

Intermediate Thermodynamics

Fugacity

Definitions

The specific Gibbs function for a simple compressible substance is:

$$dg = v dP - s dT \quad (1)$$

As in a pure substance the specific Gibbs function equals the chemical potential, we can write for an isothermal process:

$$d\mu_T = v dP \quad (2)$$

and replacing by the ideal gas EOS we obtain:

$$d\mu_{T,ideal} = \frac{RT dP}{P} = RT d \ln P \quad (3)$$

From Eq. (3) we can calculate the chemical potential of a pure substance that behaves as an ideal gas. For a real gas we can use an EOS and calculate the chemical potential by integration. This approach is not followed. Instead, a new thermodynamic property is defined such that the form of Eq. (3) still holds for a real gas. This new function is the *fugacity* f , defined as:

$$d\mu_{T,real} = RT d \ln f \quad (4)$$

In addition, as the real gas and the ideal gas behave the same at very low pressure, it is obvious that:

$$\lim_{P \rightarrow 0} \frac{f}{P} = 1 \quad (5)$$

Therefore, with the definition of Eq. (4) and with the reference value of $f=0$ at zero pressure the fugacity is completely defined.

Evaluating the fugacity

Using the definition of the isothermal chemical potential, Eq. (2), and the fugacity, Eq. (4) we can write:

$$d \ln f = \frac{v dP}{RT} \quad (6)$$

Eq. (6) in conjunction with an EOS (explicit in the specific volume) can be used to calculate the fugacity. Integrating between two pressures we get:

$$RT \ln \frac{f}{f_0} = \int_{P_0}^P v dP \quad (7)$$

If the EOS is explicit in pressure, we can use the relation:

$$d(vP) = v dP + P dv \quad (8)$$

Replacing Eq. (8) in Eq. (6) and integrating we get:

$$RT \ln \frac{f}{f_0} = P v - P_0 v_0 - \int_{v_0}^v P dv \quad (9)$$

Using the Redlich-Kwong EOS, $p = \frac{RT}{v-b} - \frac{a}{\sqrt{T} v (v+b)}$, we can use Eq. (9) to obtain:

$$RT \ln \frac{f}{f_0} = P v - P_0 v_0 - RT \ln \frac{v-b}{v_0-b} - \frac{a}{b\sqrt{T}} \ln \frac{(v+b)v_0}{(v_0+b)v} \quad (10)$$

Taking $P_0 \rightarrow 0$ the gas behaves as ideal, and we can write:

$$\ln f = \frac{Pv}{RT} - 1 + \ln \frac{RT}{v-b} - \frac{a}{bRT^{3/2}} \ln \frac{(v+b)}{v} \quad (11)$$

and replacing by the definition of the pressure we get:

$$\ln f = \frac{b}{v-b} + \ln \frac{RT}{v-b} - \frac{a}{RT^{3/2}} \left[\frac{1}{v+b} + \frac{1}{b} \ln \frac{(v+b)}{v} \right] \quad (12)$$

A similar procedure using Van der Waals EOS leads to:

$$\ln f = \frac{b}{v-b} + \ln \frac{RT}{v-b} - \frac{2a}{RTv} \quad (13)$$

Example:

Determine the fugacity, in bars, for R134a for a Redlich-Kwong gas at 90 °C and 10 bar. Compare against Van der Waals EOS.

The constants in RK EOS must be first evaluated. Using the standard conditions

$(\partial P/\partial v)_{T_c} = (\partial^2 P/\partial v^2)_{T_c} = 0$ the constants are:

$$p = \frac{RT}{v-b} - \frac{a}{\sqrt{T} v (v+b)}, \quad a = 0.42748 \frac{R^2 T_c^{2.5}}{P_c}, \quad b = 0.08664 \frac{RT_c}{P_c}$$

In R134, ($C_2F_4H_2$), we have $T_c = 374.3 K$, $P_c = 40.6 \text{ bar}$, $M = 102.3 \text{ kg / kmol}$. From direct substitution we get:

$$a = 197.1 \frac{\text{bar m}^3 \text{K}^{2.5}}{\text{kmol}^2}, \quad b = 0.06634 \frac{\text{m}^3}{\text{kmol}}$$

Calculating the specific volume from directly from the EOS ($v = 2.724 \text{ m}^3 / \text{kg}$) and replacing in Eq. (12) we get $f = 9.09 \text{ bar}$. A similar procedure leads to a value of f for a Van der Waals gas $f = 9.21 \text{ bar}$.

Evaluation of the fugacity from tables or EOS's is usually done using the *fugacity coefficient* ϕ , defined as:

$$\phi \equiv \frac{f}{p} \tag{14}$$

that can be differentiated to obtain:

$$d \ln \phi = d \ln f - d \ln p \tag{15}$$

and combining Eq. (15) with Eq. (6) we get:

$$d \ln \phi = \left(\frac{v}{RT} - \frac{1}{P} \right) dP \tag{16}$$

Integration of Eq. (16) at constant temperature from zero pressure ($\phi = 1$) to a state pressure P gives:

$$\ln \frac{f}{P} = \int_0^P \left(\frac{v}{RT} - \frac{1}{P} \right) dP \tag{17}$$

which relates PvT data with the fugacity. Eq. (17) can be integrated numerically from data or an EOS of state can be used to evaluate the integral analytically. If we replace the definition of the Z factor in Eq. (17) we obtain:

$$\ln \frac{f}{P} = \int_0^P \left(\frac{v}{RT} - \frac{1}{P} \right) dP = \int_0^P \left(\frac{Z-1}{P} \right) dP \quad (18)$$

or, in terms of reduced properties,

$$\ln \frac{f}{P} = \int_0^{P_r} \left(\frac{Z-1}{P_r} \right) dP_r \quad (19)$$

Recall that the integral in Eq. (19) has been already solved if we evaluated residual or departure functions for the entropy, Eq. (47) in notes “Thermodynamic Properties”. Examination of the Z chart shows that for P_r smaller than 0.4 the Z - P_r curves are straight lines with slope $(Z-1)/P_r$. Then the integral in Eq. (19) can be readily evaluated:

$$\ln \frac{f}{P} = \int_0^{P_r} \left(\frac{Z-1}{P_r} \right) dP_r = \left(\frac{Z-1}{P_r} \right) \int_0^{P_r} dP_r = Z-1 \quad (20)$$

that can be written as:

$$\frac{f}{P} = e^{Z-1} \cong 1 + (Z-1) + \frac{(Z-1)^2}{2!} + \frac{(Z-1)^3}{3!} + \dots \quad (21)$$

for $Z > 0.9$ the series on Eq. (21) can be approximated well as:

$$\frac{f}{P} = Z \quad (22)$$

so at low pressures and for Z close to 1 we can use Eq. (22) with fair accuracy.

To obtain f from tabular data we integrate Eq. (4) between a reference state and the state of interest along a isotherm, to get:

$$\mu_{T,P} - \mu_{T,P_{ref}} = RT \ln \frac{f}{f_{ref}} \quad (23)$$

As the chemical potential is the specific Gibbs function for a pure substance, we can write:

$$\ln \frac{f}{f_{ref}} = \frac{g - g_{ref}}{RT} \quad (24)$$

We can use Eq. (24) to evaluate the fugacity of a real gas if we use a reference state with low enough pressure such that the reference fugacity is the pressure (ideal gas) and recalling that $g = h - Ts$. Then Eq. (24) becomes:

$$\ln \frac{f}{P_{ref}} = \frac{1}{R} \left[\frac{h - h_{ref}}{T} - (s - s_{ref}) \right] \quad (25)$$

Eq. (25) is used in the following way: a reference state is chosen at the lowest pressure available at the state temperature. If the pressure is not low enough to be in the ideal gas region, extrapolation of the properties to a lower pressure region might be necessary. Then the evaluation of h and s from tables allow the calculation of f .

f can be also estimated from a three-parameter principle of corresponding states using Pitzer acentric factor ω . Due to the close relation between Z and f , the fugacity coefficient is tabulated as:

$$\log_{10} \frac{f}{P} = \left(\log_{10} \frac{f}{P} \right)^0 + \omega \left(\log_{10} \frac{f}{P} \right)^1 \quad (26)$$

Eq. (23) for a real gas can be simplified for the case of an ideal gas:

$$\left(\mu_{T,P} - \mu_{T,P_{ref}} \right)_{ig} = RT \ln \frac{P}{P_{ref}} \quad (27)$$

where the reference state is usually chosen at unit pressure, usually 1 atm. This allows us to write the following two relations:

$$\left(\mu_{T,P} \right)_{ig} = \left(g_{T,P} \right)_{ig} = g_T^0 + RT \ln P \quad (28)$$

$$\mu_{T,P} = g_T^0 + RT \ln f \quad (29)$$

Subtracting Eq. (28) from Eq. (29) we obtain:

$$\mu_{T,P} - \left(\mu_{T,P} \right)_{ig} = RT \ln \frac{f}{P} \quad (30)$$

Liquids and solids

From Eq. (6) we can obtain the change in fugacity between the saturation liquid state and a compressed state (of course at higher pressure):

$$d \ln f = \frac{v dP}{RT} \Rightarrow \ln \frac{f}{f_{sat}} \Big|_{liq} = \frac{1}{RT} \int_{P_{sat}}^P v dP \quad (31)$$

As no approximation has been made so far, Eq. (31) applies also to solids using a reference pressure other than the saturation pressure, and the corresponding fugacity.

Most liquids and solids have fairly constant specific volume over wide ranges of pressure variations, i.e. are essentially incompressible, thus we can approximate:

$$\ln \frac{f}{f_{sat}} \Big|_{liq} \cong \frac{v(P - P_{sat})}{RT} \quad (32)$$

In addition to assuming that the specific volume is constant, notice that specific volumes of liquids and solids are much smaller than the corresponding specific volumes of gases at the same pressure, for small pressures. Thus we can write for small pressure changes:

$$f^{liq} \cong f_{sat}^{liq} \quad (33)$$

We want now to relate the fugacity of saturated vapor with the fugacity of saturated liquid. To this end we will use Eq. (1) and the fact that phase changes are isobaric and isothermal (see also properties of the saturation state in notes “Property Relations”):

$$dg = d\mu = v dP - s dT = 0 \quad (34)$$

and combining Eq. (34) with Eq. (4), $d\mu = RT d \ln f$ we obtain:

$$f_{sat}^{vap} = f_{sat}^{liq} \quad (35)$$

which is a consequence of equilibrium considerations. Thus, Eq. (33) can be rewritten as:

$$f^{liq} \cong f_{sat}^{liq} \quad (36)$$

furthermore, if P_{sat} is small enough so that the vapor behaves as an ideal gas we have:

$$f^{liq} \cong P_{sat}(T) \quad (37)$$

Real gas mixtures

Recall that from Eq. (38) in Homogeneous Mixtures we have that the partial molar volume is related to the Gibbs function by:

$$\left. \frac{\partial \mu_i}{\partial P} \right|_{T,N} = \left. \frac{\partial V}{\partial N_i} \right|_{T,P,N_j} = \bar{v}_i \quad (38)$$

For an ideal gas, we can express the total volume as:

$$V = (N_1 + N_2 + \dots + N_i + \dots) \frac{RT}{P} \quad (39)$$

and from Eq. (38) we have:

$$\bar{v}_i = \left. \frac{\partial V}{\partial N_i} \right|_{T,P,N_j} = \frac{RT}{P} \quad (40)$$

and using again Eq. (38) the relation between the chemical potential and the pressure is:

$$\left. \frac{\partial \mu_i}{\partial P} \right|_{T,N} = \frac{RT}{P} \quad (41)$$

and thus:

$$d\mu_i = RT d \ln p \quad (42)$$

Recall also that Dalton's Law states that ("any gas is a vacuum to any other gas mixed with it"):

$$p_i = x_i p \quad (43)$$

as at constant x_i we have $dp_i/p_i = (x_i dp)/x_i p \Rightarrow d \ln p_i = d \ln p$ we obtain

$$d\mu_{i,ig} = RT d \ln p_i \quad (44)$$

which is equivalent to Eq. (4) valid for a pure substance. Integration yields (compare to Eq. (27) for a pure substance):

$$\left(\mu_{i,T} - \mu_{ref} \right)_{ig} = RT \ln \frac{p_i}{p_{i,ref}} \quad (45)$$

where the reference value is usually selected at the ideal gas value at unit pressure (usually 1 atm) and thus:

$$\mu_{i,T,ig} = g_T^0 + RT \ln p_i \quad (46)$$

In a real gas mixture we use the same type of definition for the fugacity as was done in a pure substance (recall Eq. (23)), and then we can write:

$$d\mu_i = d\bar{g}_i = RT d \ln \tilde{f}_i \quad (47)$$

where p_i is defined in Eq. (43). To evaluate f_i we make use of Eq. (38), that allows us to write:

$$d\mu_{i,T} = \bar{v}_i dP \quad (48)$$

that can be replaced into Eq. (47) yielding:

$$RT d \ln \tilde{f}_i = \bar{v}_i dP \quad (49)$$

and integrating between a low pressure state to a given state we obtain:

$$RT \ln \frac{\tilde{f}_i}{\tilde{f}_i^*} = \int_{P^*}^P \bar{v}_i dP \quad (50)$$

A similar equation can be easily derived for an ideal gas, resulting in:

$$RT \ln \frac{P}{P^*} = \int_{P^*}^P \frac{RT}{P} dP \quad (51)$$

using Eqs. (50) and (51) yields:

$$RT \ln \frac{\tilde{f}_i}{P} = RT \ln \frac{\tilde{f}_i^*}{P^*} + \int_{P^*}^P \left(\bar{v}_i - \frac{RT}{P} \right) dP \quad (52)$$

we want to find the limit for $P^* \rightarrow 0$. Note that:

$$\lim_{P^* \rightarrow 0} \frac{\tilde{f}_i}{P^*} = \lim_{P^* \rightarrow 0} \frac{x_i \tilde{f}_i}{x_i P^*} = \lim_{P^* \rightarrow 0} \frac{x_i \tilde{f}_i}{p_i} = x_i \quad (53)$$

and then we can write:

$$\ln \bar{f}_i = \ln x_i P + \int_0^P \left(\frac{\bar{v}_i}{RT} - \frac{1}{P} \right) dP \quad (54)$$

notice the similarity with Eq. (17), $\ln \frac{f}{P} = \int_0^P \left(\frac{v}{RT} - \frac{1}{P} \right) dP$. Introducing the fugacity coefficient for mixtures we have:

$$\ln \frac{\bar{f}_i}{x_i P} = \ln \bar{\phi}_i = \int_0^P \left(\frac{\bar{v}_i}{RT} - \frac{1}{P} \right) dP \quad (55)$$

Notice that we need the partial molar volumes as a function of pressure for each temperature to calculate the fugacities of the components. If such data is not available we will need to make suitable approximations.

Duhem-Margules relation

It is possible to obtain an important relation for the variation of the component fugacities as a function of the composition for fixed pressure and temperature. In a binary system with components 1 and 2, the Gibbs-Duhem relation (Eq. (36) in Homogeneous Mixtures) states:

$$x_1 d\mu_1 + x_2 d\mu_2 = 0 \quad (56)$$

and from Eq. (47) we have:

$$x_1 d \ln \bar{f}_1 + x_2 d \ln \bar{f}_2 = 0 \quad (57)$$

As the fugacity is only a function of composition at constant pressure and temperature, we can write:

$$d \ln \bar{f}_i = \frac{\partial \ln \bar{f}_i}{\partial x_i} dx_i \quad (\text{constant } T, P) \quad (58)$$

and replacing into Eq. (57) gives:

$$x_1 \frac{\partial \ln \bar{f}_1}{\partial x_1} dx_1 + x_2 \frac{\partial \ln \bar{f}_2}{\partial x_2} dx_2 = 0 \quad (59)$$

and since $dx_1 = -dx_2$ for a two-component system we have:

$$x_1 \frac{\partial \ln \tilde{f}_1}{\partial x_1} = x_2 \frac{\partial \ln \tilde{f}_2}{\partial x_2} \quad (60)$$

or

$$\left. \frac{\partial \ln \tilde{f}_1}{\partial \ln x_1} \right|_{P,T} = \left. \frac{\partial \ln \tilde{f}_2}{\partial \ln x_2} \right|_{P,T} \quad (61)$$

that are the *Duhem-Margules* relations. For low pressure we can replace the component fugacities by the partial pressure to get:

$$\left. \frac{\partial \ln p_1}{\partial \ln x_1} \right|_{P,T} = \left. \frac{\partial \ln p_2}{\partial \ln x_2} \right|_{P,T} \quad (62)$$

or, using Eq. (60),

$$x_1 \left. \frac{\partial \ln p_1}{\partial x_1} \right|_{P,T} = -x_2 \left. \frac{\partial \ln p_2}{\partial x_1} \right|_{P,T} \quad (63)$$

As a consequence of the Duhem-Margules relation, partial pressure – composition plots have a trend as shown in Fig. 1.

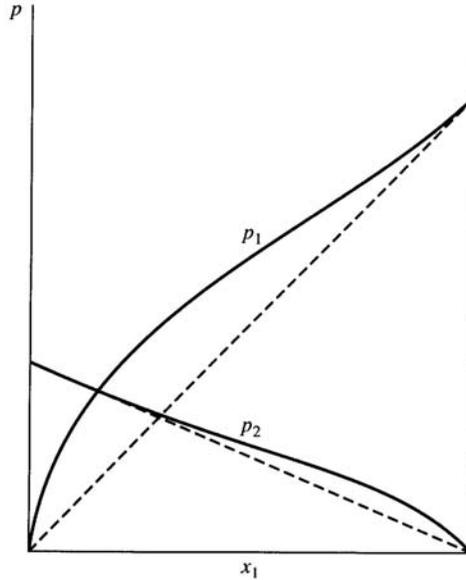


Figure 1: typical partial pressure plot for a two-component system.

Ideal Solutions

Going back to Eq. (46), the chemical potential in an ideal-gas mixture can be written as:

$$\mu_{i,ig} = g_T^0 + RT \ln p_i \quad (64)$$

From the definition of partial pressure we have that $p_i = x_i p$, so Eq. (64) can be rewritten as:

$$\mu_{i,ig} = g_T^0 + RT \ln P + RT \ln x_i = \mu_i^* + RT \ln x_i \quad (65)$$

or, in general,

$$\mu_i = \mu_i^* + RT \ln x_i \quad (66)$$

where μ_i^* is the Gibbs function of the pure substance at T and the total pressure P . Eq. (66) represents the definition of an *ideal solution*: a solution is an ideal solution if the chemical potential of every component can be expressed as a linear function of the logarithm of its mole fraction. Of course, ideal-gas mixtures satisfies the definition. Many other non-ideal liquid and gaseous mixtures behave like ideal mixtures at least in a range of compositions.

We will develop some relations for ideal solution, and then discuss the case of real solutions.

From Eq. (30) of Homogeneous Mixtures, the enthalpy of formation was expressed as:

$$\Delta H = \sum_i N_i (\bar{h}_i - h_i) \quad (67)$$

In an ideal solution, this expression can be derived from manipulation of Eq. (37) of Homogeneous Mixtures:

$$\left. \frac{\partial \mu_i / T}{\partial T} \right|_{P,N} = \frac{1}{T} \left. \frac{\partial \mu_i}{\partial T} \right|_{P,N} - \frac{\mu_i}{T^2} = -\frac{\bar{s}_i}{T} - \frac{\mu_i}{T^2} = -\frac{\bar{h}_i}{T^2} \quad (67)$$

and a similar derivation for a pure component results in:

$$\frac{\partial g_i / T}{\partial T} = -\frac{h_i}{T^2} \quad (68)$$

Now, differentiating Eq. (66) respect to temperature at constant pressure after dividing by T we obtain:

$$\frac{\partial \mu_i / T}{\partial T} - \frac{\partial \mu_i^* / T}{\partial T} = \frac{\partial \mu_i / T}{\partial T} - \frac{\partial g_i / T}{\partial T} = 0 \quad (69)$$

which implies in conjunction with Eqs. (67) and (68) that $\bar{h}_i = h_i$ in an ideal solution, and therefore the heat or enthalpy of mixing will be:

$$\Delta H = \sum_i N_i (\bar{h}_i - h_i) = 0 \quad (70)$$

In a similar manner, differentiation of Eq. (66) with respect to pressure at constant temperature yields:

$$\left. \frac{\partial \mu_i}{\partial P} \right|_T - \left. \frac{\partial g_i}{\partial P} \right|_T = 0 \quad (71)$$

and using $\partial \mu_i / \partial P = \bar{v}_i$ we obtain:

$$\bar{v}_i = v_i \quad (72)$$

so the partial molar volume is the pure specific volume.

Differentiation of Eq. (66) with respect to temperature leads to:

$$\frac{\partial \mu_i}{\partial T} = \frac{\partial g_i}{\partial T} + R \ln x_i = 0 \quad (73)$$

and using Eq. (37) in Homogeneous Mixtures we obtain:

$$\bar{s}_i = s_i - R \ln x_i \quad (74)$$

In consequence, according to Eqs. (70), (72), and (74) we can write for an *ideal solution*:

$$h_{mixt} = \sum_i x_i \bar{h}_i = \sum_i x_i h_{i,pure} \quad (\Delta h_{mix} = 0) \quad (75)$$

$$v_{mixt} = \sum_i x_i \bar{v}_i = \sum_i x_i v_{i,pure} \quad (\Delta v_{mix} = 0) \quad (76)$$

$$s_{mixt} = \sum_i x_i \bar{s}_i = \sum_i x_i s_{i,pure} - \underbrace{R \sum_i x_i \ln x_i}_{\Delta s_{mix}} \quad (77)$$

$$g_{mixt} = h_{mix} - (Ts)_{mix} = \sum_i x_i h_{i,pure} - \sum_i x_i s_{i,pure} + \underbrace{RT \sum_i x_i \ln x_i}_{\Delta g_{mix}} \quad (78)$$

To calculate the fugacity of an ideal solution let's recall the definitions of the fugacity, Eq. (47) $d\mu_i = RTd \ln \tilde{f}_i$, and of the chemical potential for an ideal solution, Eq. (66), $\mu_i = \mu_i^* + RT \ln x_i$. Differentiating Eq. (66) at constant temperature and equating the chemical potentials we obtain:

$$RTd \ln \tilde{f}_i = RTd \ln x_i \quad (79)$$

and upon integration between states 1 and 2 with different composition we obtain:

$$\frac{\tilde{f}_{i,2}}{\tilde{f}_{i,1}} = \frac{x_{i,2}}{x_{i,1}} \quad (80)$$

where if we choose state 1 with a pure substance i , ie $x_i = 1$, $\tilde{f}_i = f_{i,P}$ (fugacity of pure component i at the total pressure), then:

$$\tilde{f}_i = x_i f_{i,P} \quad (81)$$

which is known as Lewis-Randall rule, which states that the partial molar fugacity in an ideal solution is the pure substance fugacity multiplied by the molar fraction.

In a binary solution with components A and B we have $x_A + x_B = 1$, and thus Eq. (75) reduces to:

$$h_{mixt} = \sum_i x_i h_{i,pure} = x_A h_A + (1 - x_A) h_B \quad (82)$$

that can be easily interpreted in a $x-h$ diagram, as shown in Fig. 2.

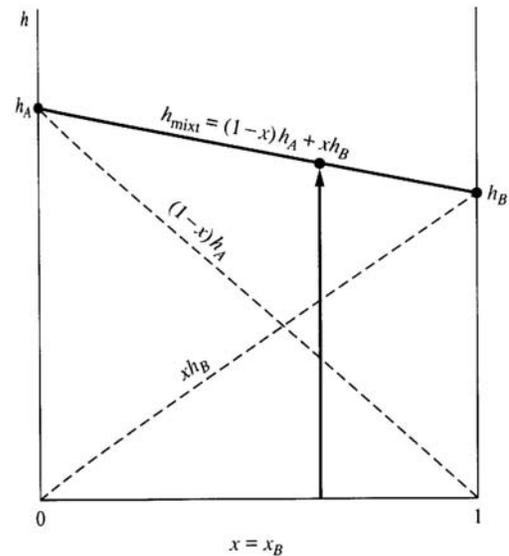


Figure 2: molal enthalpy-composition

The entropy of the ideal mixture is shown in Fig. 3. Notice that the mixture entropy is always larger than the individual entropies. A similar statement is true for the Gibbs function but with lower Gibbs function after the mixture.

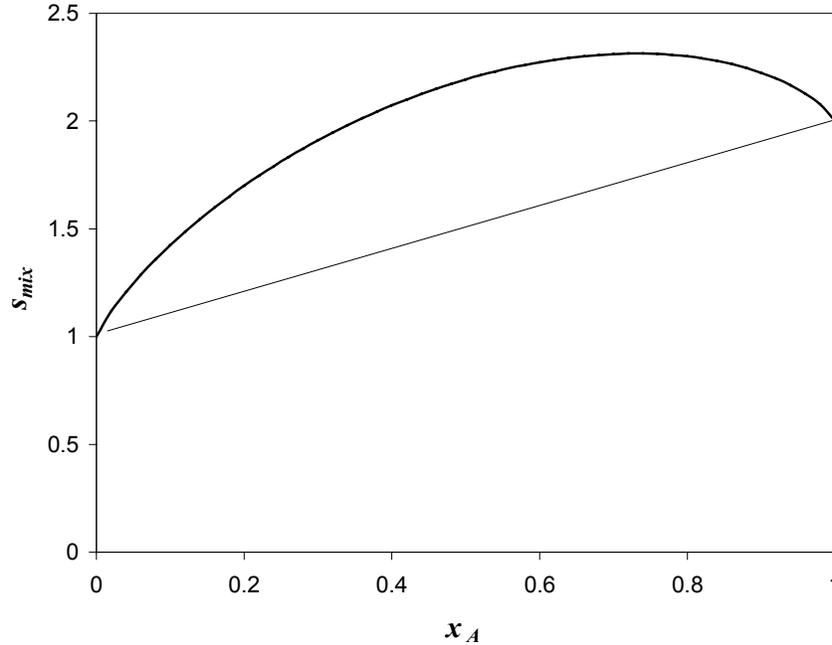


Figure 3: molal entropy vs. composition diagram

Heat/work interactions in ideal solutions

Let's analyze the case of an ideal solution undergoing a process in which heat and work interactions occur. Consider an internally reversible process in which the volume is changed isothermally in a flow device (compressor or turbine). In this case the heat transfer can be calculated from:

$$\dot{Q} = T\Delta S = T \sum_i N_i (\bar{s}_{i,2} - \bar{s}_{i,1}) \quad (82)$$

and the work is calculated from:

$$\dot{W} = m(\Delta h + \Delta ke + \Delta pe) - \dot{Q} \quad (83)$$

As shown by Eqs. (82) and (83), evaluation of mixture properties, namely h and s , is necessary. These property data might not be readily available and some modeling will be necessary to estimate the changes in enthalpy and entropy. In the case of an ideal solution we have:

$$\Delta \bar{s}_i = (s_i - R \ln x_i)_2 - (s_i - R \ln x_i)_1 = \Delta s_i \quad (84)$$

thus Eq. (82) reduces to:

$$\dot{Q} = T \Delta S = T \sum_i \dot{N}_i (s_{i,2} - s_{i,1}) = \dot{N} T \sum_i x_i (s_{i,2} - s_{i,1}) \quad (85)$$

The change in enthalpy is calculated from Eq. (75) as:

$$\Delta h_m = \sum_i x_i (h_{i,2} - h_{i,1}) \quad (86)$$

Example: a gas mixture consisting of 70 % molar methane and 30 % nitrogen is compressed reversibly and isothermally from 10 bar to 100 bar at 250 K. Flow rate is $0.2 \text{ m}^3/\text{min}$. Determine a) the heat transfer, b) the power requirement assuming ideal solution and ideal gas.

The pure component properties are taken from tables at 10 bar and at 100 bar, 250 K, We have: Nitrogen at 10 bar: $v = 73.6 \text{ cm}^3/\text{g}$, $h = 356.3 \text{ kJ/kg}$, $s = 5.962 \text{ kJ/kg K}$. Nitrogen at 100 bar: $v = 7.12 \text{ cm}^3/\text{g}$, $h = 330.4 \text{ kJ/kg}$, $s = 5.190 \text{ kJ/kg K}$. Methane at 10 bar: $v = 125.4 \text{ cm}^3/\text{g}$, $h = 1077.9 \text{ kJ/kg}$, $s = 10.002 \text{ kJ/kg K}$. Methane at 100 bar: $v = 8.88 \text{ cm}^3/\text{g}$, $h = 928.5 \text{ kJ/kg}$, $s = 8.364 \text{ kJ/kg K}$.

The molar flow rate can be calculated from $\dot{N} = \dot{V}_m / v_m$, with $\dot{V}_m = 0.2 \text{ m}^3/\text{min}$ and v_m the specific molar volume. For an ideal solution, see Eq. (76),

$$v_m = x_1 v_1 + x_2 v_2 = (0.7 \cdot 125.4 + 0.3 \cdot 73.6) \frac{1}{10^3} = 2.026 \frac{\text{m}^3}{\text{kmol}}$$

thus the molar flow rate is:

$$\dot{N} = \frac{0.2}{2.026} = 0.0987 \frac{\text{kmol}}{\text{min}}$$

a) The heat transfer can now be evaluated from Eq. (85):

$$\dot{Q} = 0.0987 \cdot 250 [0.7(8.364 - 10.002) + 0.3(5.190 - 5.962)] = -624 \frac{\text{kJ}}{\text{min}}$$

b) The work is:

$$W = \dot{N} \Delta h - \dot{Q} = \dot{N} (x_1 \Delta h_1 + x_2 \Delta h_2) - \dot{Q} = 427 \frac{\text{kJ}}{\text{kmol}} = 7.12 \text{ kW}$$

For the ideal gas model we have that the volume is:

$$v_m = \frac{RT}{P} = \frac{0.08314 \cdot 250}{10} = 2.079 \frac{\text{m}^3}{\text{kmol}}$$

and the molar flow rate is:

$$N = \frac{0.2}{2.079} = 0.0962 \frac{\text{kmol}}{\text{min}}$$

Using Eq. (85) for the heat transfer we get:

$$\dot{Q} = T\Delta s = 0.0987 \cdot 250 \left(-R \ln \frac{P_2}{P_1} \right) = -460 \frac{\text{kJ}}{\text{min}}$$

And the work is:

$$\dot{W} = -\dot{Q} = 460 \frac{\text{kJ}}{\text{kmol}} = 7.67 \text{ kW}$$

since $\Delta h = 0$ in an isothermal process for an ideal gas.

Non-ideal solutions

Enthalpy-composition diagram

In non-ideal solutions the enthalpy of mixing is non-zero, and therefore the molal enthalpy vs. composition diagram will no longer be a straight line. Fig. 4 shows a typical molal enthalpy – composition diagram for a solution with positive enthalpy of formation.

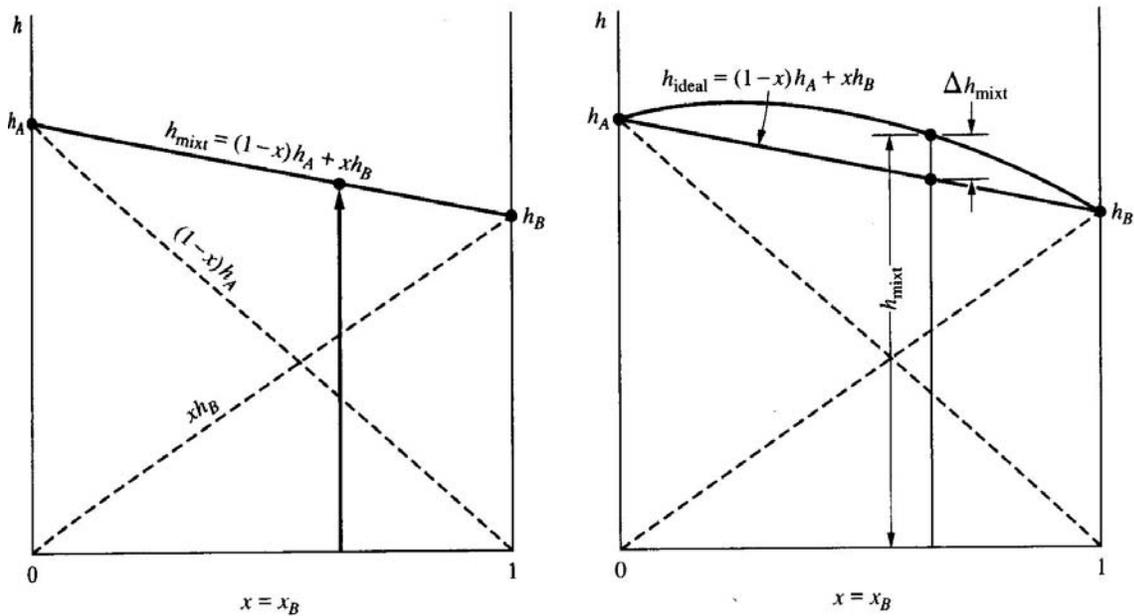


Figure 4: molal enthalpy vs. composition diagrams for an ideal solution (left) and a real solution (right).

Notice in Fig. 4 that the enthalpy of mixing can be defined as the difference between the molal enthalpy for a real solution minus the molal enthalpy for an ideal solution. Using Eq. (70) on a molar basis:

$$\Delta h_{mix} = \sum_i x_i (\bar{h}_i - h_i) = \sum_i x_i \bar{h}_i - \sum_i x_i h_i = h_{mix} - [(1-x)h_A + xh_B] \quad (87)$$

The enthalpy of mixing is the amount of heat that needs to be added or extracted from a closed system to keep the temperature of the mixture constant during the formation of a solution. A negative enthalpy of mixing implies that heat must be removed from the system to keep it at constant temperature or, under adiabatic conditions, the temperature of the system will increase. Conversely, heat must be added to undergo an isothermal mixing if the enthalpy of mixing is positive.

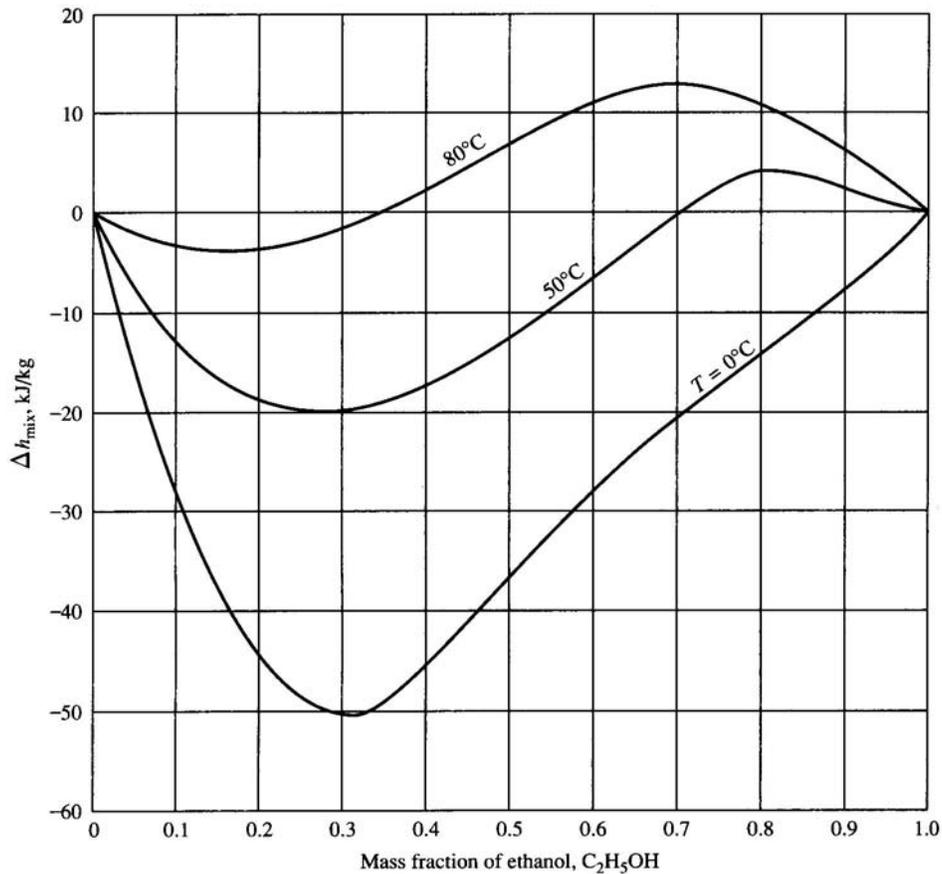


Figure 5: enthalpy of mixing vs. composition diagram for a water/ethanol solution.

Fig. 5 shows the enthalpy of mixing as a function of composition for a binary solution of ethanol and water for three different temperatures. Notice that at 0 °C the

enthalpy of mixing is negative for all compositions, thus heat has to be removed from the system to keep it at constant temperature. This type of enthalpy of mixing/composition diagram can be used to solve problems involving real mixtures. Note that the composition is given in mass fraction and not in molar fraction.

A second (and preferred) format in which the data may be available is in mixture (molal) enthalpy vs. composition diagram for several temperatures, at a given pressure. Temperatures are interpolated for use in actual problems from the temperatures of the diagram. This type of diagram is shown in Fig. 6 for a ethanol/water binary system.

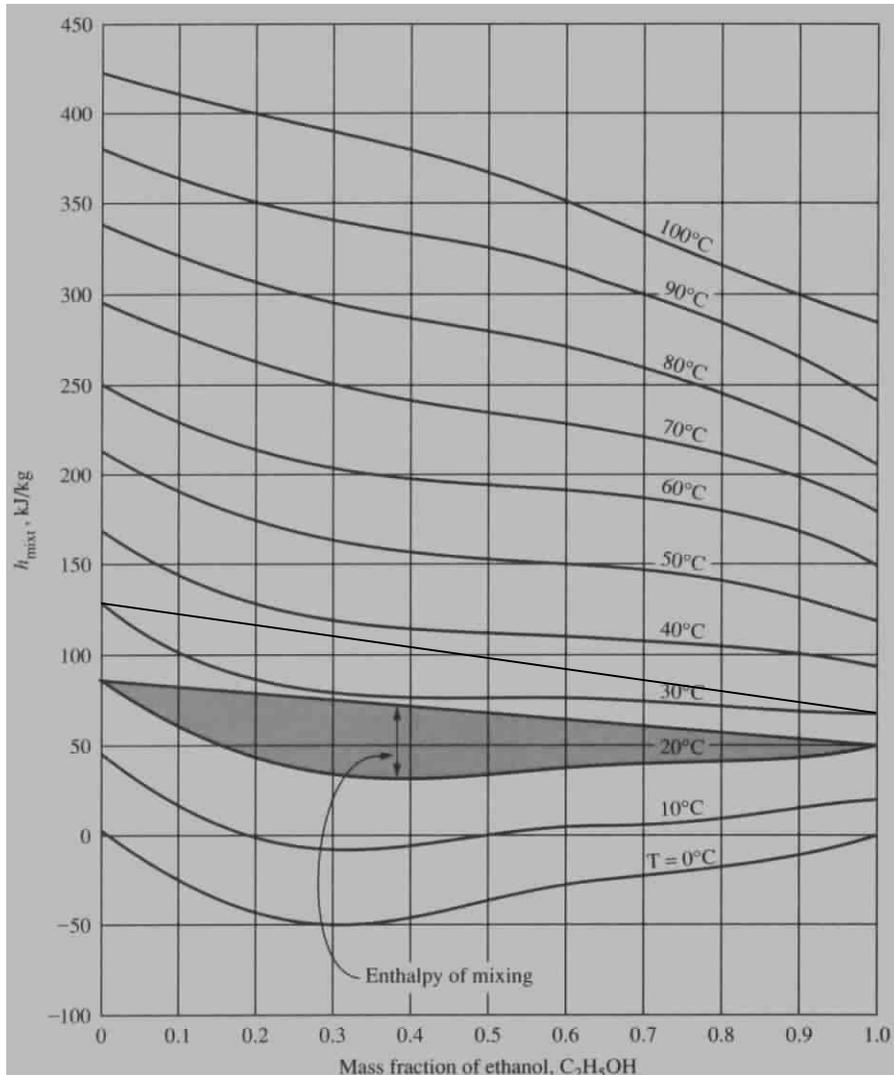


Figure 6: molal enthalpy vs. composition diagram for a water/ethanol solution.

Example: the mixing of two fluid streams.

Two streams of water and ethanol are mixed in an adiabatic chamber. The flow rates are 0.7 kg/s of water and 0.3 kg/s of ethanol. Inlet temperatures are 70 °C for ethanol and 10 °C for water. Find the temperature of the exit mixture assuming a) ideal solution and b) real solution. c) What is the amount of heat that should be removed from the mixer to overcome the heat of mixing?

The temperature at the exit can be found using the mass and energy conservation equations:

$$m_w + m_e = m_{mixt}$$

$$m_w h_w + m_e h_e = m_{mixt} h_{mixt}$$

mass conservation implies that $m_{mixt} = 1 \text{ kg/s}$. From the diagram for ethanol and water, we have, $h_w = 45 \text{ kJ/kg}$, $h_e = 180 \text{ kJ/kg}$. Thus, the mixture enthalpy will be:

$$h_{mixt} = \frac{m_w h_w + m_e h_e}{m_{mixt}} = \frac{0.7 \cdot 45 + 0.3 \cdot 180}{1} = 85.5 \text{ kJ/kg}$$

- assuming ideal solution, for a mass fraction of ethanol of 0.3, we can interpolate the temperature values of the diagram of Fig. 5, using straight lines. For 20 °C, $x_m=0.3$ we have an enthalpy of 75 kJ/kg. For 30 °C we have an enthalpy of 110 kJ/kg. Interpolation gives a temperature of 23 °C.
- for a real solution, we have 80 kJ/kg for 30 °C and 120 kJ/kg for 40 °C. Interpolation results in a temperature of 31.3 °C.

For question c), the energy equation writes:

$$m_w h_w + m_e h_e + \dot{Q} = m_{mixt} h_{mixt}$$

where the mixture enthalpy must be such that the temperature is that of the ideal solution (in which case the enthalpy of mixing is zero and there is no overheating in the mixer). For $T_{mixt} = 20 \text{ °C}$ we get from Fig. 5 that $h_{mixt} = 35 \text{ kJ/kg}$, and for $T_{mixt} = 30 \text{ °C}$ we get $h_{mixt} = 65 \text{ kJ/kg}$. Thus, for $T_{mixt} = 23 \text{ °C}$ we obtain by interpolation $h_{mixt} = 44 \text{ kJ/kg}$. Replacing into the energy equation results in:

$$\dot{Q} = m_{mixt} h_{mixt} - m_w h_w - m_e h_e = 1 \cdot 44 - 0.7 \cdot 45 - 0.3 \cdot 180 = -41.5 \text{ W}$$