c^1\Sigma^+$

13.55

The selection rules are:

$$\Delta\Lambda = 0, \pm 1$$

$$\Delta S = 0$$

$$g \leftrightarrow u$$

State	Λ	S
$^3\Sigma_g$	0	1
$^1\Delta_g$	2	0

13.57

The selection rules are:

$$\Delta\Lambda = 0, \pm 1$$

$$\Delta S = 0$$

$$g \leftrightarrow u$$

vertical mirror symmetry (+/-) does not change

N_2 ground state is $^1\Sigma_g^+$ Allowed transitions are to $^1\Sigma_u^+$ and $^1\Pi_u$

O_2 ground state is $^3\Sigma_g^-$ Allowed transitions are to $^3\Sigma_u^-$ and $^3\Pi_u$

13.59

$$v_{v'-0} = v_{00} + v'(\omega'_e - \omega'_e x'_e) - (v')^2 \omega'_e x'_e$$

$$\Rightarrow \frac{v_{v'-0} - v_{00}}{v'} = (\omega'_e - \omega'_e x'_e) - (v') \omega'_e x'_e$$

$$v_{00} = 39,699.1 \text{ cm}^{-1}$$

Plotting $\frac{v_{v'-0} - v_{00}}{v'}$ vs. v' and using linear regression gives

$$(\text{slope}) -7.280 = -\omega'_e x'_e \Rightarrow \omega'_e x'_e = 7.3 \text{ cm}^{-1}$$

$$(\text{intercept}) 1094.84 = (\omega'_e - \omega'_e x'_e) \Rightarrow \omega'_e = 1102.1 \text{ cm}^{-1}$$

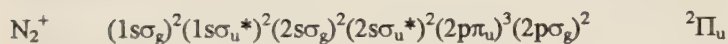
13.61

a) Plotting the data and doing linear regression gives an intercept of $57,214 \text{ cm}^{-1}$. This value is the dissociation energy of O_2 .

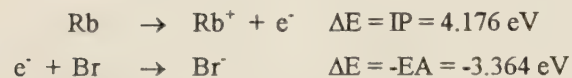
b) D_0 equals dissociation energy minus atomic energy

$$D_0 = 57,214 \text{ cm}^{-1} - 15,868 \text{ cm}^{-1} = 41,346 \text{ cm}^{-1} = 5.13 \text{ eV}$$

13.63



13.65



13.67

$$\begin{aligned} \omega_e &= 364.6 \text{ cm}^{-1} \\ R_e &= 2.3609 \times 10^{-8} \text{ cm} \\ \text{IP-EA} &= 1.523 \text{ eV} \\ \mu &= 2.30328 \times 10^{-23} \text{ g} \end{aligned}$$

For equations, see example 13.12

$$B = 2 + \frac{k_e R_e^3 (4\pi\epsilon_0)}{e^2} = 8.1966$$

$$k_e = \mu (2\pi c \omega_e)^2 = 108636.1 \text{ g/s}^2$$

$$A = \frac{e^2 \exp[B]}{(4\pi\epsilon_0) B R_e} = 4.32556 \times 10^{-16} \text{ J} = 2700.04 \text{ eV}$$

$$D_e = -E_e(R_e) = 3.83 \text{ eV}$$

13.69

$$\mu_0 = 6.32 \text{ debye}$$

$$R_e = 1.5639 \times 10^{-10} \text{ m}$$

$$\% \text{ ionic} = \frac{100\mu_0}{eR_e} = 84.14\%$$

13.71

$$P = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{\rho} = \frac{4\pi L}{3} \left(\alpha + \frac{\mu_o^2}{3kT} \right) \text{ (equation 13.55)}$$

Plotting P vs. $\frac{1}{T}$ and using linear regression gives

$$(\text{slope}) \quad \frac{4\pi L}{3} \frac{\mu_o^2}{3k} = 7060.6 \text{ cm}^3 \text{ K} \Rightarrow \mu_o = 1.08 \text{ D} \quad \text{and}$$

$$(\text{y-intercept}) \quad \frac{4\pi L}{3} \alpha = 25547 \text{ cm}^3 \Rightarrow \alpha = 1.013 \times 10^{-23} \text{ cm}^3$$

13.73

$$\mu = 2.3033 \times 10^{-26} \text{ kg}$$

$$R_e = 2.3609 \times 10^{-10} \text{ m}$$

$$I = \mu R_e^2 = 1.2838 \times 10^{-45} \text{ kg} \cdot \text{m}^2$$

$$\varepsilon = 250,000 \frac{\text{V}}{\text{m}}$$

$$\mu_0 = 9.00 \text{ Debye}$$

$$\Delta E(M=0 \text{ to } 1) = \frac{3I\mu_0^2\varepsilon^2}{10\hbar^2} = 1.9506 \times 10^{-24} \text{ J}$$

$$\nu = \frac{\Delta E}{h} = 2.94 \text{ GHz}$$

13.75

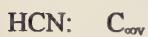
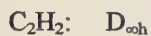
a) non-zero b) 0 c) non-zero d) 0

b) and d) are odd functions

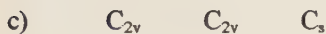
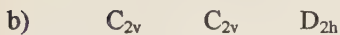
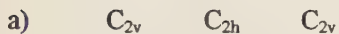
CHAPTER 14 Polyatomic Molecules

SECTION 14.2

14.1



14.3



14.5

The S_8 molecule has the following symmetry elements:

C_4 principal axis

4 C_2 axes perpendicular to C_4

no σ_h

4 σ_d and S_8 (the symmetry element, not the actual molecule) parallel to C_4

Therefore, the point group is D_{4d} .

14.7

a) D_{3h}

b) D_{3d}

c) C_2

d) C_{2h}

14.9

Hexamethylbenzene (see the first figure in problem 14.11) has the following symmetry elements:

C_3 principal axis

3 C_2 axes perpendicular to C_3

no σ_h

3 σ_d and S_6 parallel to C_3

Therefore, the point group is D_{3d} .

14.11

a)

Figure 1 has the following symmetry elements:

C_3 principal axis
3 C_2 axes perpendicular to C_3
no σ_h
3 σ_d and S_6 parallel to C_3

Therefore, the point group is D_{3d} .

Figure 2 has the following symmetry elements:

C_2 principal axis
2 σ_v parallel to C_2

Therefore, the point group is C_{2v} .

b)

The cyclohexane "chair" is the same as figure 1 (D_{3d}), and the cyclohexane "boat" is the same as figure 2 (C_{2v}).

SECTION 14.3 and 14.4

14.13

From the C_{3v} character table, $A_2 \otimes E$ is

A_2	1	1	-1
E	2	-1	0
	2	-1	0

This direct product is E.

From the D_{3h} character table, $A_1'' \otimes A_2''$ is

A_1''	1	1	1	-1	-1	-1
A_2''	1	1	-1	-1	-1	1
	1	1	-1	1	1	-1

This direct product is A_2' .

From the T_d character table, $A_2 \otimes T_1$ is

A_2	1	1	1	-1	-1
T_1	3	0	-1	1	-1
	3	0	-1	-1	1

This direct product is T_2 .

14.15

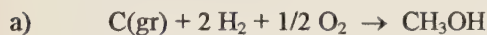
For the integrals to be non-zero, the integrand must be symmetric, i.e.

$$\Gamma_{\psi} \otimes (x, y, z) \otimes \Gamma_{\psi^*} = \Gamma_s \quad (\Gamma_s \text{ means all 1's in the representation})$$

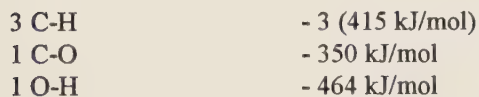
The point groups where x, y, or z fall in Γ_s are C_s and C_{nv} .

SECTION 14.5

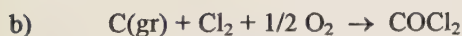
14.17



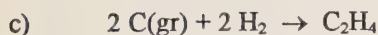
$$\Delta H = \Sigma(\text{bonds broken}) - \Sigma(\text{bonds made})$$



$$\Delta H = 1833 - 2059 = -226 \text{ kJ/mol}$$



$$\Delta H = 1202 - 1376 = -174 \text{ kJ/mol}$$



$$\Delta H = 2304 - 2275 = 29 \text{ kJ/mol}$$

SECTION 14.6, 14.7, and 14.8

14.19

The point group for this hypothetical molecule is C_{2h} .

function	E	C_2	i	σ_h	symmetry
X_1	1	1	1	1	a_g
X_2	1	-1	-1	1	b_u
X_3	1	1	-1	-1	a_u
X_4	1	-1	1	-1	b_g

The point group for butadiene is C_{2h} .

$$X_1 = (C_A p_z) + (C_B p_z) + (C_C p_z) + (C_D p_z)$$

$$X_2 = (C_A p_z) + (C_B p_z) - (C_C p_z) - (C_D p_z)$$

$$X_3 = (C_A p_z) - (C_B p_z) - (C_C p_z) + (C_D p_z)$$

$$X_4 = (C_A p_z) - (C_B p_z) + (C_C p_z) - (C_D p_z)$$

function	E	C_2	i	σ_h	symmetry	nodes
X_1	1	1	-1	-1	$1a_u$	0
X_2	1	-1	1	-1	$1b_g$	1
X_3	1	1	-1	-1	$2a_u$	2
X_4	1	-1	1	-1	$2b_g$	3

	$1a_u$	$1b_g$	$2a_u$	$2b_g$	State
E ↑	4	↑↓		↓	1A_g
	3	↑↓		↑	3A_g
	2	↑↓	↓		1B_u
	1	↑↓	↑		3B_u
	gr	↑↓	↑↓		1A_g

The total state comes from the direct product of the configuration for each electron. For example, the state of the ground level is $a_u \otimes a_u \otimes b_g \otimes b_g = a_g$. $S = 0$ implies it is a singlet state. Thus, the total state is 1A_g .

The selection rules for electric dipole transitions require $\Delta S = 0$ and $g \longleftrightarrow u$, so the only allowed transition is 1A_g to 1B_u .

14.23

BH₃ has eight electrons

BH ₃	$(1a_1')^2(2a_1')^2(1e')^4$	term symbol $^1A_1'$
BH ₃ ⁺	$(1a_1')^2(2a_1')^2(1e')^3$	term symbol $^2E'$
BH ₃ ⁻	$(1a_1')^2(2a_1')^2(1e')^4(1a_2'')^1$	term symbol $^2A_2''$

14.25

NH ₂ ⁺	$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2$	term symbol 1A_1
NH ₂ ⁻	$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$	term symbol 1A_1
BH ₂ ⁻	$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2$	term symbol 1A_1
CH ₂ ⁻	$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^1$	term symbol 2B_1

14.27

In the first excited state, 1 electron is promoted from e_{1g} to b_{2g}

e _{1g}	2	1	-1	-2	0	0	2	1	-1	-2	0
b _{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1
e _{2g}	2	-1	-1	2	0	0	2	-1	-1	2	0

The final state is $^1E_{2g}$ or $^3E_{2g}$

SECTION 14.9 and 14.10

14.29

linear molecules: 3N-5 normal modes
 non-linear molecules 3N-6 normal modes

H₂O₂: 3 (4) - 6 = 6 vibrational modes

C₂H₂: 3 (4) - 5 = 7 vibrational modes

C₂H₄: 3 (6) - 6 = 12 vibrational modes

C₂H₃Cl: 3 (6) - 6 = 12 vibrational modes

C₆H₅Cl: 3 (12) - 6 = 30 vibrational modes

14.31

$$\omega_{e1} = 830 \text{ cm}^{-1}$$

$$\omega_{e2} = 490 \text{ cm}^{-1}$$

$$\omega_{e3} = 1110 \text{ cm}^{-1}$$

$$\nu = \frac{E_{\text{vib}}}{hc} = \sum_1^3 (\nu_i + 1/2)\omega_{ei}$$

$$(0, 0, 0) \quad \nu = 1215 \text{ cm}^{-1}$$

$$(0, 1, 0) \quad \nu = 1705 \text{ cm}^{-1}$$

$$(1, 0, 0) \quad \nu = 2045 \text{ cm}^{-1}$$

$$(0, 2, 0) \quad \nu = 2195 \text{ cm}^{-1}$$

$$(0, 0, 1) \quad \nu = 2325 \text{ cm}^{-1}$$

$$(1, 1, 0) \quad \nu = 2535 \text{ cm}^{-1}$$

$$(0, 3, 0) \quad \nu = 2685 \text{ cm}^{-1}$$

$$(0, 1, 1) \quad \nu = 2815 \text{ cm}^{-1}$$

$$(2, 0, 0) \quad \nu = 2875 \text{ cm}^{-1}$$

14.33

Point group C_{2v}

ground state is given by representation a_1

$(0, 0, 0, 1, 0, 0)$ is b_1	$a_1 \otimes b_1 = b_1$	B_1 is an allowed transition
$(1, 0, 0, 0, 0, 1)$ is $a_1 \otimes b_2 = b_2$	$a_1 \otimes b_2 = b_2$	B_2 is an allowed transition
$(0, 0, 0, 0, 1, 1)$ is $b_1 \otimes b_2 = a_2$	$a_1 \otimes a_2 = a_2$	A_2 is NOT an allowed transition

14.35

A mode will be IR active if the dipole moment changes. From Figure 14.12, modes Q_3 and Q_5 show a change in dipole moment, so they are IR active.

14.37

Point group D_{2h}

IR active - b_{1y} , $2b_{2u}$, and $2b_{3u}$

Raman active - $3a_g$, $2b_{1g}$, and $1b_{2g}$

a_u is inactive

$b_{1u} \otimes b_{1u} = a_g$, so this overtone is not IR active

$a_u \otimes b_{1g} = B_{1u}$, so this overtone is IR active

14.39

$$\tilde{\nu}_i = \frac{1}{\lambda} = \frac{1}{600 \text{ nm}} = 16667 \text{ cm}^{-1}$$

Scattered frequency will equal the incident frequency minus the fundamental

$$\lambda_1 = \frac{1}{\tilde{\nu}_i - \omega_1} = \frac{1}{(16667 - 1151) \text{ cm}^{-1}} = 645 \text{ nm}$$

$$\lambda_2 = \frac{1}{\tilde{\nu}_i - \omega_2} = \frac{1}{(16667 - 524) \text{ cm}^{-1}} = 620 \text{ nm}$$

$$\lambda_3 = 654 \text{ nm}$$

SECTION 14.11

14.41

Axis 1 is along the C=C double bond.

Axis 2 is perpendicular to the plane of the molecule through the center of the C=C bond.

Axis 3 is perpendicular to the C=C bond in the plane of the molecule and through the center of the C=C bond.

14.43

Case 1: Axis through 1 corner and center of mass

$$I = m(0)^2 + 2m\left(\frac{a}{2}\right)^2 = \frac{1}{2}ma^2$$

Case 2: Axis through center of mass and parallel to one side

let x = distance from corner to axislet $.5x$ = distance from parallel side to axis

$$x^2 = \left(\frac{x}{2}\right)^2 + \left(\frac{a}{2}\right)^2 \Rightarrow \frac{3}{4}x^2 = \frac{1}{4}a^2 \Rightarrow x^2 = \frac{1}{3}a^2$$

$$I = mx^2 + 2m\left(\frac{x}{2}\right)^2 = m\left(\frac{1}{3}a^2\right) + 2m\left(\frac{1}{12}a^2\right) = \left(\frac{1}{3} + \frac{1}{6}\right)ma^2 = \frac{1}{2}ma^2$$

14.45

Axis a is perpendicular to the plane of the molecule and through the center of the molecule.Axes b, c are in the plane of the molecule. These moments are the same - see problem 14.43

$$I_a = 3 m_y (R)^2 = 3m_y R^2$$

$I_b = I_c = 2 m_y (x)^2 = \frac{3}{2} m_y R^2$ - To calculate the value of x , consider a right triangle with legs x and $.5R$ and hypotenuse R .

None of these moments can be measured with microwave spectroscopy because the molecule lacks a permanent dipole moment.

14.47

$$R_{12} = 162.9 \times 10^{-12} \text{ m}$$

$$R_{23} = 116.3 \times 10^{-12} \text{ m}$$

m_1 = mass of chlorine atom

m_2 = mass of carbon atom

m_3 = mass of nitrogen atom

$$I = \frac{(m_1 m_2 + m_1 m_3) R_{12}^2 + 2 m_1 m_3 R_{12} R_{23} + (m_1 m_3 + m_2 m_3) R_{23}^2}{m_1 + m_2 + m_3} = 1.405 \times 10^{-45} \text{ kg} \cdot \text{m}^2$$

14.49

$$R_{12} = R_{\text{HC}}$$

$$R_{23} = R_{\text{CN}}$$

molecule 1: $^1\text{H}^{12}\text{C}^{14}\text{N}$

$$B = 44.3160 \text{ GHz}$$

$$I = \frac{h}{8\pi^2 B} = 0.11404 \text{ amu} \cdot \text{nm}^2$$

 m_1 = mass of hydrogen atom m_2 = mass of carbon-12 atom m_3 = mass of nitrogen atom

$$I = \frac{(m_1 m_2 + m_1 m_3) R_{12}^2 + 2 m_1 m_3 R_{12} R_{23} + (m_1 m_3 + m_2 m_3) R_{23}^2}{m_1 + m_2 + m_3} = 0.11404 \text{ amu} \cdot \text{nm}^2$$

molecule 2: $^1\text{H}^{13}\text{C}^{14}\text{N}$

$$B' = 43.1698 \text{ GHz}$$

$$I' = \frac{h}{8\pi^2 B'} = 0.11707 \text{ amu} \cdot \text{nm}^2$$

 m'_1 = mass of hydrogen atom m'_2 = mass of carbon-13 atom m'_3 = mass of nitrogen atom

$$I' = \frac{(m'_1 m'_2 + m'_1 m'_3) R_{12}'^2 + 2 m'_1 m'_3 R_{12}' R_{23}' + (m'_1 m'_3 + m'_2 m'_3) R_{23}'^2}{(m'_1 + m'_2 + m'_3)'} = 0.11707 \text{ amu} \cdot \text{nm}^2$$

Solve the equations I and I' simultaneously using a computer to get R_{12} and R_{23}

$$R_{12} = 0.1067 \text{ nm}$$

$$R_{23} = 0.1156 \text{ nm}$$

14.51

$$R_{12} = R_{\text{OC}}$$

$$R_{23} = R_{\text{CS}}$$

molecule 1: $^{16}\text{O}^{12}\text{C}^{32}\text{S}$

$$B = 6.08149 \text{ GHz}$$

$$I = \frac{h}{8\pi^2 B} = 0.83101 \text{ amu} \cdot \text{nm}^2$$

 m_1 = mass of oxygen - 16 atom m_2 = mass of carbon atom m_3 = mass of sulfur atom

$$I = \frac{(m_1 m_2 + m_1 m_3) R_{12}^2 + 2 m_1 m_3 R_{12} R_{23} + (m_1 m_3 + m_2 m_3) R_{23}^2}{m_1 + m_2 + m_3} = 0.83101 \text{ amu} \cdot \text{nm}^2$$

molecule 2: $^{18}\text{O}^{12}\text{C}^{32}\text{S}$

$$B' = 5.70483 \text{ GHz}$$

$$I' = \frac{h}{8\pi^2 B'} = 0.88588 \text{ amu} \cdot \text{nm}^2$$

 m'_1 = mass of oxygen - 18 atom m'_2 = mass of carbon atom m'_3 = mass of sulfur atom

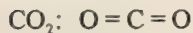
$$I' = \frac{(m'_1 m'_2 + m'_1 m'_3) R_{12}^2 + 2 m'_1 m'_3 R_{12} R_{23} + (m'_1 m'_3 + m'_2 m'_3) R_{23}^2}{(m'_1 + m'_2 + m'_3)} = 0.88588 \text{ amu} \cdot \text{nm}^2$$

Solve the equations I and I' simultaneously using a computer to get R_{12} and R_{23}

$$R_{12} = 0.1155 \text{ nm}$$

$$R_{23} = 0.1566 \text{ nm}$$

14.53



R_{CO} = bond length

m_{O} = mass of oxygen atom

$$B = 0.3937 \text{ cm}^{-1} = 1.180 \times 10^{10} \text{ Hz}$$

$$I = 2m_{\text{O}}R_{\text{CO}}^2$$

$$B = \frac{h}{8\pi^2 I}$$

$$\Rightarrow I = \frac{h}{8\pi^2 B} = 2m_{\text{O}}R_{\text{CO}}^2$$

$$\Rightarrow R_{\text{CO}} = \left(\frac{h}{16m_{\text{O}}\pi^2 B} \right)^{1/2} = 115.7 \text{ pm}$$

14.55

$$m_{\text{H}} = 1.67 \times 10^{-27} \text{ kg}$$

From Figure 14.16, the distance between successive peaks is approximately $2B$

distance between peaks = 4.0 mm

scale = 42.5 mm / 100 cm^{-1}

$$2B = \frac{4.0 \text{ mm}}{42.5 \text{ mm} / 100 \text{ cm}^{-1}} \Rightarrow B = 9.4 \text{ cm}^{-1}$$

$$B = \frac{h}{8\pi^2 Ic} \Rightarrow I = \frac{h}{8\pi^2 Bc} = \frac{8}{3} m_{\text{H}} R^2 \quad (\text{from problem 14.54})$$

$$\Rightarrow R = \left(\frac{3h}{64\pi^2 m_{\text{H}} Bc} \right)^{1/2} = 0.82 \text{ angstroms}$$

14.57

The A axis is along the C=O bond in formaldehyde

$$A = 282.106 \times 10^9 \text{ Hz}$$

$$m_H = 1.6735 \times 10^{-27} \text{ kg}$$

$$R_{CH} = 0.107 \times 10^{-9} \text{ m}$$

α = HCH angle

$$I_A = \frac{h}{8\pi^2 A} = 2m_H \left(R_{CH} \sin \frac{\alpha}{2} \right)^2 \Rightarrow \sin \frac{\alpha}{2} = \left(\frac{h}{16m_H \pi^2 A} \right)^{1/2} \frac{1}{R_{CH}}$$

$$\Rightarrow \alpha = 2 \arcsin \left[\left(\frac{h}{16m_H \pi^2 A} \right)^{1/2} \frac{1}{R_{CH}} \right] = 2 \arcsin(0.8811) = 123.54^\circ$$

SECTION 14.12

14.59

$$I_{CCl_3} = \frac{8}{3} m_{Cl} R_{C-Cl}^2 = \frac{8}{3} \left(\frac{34.96885 \times 10^{-3} \text{ kg}}{L} \right) (0.178 \times 10 \text{ m})^2 = 4.906 \times 10^{-45} \text{ kg} \cdot \text{m}^2$$

$$I_{CH_3} = 5.302 \times 10^{-47} \text{ kg} \cdot \text{m}^2$$

(see problem 14.56)

$$I_{\text{rel}} = \frac{I_1 I_2}{I_1 + I_2} = \frac{I_{CH_3} I_{CCl_3}}{I_{CH_3} + I_{CCl_3}} = 5.245 \times 10^{-47} \text{ kg} \cdot \text{m}^2$$

$$\begin{aligned}
H_{m,n} &= \int \psi_m^*(\phi) [H] \psi_n(\phi) d\phi \\
&= \frac{1}{2\pi} \int_0^{2\pi} \exp[-im\phi] \left[\frac{\hbar^2}{8\pi^2 I} \frac{\partial^2}{\partial \phi^2} + \frac{1}{2} V_3 (1 - \cos 3\phi) \right] \exp[in\phi] d\phi \\
&= \frac{1}{2\pi} \left(\frac{\hbar^2 n^2}{8\pi^2 I} + \frac{1}{2} V_3 \right) \int_0^{2\pi} \exp[i(n-m)\phi] d\phi - \frac{1}{4\pi} \frac{V_3}{2} \int_0^{2\pi} \exp[i(n-m)\phi] (\exp[3i\phi] + \exp[-3i\phi]) d\phi \\
&= \frac{1}{2\pi} \left(\frac{\hbar^2 n^2}{8\pi^2 I} + \frac{1}{2} V_3 \right) 2\pi \delta_{m,n} - \frac{1}{4\pi} \frac{V_3}{2} 2\pi [\delta_{m,n+3} + \delta_{m,n-3}] \\
\Rightarrow H_{m,m} &= \left(\frac{\hbar^2 m^2}{8\pi^2 I} + \frac{1}{2} V_3 \right) \text{ and } H_{m,m\pm 3} = -\frac{V_3}{4}
\end{aligned}$$

CHAPTER 15 *Statistical Mechanics*

SECTION 15.1-15.3

15.1

$$g(\epsilon) \propto \epsilon^{1/2} \quad (\text{equation 15.26})$$

$$\int_0^{\infty} x^n \exp[-ax] dx = \frac{\Gamma(n+1)}{a^{n+1}} \quad (\text{use a standard set of tables to evaluate the gamma function})$$

$$\langle \epsilon \rangle = \frac{\int_0^{\infty} \epsilon^{3/2} \exp[-\epsilon/kT] d\epsilon}{\int_0^{\infty} \epsilon^{1/2} \exp[-\epsilon/kT] d\epsilon} = \frac{\cancel{\Gamma\left(\frac{5}{2}\right)} \left(\frac{1}{kT}\right)^{5/2}}{\cancel{\Gamma\left(\frac{3}{2}\right)} \left(\frac{1}{kT}\right)^{3/2}} = kT \frac{\cancel{3\sqrt{\pi}}/4}{\cancel{\sqrt{\pi}}/2} = \frac{3}{2} kT$$

SECTION 15.4-15.6

15.3

$$S_m = R \ln (g_N)$$

$$g_N = 2I + 1$$

$$I_B = 3/2$$

$$I_F = 1/2$$

$$g_B = 4$$

$$g_F = 2$$

$$g(\text{BF}_3) = g_B g_F^3 = 32$$

$$S_m (\text{BF}_3) = R \ln (32) = 28.815 \text{ J/K}$$

15.5

$$z_{\text{nsr}} = \sum_{\text{even } J} (2J+1) \exp\left[\frac{-J(J+1)\theta_r}{T}\right] + 3 \sum_{\text{odd } J} (2J+1) \exp\left[\frac{-J(J+1)\theta_r}{T}\right]$$

or

$$z_{\text{nsr}} = \frac{g_N T}{\sigma \theta_r} \quad (\text{approximate})$$

$$\theta_r = 85.35 \text{ K}$$

$$\sigma = 2$$

$$g_N = 4$$

T (K)	z (exact)	z (approximate)
100	2.663	2.343
500	12.4067	11.7165

15.7

$$\theta_r = 85.35 \text{ K}$$

$$T = 200 \text{ K}$$

$$\langle E_{\text{rot}} \rangle = RT^2 \frac{\partial \ln z_{\text{nsr}}}{\partial T} = \frac{RT^2}{z_{\text{nsr}}} \frac{\partial z_{\text{nsr}}}{\partial T}$$

$$\frac{\partial z_{\text{nsr}}}{\partial T} = \sum_{\text{even } J} \frac{J(J+1)(2J+1)\theta_r}{T} \exp\left[\frac{-J(J+1)\theta_r}{T}\right] = 5.021 \times 10^{-3} / \text{K}$$

$$z_{\text{nsr}} = 13881 \text{ (from problem 15.6)}$$

$$\Rightarrow \langle E_{\text{rot}} \rangle = 1203 \text{ J}$$

15.9

J'' = initial state

J' = final state

Stokes ($J' = J'' + 2$)

$$\tilde{\nu}_s(S) = \tilde{\nu}_i - \tilde{B}[(J'' + 2)(J'' + 3) - J''(J'' + 1)] = \tilde{\nu}_i - \tilde{B}(4J'' - 2)$$

Anti-Stokes ($J' = J'' - 2$)

$$\tilde{\nu}_s(aS) = \tilde{\nu}_i - \tilde{B}[(J'' - 2)(J'' - 1) - J''(J'' + 1)] = \tilde{\nu}_i + \tilde{B}(4J'' - 2)$$

15.11

$$I_1 = 3/2 \text{ and } I_2 = 3/2$$

Let T_1 = total molecular spin = $I_1 + I_2$, $I_1 + I_2 - 1$, ..., $|I_1 - I_2| = 3, 2, 1, 0$

$$g_T = 2T_1 + 1$$

$$g_{\text{odd}} = \sum g_T (T_1 \text{ odd}) = 3 + 7 = 10$$

$$g_{\text{even}} = \sum g_T (T_1 \text{ even}) = 1 + 5 = 6$$

$$z_{\text{nsr}} = 6 \sum_{\text{even } J} (2J + 1) \exp\left[\frac{-J(J+1)\theta_r}{T}\right] + 10 \sum_{\text{odd } J} (2J + 1) \exp\left[\frac{-J(J+1)\theta_r}{T}\right]$$

$$\frac{\text{odd}}{\text{even}} = \frac{10}{6} = \frac{5}{3}$$

15.13

$$\frac{g_N}{z_{\text{nsr}}} = \left(\frac{N_{J''}}{N} \right) \frac{1}{2J+1} \exp \left[\frac{J(J+1)\theta_r}{T} \right]$$

$$\theta_r = 3.0 \text{ K}$$

$$T = 300 \text{ K}$$

$$\left(\frac{N_{J''}}{N} \right) = \text{relative int ensity}$$

$$\frac{g_N}{z_{\text{nsr}}} = 1.000 \text{ for even } J'' \text{ and } \frac{g_N}{z_{\text{nsr}}} \cong 1.67 \text{ for odd } J''$$

$$\Rightarrow \frac{\text{odd}}{\text{even}} = \frac{1.67}{1} = \frac{5}{3} \Rightarrow I = \frac{3}{2} \text{ (as in problem 15.11)}$$

SECTION 15.7

15.15

$$T = 5 \text{ K}$$

$$C_{\text{pm}} = 0.0012 \text{ J/K}$$

$$\theta_D = \left(\frac{36\pi^4 R}{15C_{\text{vm}}} \right)^{1/3} T$$

$$C_{\text{pm}} \cong C_{\text{vm}} \Rightarrow \theta_D = 587 \text{ K}$$

rearranging the equation above and using $T = 10 \text{ K}$ gives

$$C_{\text{vm}} = \frac{36\pi^4 R}{15\theta_D^3} T^3 = 0.0096 \text{ J / K}$$

15.17

$$\theta_E = \frac{h\nu_E}{k}$$

$$\theta_D = \frac{h\nu_m}{k}$$

$$\nu_E = \langle \nu_m \rangle = \frac{\int_0^{\nu_m} \nu g(\nu) d\nu}{\int_0^{\nu_m} g(\nu) d\nu} = \frac{\int_0^{\nu_m} \nu^3 d\nu}{\int_0^{\nu_m} \nu^2 d\nu} = \frac{3}{4} \nu_m$$

$$\Rightarrow \theta_E = \frac{3}{4} \theta_D$$

$$u = \frac{3}{4} \theta_D \frac{1}{T} = \frac{9}{4}$$

$$\frac{C_{vm}}{3R} = \frac{u^2 \exp[u]}{(\exp[u] - 1)^2} = 0.667 \quad (\text{Einstein Theory})$$

$$\frac{C_{vm}}{3R} = D \left(\frac{\theta_D}{T} \right) = 0.67 \quad (\text{Debye Theory and Figure 15.10})$$

SECTION 15.8

15.19

$$u = \frac{h\nu}{kT}$$

$$\rho(\nu)d\nu = \frac{8\pi k^4 T^4 u^3 du}{h^3 c^3 (\exp[u] - 1)}$$

$$\Rightarrow \rho(u) = \frac{8\pi k^3 T^3 u^3}{h^2 c^2 (\exp[u] - 1)}$$

$$\frac{\partial \rho}{\partial u} = 0 \Rightarrow u = 3(1 - \exp[-u])$$

Solving this equation numerically gives

$$u = 2.8214$$

$$\Rightarrow \nu_{\max} = 2.8214 \frac{kT}{h}$$

Anti-Stokes ($J' = J'' - 2$)

$$\tilde{\nu}_s(\text{aS}) = \tilde{\nu}_i - \tilde{B}[(J'' - 2)(J'' - 1) - J''(J'' + 1)] = \tilde{\nu}_i + \tilde{B}(4J'' - 2)$$

CHAPTER 16 *Structure of Condensed Phases*

SECTION 16.1

16.1

$$a = b \neq c$$

$$\alpha = \beta = 90 \text{ degrees}$$

$$\gamma = 120 \text{ degrees}$$

$$V = \vec{a} \cdot \vec{b} \times \vec{c} = abc \left[1 - \cos^2(\alpha) - \cos^2(\beta) - \cos^2(\gamma) + 2 \cos(\alpha) \cos(\beta) \cos(\gamma) \right]^{1/2} = abc \sqrt{0.75} = 0.866a^2c$$

16.3

$$V \cong abc = 7.079 \times 10^{-22} \text{ cm}^3$$

$$m = \rho V = 1.097 \times 10^{-21} \text{ g}$$

$$M. W. = 314.3 \text{ g/mol}$$

$$n = \frac{(m)L}{M. W. + 18(x)} = 2.0 \text{ if } x = 1$$

This implies that the salt has one attached water molecule and two molecules per unit cell

16.5

$$C_{5v} (\text{Schoenflies}) = 5m (\text{herman-Mauguin})$$

5-fold rotation axis implies 5

mirror plane implies m

SECTION 16.2

16.9

$$n = 1$$

$$\theta = 10^\circ$$

$$\lambda = 1.54 \text{ \AA}$$

$$d = \frac{\lambda}{2 \sin \theta} = 4.43 \text{ \AA}$$

As θ , and thus $\sin \theta$, decreases, d increase further.

16.11

For a body-centered cell, $h + k + l$ is even:

110, 200, 211, 220, 301, 222, 321, 400

For a face-centered cell, h , k , and l are all even or all odd:

111, 200, 220, 311, 222, 400

16.13

$a = 3.4$ angstroms

$\lambda = 1.8$ angstroms

$$d_{hkl} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}$$

$$\theta = \sin^{-1} \left(\frac{\lambda}{2d_{hkl}} \right)$$

Σhkl must be even

hkl	d_{hkl} (angstroms)	θ
110	2.40	22
200	1.70	32
211	1.39	40
220	1.20	49
301	1.08	57
222	0.98	67
321	0.91	82
400	0.85	---

16.15

$$a = 5.64 \text{ angstroms}$$

$$\text{Na-Cl separation} = \frac{1}{2} a = 2.82 \text{ angstroms}$$

$$\text{Na-Na separation} = \frac{\sqrt{2}}{2} a = 3.99 \text{ angstroms}$$

$$m_{\text{Na}} = 22.9 \text{ g/mol}$$

$$m_{\text{Cl}} = 35.45 \text{ g/mol}$$

$$\rho = \frac{\frac{1}{2}(m_{\text{Na}} + m_{\text{Cl}})}{\left(\frac{1}{2}a\right)^3 \text{L}} = 2.164 \text{ g/cm}^3$$

SECTION 16.3

16.17

$$a = 5.462 \text{ angstroms}$$

$$m_{\text{Ca}} = 40.08 \text{ g/mol}$$

$$m_{\text{Cl}} = 18.99 \text{ g/mol}$$

$$\rho = \frac{(4m_{\text{Na}} + 8m_{\text{Cl}})}{(a)^3 \text{L}} = 3.182 \text{ g/cm}^3$$

16.19

$$\Delta_f H = -435.9 \text{ kJ/mol}$$

$$\Delta_{\text{sub}} H = 90.0 \text{ kJ/mol}$$

$$D_o(\text{Cl}_2) = 238.8 \text{ kJ/mol}$$

$$\text{IP}(\text{K}) = 418.8 \text{ kJ/mol}$$

$$\text{EA}(\text{Cl}) = 348.8 \text{ kJ/mol}$$

$$\Delta_c U = -\Delta_f H + \Delta_{\text{sub}} H + \frac{D_o(\text{Cl}_2)}{2} + \text{IP}(\text{K}) - \text{EA}(\text{Cl}) = 715.3 \text{ kJ/mol}$$

16.21

$$\frac{\partial E(R)}{\partial R} \bigg|_{R=R_e} = 0 = \frac{q^2 ML}{R_e^2} - \frac{A}{\rho} \exp\left[-\frac{R_e}{\rho}\right] \Rightarrow A = \frac{\rho q^2 ML}{R_e^2} \exp\left[\frac{R_e}{\rho}\right]$$

$$\Delta U_c = -E(R_e) = \frac{q^2 ML}{R_e} - \frac{\rho q^2 ML}{R_e^2} \exp\left[\frac{R_e}{\rho}\right] \exp\left[-\frac{R_e}{\rho}\right] = \frac{q^2 ML}{R_e} \left(1 - \frac{\rho}{R_e}\right)$$

16.23

$$m = 137.22 \text{ g/mol}$$

$$\rho = \frac{2m}{La^3} = 3.595 \text{ g/cm}^3$$

16.25

$$E = \frac{n^2 h^2}{8mV^{2/3}}$$

let $n = n_f$ at $E = E_f$ with N electrons in a volume V

$$\left(\frac{4}{3}\pi n_f^3\right) \frac{1}{8} = \frac{NV}{2}$$

(1/8 for the positive octant, $N/2$ due to electron + or -)

$$\Rightarrow \frac{n_f^3}{V} = \frac{3N}{\pi} \Rightarrow E_f = \frac{h^2}{8m} \left(\frac{3N}{\pi}\right)^{2/3}$$

sodium has one valence electron per atom

$$\frac{N}{L} = \frac{\rho}{M.W} \Rightarrow N = 2.54 \times 10^{22} \text{ e}^{-1} / \text{cm}^3$$

$$\Rightarrow E_f = 3.15 \text{ eV}$$

SECTION 16.4

16.29

- a) methyl group on polyethylene

$$\delta = 8.85 + 2(9.51) + 2(-2.34) + 2(0.28) + 2(0.03) + (-0.96) - 2.35 = 20.5 \text{ ppm}$$

- b) ethyl group on polyethylene

$$\delta = 8.85 + 9.51 + 2(-2.34) + 2(0.28) + 2(0.03) - 2.35 = 11.8 \text{ ppm}$$

- c) propyl group on polyethylene

$$\delta = 8.85 + 9.51 - 2.34 + 2(0.28) + 2(0.03) - 2.35 = 14.3 \text{ ppm}$$

- d) butyl group on polyethylene

$$\delta = 8.85 + 9.51 - 2.34 + 0.28 + 2(0.03) - 2.35 = 14.0 \text{ ppm}$$

- e) For longer groups, the shift will stay near 14.0 ppm

16.31

$$I_{38} = 15$$

$$I_{30} = 747$$

$$\% \text{branching} = 100 \left(\frac{I_{38}}{I_{30} + 7I_{38}} \right) = 1.76\%$$

$$\text{average run length} = \frac{I_{30} + 6I_{38}}{I_{38}} = 56$$

16.33

Most bonds are m (meso), except where there is a change in stereochemistry, which are r (racemic)

Here there would be 98 m followed by 2 r (on average).

Per hundred units this would mean 2 mrr, 2 mmr, and 96 mmm groups

16.35

a) BBB

$$\delta = 3(8.85) + 3(9.51) + 4(-2.34) + 4(0.28) + 3(-3.04) - 2.35 = 35.4 \text{ ppm}$$

EBB

$$\delta = 3(8.85) + 3(9.51) + 3(-2.34) + 3(0.28) + 3(-3.04) - 2.35 = 37.4 \text{ ppm}$$

EBE

$$\delta = 3(8.85) + 3(9.51) + 2(-2.34) + 2(0.28) + 3(-3.04) - 2.35 = 39.5 \text{ ppm}$$

b) frequency equals $\sum n_i P_i$, where n_i is the degeneracy of permutations. $P = 0.5$ in both cases

$$f(\text{BBB}) = (0.5)^3 = 0.125$$

$$f(\text{EBB}) = 2(0.5)^2(0.5) = 0.250$$

$$f(\text{EBE}) = (0.5)^3 = 0.125$$

Relative intensities are 1:2:1

c) $f(\text{BBB}) = 8$

$$f(\text{EBB}) = f(\text{BEE}) = 2$$

$$f(\text{EBE}) = 0$$

Relative intensities are 4:1:0

$$\text{compliance} = \frac{\text{area}}{\text{force}} = \frac{\text{m}^2}{\text{N}} = \frac{\text{m}^2}{\text{kg} \cdot \text{m} \cdot \text{s}^{-2}} = \frac{\text{m} \cdot \text{s}^2}{\text{kg}}$$

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