
1. GENERALTY

1.1 The phase equilibrium

1.1.1 Equilibrium

Thermodynamic definition: a system is in equilibrium if its free energy is at the minimum.

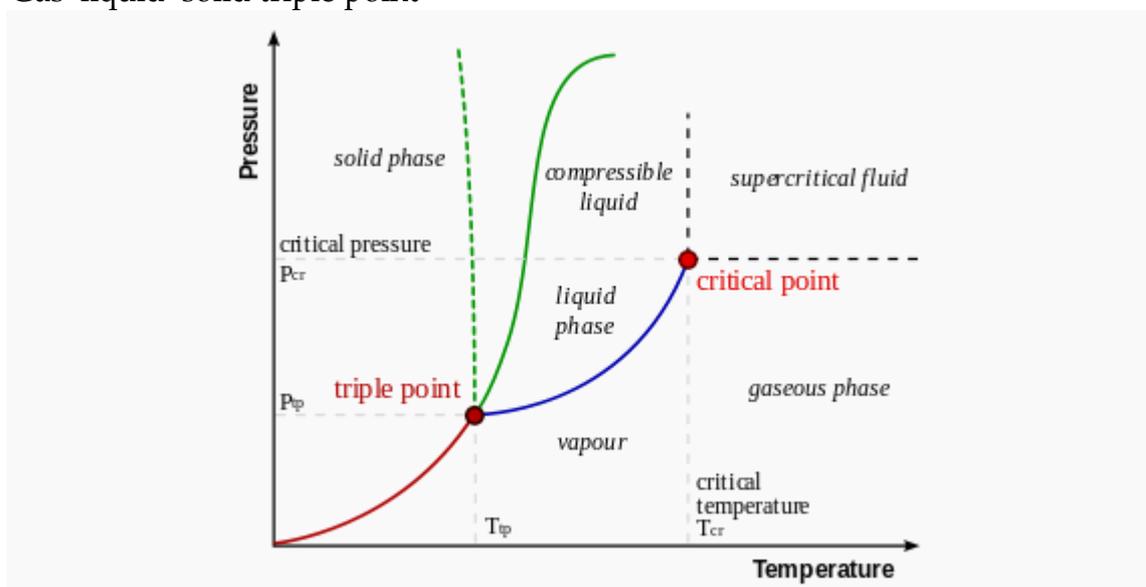
- The characteristics of the system do not change with time, i.e., the system is stable
- If you change the temperature, pressure, or composition, the free energy will change the specific phase(s) present may (or may not) change but the phase assemblage

Definition: Transformation = state change

- A) The transformation of matter from solid state to liquid state = **fusion**
- B) Transformation of matter from liquid state to solid state = **solidification**
- C) Transformation of matter from liquid state to vapor state = **vaporization**
- D) Transformation of matter from vapor state to liquid state = **condensation**
- E) Transformation of matter directly from solid state to vapor state = **sublimation**

1.1.2 Triple points of substance

Gas-liquid-solid triple point



A typical phase diagram. The solid green line applies to most substances; the dotted green line gives the anomalous behaviour of water

The single combination of pressure and temperature at which liquid as water, solid as ice and water vapor can coexist in a stable equilibrium occurs at exactly 273.16 K (0.01°C) and a partial vapor pressure of 611.73 Pa (0.0060373 atm). At that point, it is possible to change all of the substance to ice, water, or vapor by making arbitrarily small changes in pressure and temperature. Even if the total pressure of a system is well above triple point of water, provided the partial pressure of the water vapor is 611.73 Pa then the system can still be brought to the triple point of water. Strictly speaking, the surfaces separating the different phases should also be perfectly flat, to negate the effects of surface tensions.

The gas–liquid–solid triple point of water corresponds to the minimum pressure at which liquid water can exist. At pressures below the triple point, solid ice when heated at constant pressure is converted directly into water vapor in a process known as sublimation. Above the triple point, solid ice when heated at constant pressure first melts to form liquid water, and then evaporates or boils to form vapor at a higher temperature.

For most substances the gas–liquid–solid triple point is also the minimum temperature at which the liquid can exist. For water, however, this is not true because the melting point of ordinary ice decreases as a function of pressure, as shown by the dotted green line in the phase diagram. At temperatures just below the triple point, compression at constant temperature transforms water vapor first to solid and then to liquid (water ice has lower density than liquid water, so increasing pressure leads to a liquefaction).

1.1.3 The Clapeyron relationship

The slopes of the lines on a one-component pressure-temperature phase diagram may be derived from the Clapeyron equation.

For any two phases we can write:

$$\text{For state } \alpha \quad dG_{\alpha} = V_{\alpha}dP - S_{\alpha}dT$$

$$\text{For state } \beta \quad dG_{\beta} = V_{\beta}dP - S_{\beta}dT$$

Where V_{α} is the molar volume of phase α and S_{β} is the molar entropy of phase.

$$\text{At equilibrium} \quad dG_{\alpha} = dG_{\beta} \quad \text{and} \quad V_{\alpha}dP - S_{\alpha}dT = V_{\beta}dP - S_{\beta}dT$$

$$\text{If } V_{\alpha} - V_{\beta} = \Delta V \text{ and } S_{\alpha} - S_{\beta} = \Delta S \text{ we can write} \quad \Delta V dP = \Delta S dT$$

$$\text{or} \quad \frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

but also at equilibrium $\Delta G = \Delta H - T\Delta S = 0$ and $\Delta G = G_\alpha - G_\beta$

and therefore
$$\Delta S = \frac{\Delta H}{T}$$

by this way we have $\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$ this expression, the Clapeyron equation, is entirely general and applies to any phase change in a one-component system.

We can write
$$dP = \frac{\Delta H}{\Delta V} \times \frac{dT}{T} \quad P_2 - P_1 = \frac{\Delta H}{\Delta V} (\ln T_1 - \ln T_2)$$

In case of vaporization or sublimation we can assume that since the volume of the gas formed is so much greater than that of the solid or liquid, respectively

For sublimation $\Delta V = V_g - V_s \approx V_g$ and for vaporization $\Delta V = V_g - V_L \approx V_g$

Furthermore, if we assume that the vapor is considered as ideal and work only with molar quantities, we can write

$$V_g = \frac{RT}{P} \quad \text{so that} \quad \Delta V \approx \frac{RT}{P} \quad \text{and} \quad \frac{dP}{dT} = \frac{\Delta H}{T\Delta V} = \frac{P\Delta H}{RT^2}$$

Which is the differential form of the Clausius-Clapeyron equation. Rearranging gives $\frac{dP}{P} = \frac{\Delta H dT}{RT^2}$ which, in its integrated form is

$$\ln P_2 - \ln P_1 = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

or
$$\ln \frac{P_2}{P_1} = \frac{\Delta H}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

The equation relates the values of any pair of points (p_1, T_1) and (p_2, T_2) on the vaporisation or sublimation line. By measuring experimentally the gradient of a pressure-temperature line we may therefore determine an average value for the enthalpy of vaporisation or sublimation over that temperature range.

Example 1. The densities of ice and of liquid water vary little with temperature and pressure. We can therefore use these values to calculate the change in volume $\Delta_{fus}V$ on melting and, with a value for the enthalpy of fusion ΔH^{fus} , determine the melting temperature of ice at different pressures from a rearranged form the integrated form of the Clapeyron equation

$$p_2 - p_1 = \frac{\Delta H}{\Delta V} (\ln T_2 - \ln T_1)$$

Given the density of a substance ρ , we can calculate its molar volume V

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

where M is the molar mass. The densities of ice and liquid water are 0.917 g dm^{-3} and 1.000 g dm^{-3} and the molar mass, $M = 18.02 \text{ g}$, so that the molar volumes of ice and liquid water are

$$V_{\text{ice}} = 18.02 \text{ g} / 0.917 \text{ g dm}^{-3} = 19.58 \text{ dm}^3$$

and

$$V_{\text{water}} = 18.02 \text{ g} / 1.000 \text{ g dm}^{-3} = 18.02 \text{ cm}^3$$

respectively. The volume change on melting is therefore

$$\Delta_{\text{fus}}V = V_{\text{water}} - V_{\text{ice}} = 18.02 - 19.58 = -1.56 \text{ cm}^3.$$

We must remember to convert this value into units of m^3

$$\Delta_{\text{fus}}V = -1.56 \text{ cm}^3 = -1.56 \times 10^{-6} \text{ m}^3$$

before substituting it into the Clapeyron equation.

We already know one point on the solid-liquid equilibrium line since we know that ice melts at a temperature of $T_1 = 273.15 \text{ K}$ and pressure of $p_1 = 101325 \text{ Pa}$. The enthalpy of fusion of ice $\Delta_{\text{fus}}H^\circ = 6.030 \text{ kJ mol}^{-1}$.

Thus at a pressure of 70 bar (7093000 Pa , which is typical of the pressure exerted by an ice skater

$$p_2 - p_1 = \frac{\Delta H}{\Delta V} (\ln T_2 - \ln T_1)$$

and so

$$\ln T_2 = \left(\ln T_1 + \frac{\Delta V}{\Delta H} (p_2 - p_1) \right)$$

$$\ln T_2 = \ln 273.15 + \frac{-1.56 \times 10^{-6}}{6030} (70 - 1) \times 101325 = \ln 273.15 - 1.809 \times 10^{-3} = 5.608$$

Thus at a pressure of 70 bar, the melting point of ice is $T_2 = 272.66$ K, a decrease of 0.49 K.

The melting temperature of ice is therefore lowered by the effect of increased pressure. The application of pressure to a block of ice held at a constant temperature may therefore cause melting. This is unusual; for most substances, the melting point increases with pressure. The peculiar behaviour of water arises because the density of liquid water is greater than that of ice. The contraction on melting causes results in a negative value for $\Delta_{\text{fus}}V$ and so the solid-liquid line on the pressure-temperature phase diagram of water has a negative gradient.

Example 2. Given the normal boiling temperature and enthalpy of vaporisation of a substance, we can use the Clausius-Clapeyron equation to predict the vapour pressure at a range of different temperatures.

For example, the normal boiling temperature of benzene is 353.25 K, with a standard enthalpy of vaporisation $\Delta_{\text{vap}}H^\ominus = 30.8$ kJ mol⁻¹. If we assume that the enthalpy of vaporisation varies little with temperature and pressure, we may use the integrated form of the Clausius-Clapeyron equation

$$\ln p_2 - \ln p_1 = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

to determine the vapour pressure of benzene at another temperature, such as 298.15 K.

The normal boiling temperature is the temperature at which the vapour pressure of benzene is 101325 Pa. We may therefore take $T_1 = 353.25$ K and $p_1 = 101325$ Pa and substitute into the Clausius-Clapeyron equation. This will allow us to determine a value for the vapour pressure p_2 at a temperature of $T_2 = 298.15$.

$$\ln p_2 - \ln 101325 = \frac{30.8 \times 10^3}{8.314} \left(\frac{1}{353.25} - \frac{1}{298.15} \right)$$

giving $p_2 = 14600$ Pa.

Note that we must assume that the enthalpy of vaporisation remains constant over the entire temperature and pressure range. In theory, the value quoted is only appropriate for a temperature of 353.25 K and a pressure of 10⁵ Pa. Significant variation in the enthalpy of vaporisation with temperature and pressure would be observed as a curve in the liquid-vapour equilibrium line on the benzene phase diagram.

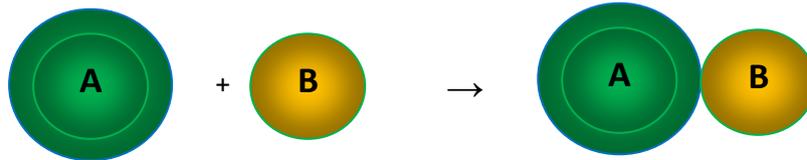
2. THE SIMPLE MIXTURES

Solute/solvent = solution

Real solution : interaction between solvent and solute

A) **Ideal solution:** No interaction between solvent and solute

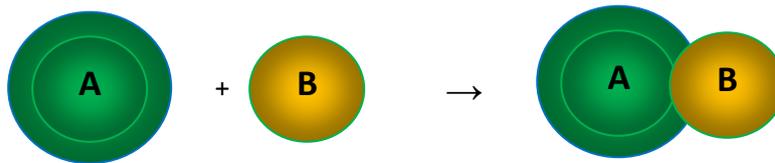
Example: 10 L of A + 5 L of B = 15 L (A+B) (Ideal solution)



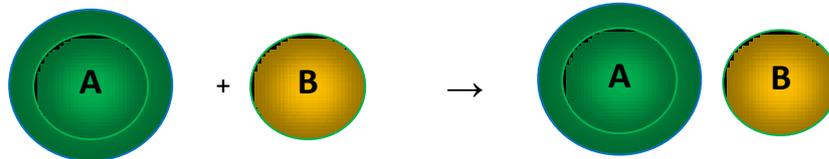
B) **Real solution**

2 cases: There are attractions or repulsion between molecules of A and molecules of B

Example: : 10 L of A + 5 L of B < 15 L (A+B) (Real solution , Attraction)



Example: 10 L of A + 5 L of B > 15 L (A+B) (Real solution , Repulsion)



2.1 The thermodynamic description of mixtures

2.1.1 Partial molar quantities

Definition

a) *The partial molar volume of a substance is the contribution to the volume that a substance makes when it is part of a mixture.*

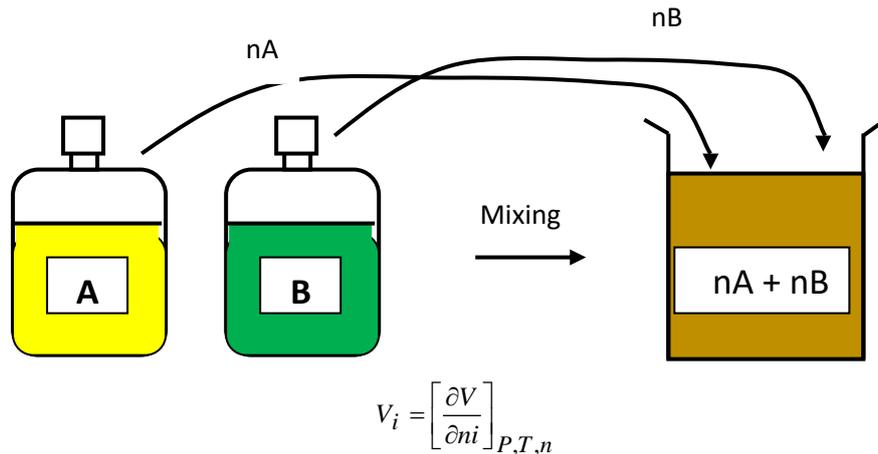
b) *The chemical potential is the partial molar Gibbs energy and enables us to express the dependence of the Gibbs energy on the composition of a mixture.*

c) *The chemical potential μ also shows how, under a variety of different conditions, the thermodynamic functions vary with composition.*

d) The Gibbs-Duhem equation shows how the changes in chemical potential of the components of a mixture are related.

A- Partial molar volume V_p

The partial molar volumes of the components of a mixture vary with composition because the environment of each type of molecule changes as the composition changes from pure A to pure B.



Where n is the amounts of all other substances present are constant.

The definition in equation 5.1 implies that, when the composition of the mixture is changed by the addition of n_A of A and n_B of B, then the total volume of the mixture changes by:

$$V_A = \left(\frac{\partial V_t}{\partial n_A} \right)_{T,P,n_B} \quad ; \quad V_B = \left(\frac{\partial V_t}{\partial n_B} \right)_{T,P,n_A}$$

$$V_t = \left(\frac{\partial V_t}{\partial n_A} \right)_{T,P,n_B} dn_A + \left(\frac{\partial V_t}{\partial n_B} \right)_{T,P,n_A} dn_B$$

$$V_t = V_A dn_A + V_B dn_B$$

Example: A liquid mixture of ethanol and water. Calculate the partial molar volume ethanol and the partial molar volume of water, if its total volume is V_t is expressed as $V_T = 18 + 2.3 n_{\text{eth}} + 0.67 n_{\text{eth}}^2$ and the mole number of ethanol is 0.23 mol and the mole number water is 1.22 mol

Solution

a) Partial molar volume of ethanol

$$V_{Eth} = \left(\frac{\partial V_t}{\partial n_{Eth}} \right)_{n_{water}, T, P}$$

b) *Partial molar volume of water*

$$V_{water} = \left(\frac{\partial V_t}{\partial n_{water}} \right)_{n_{eth}, T, P}$$

Exercise: A solution containing 150 g of ethanol/water mixture, what are the partial molar volume of ethanol and the partial molar volume of water if the total volume of this solution is expressed as function of the mole number of ethanol by the following equation:

$$V_t = 0.23 + 2.32 n_{eth} + 0.36 n_{eth}^2$$

and the mole number of ethanol is 0.23 mol

$$m_t = m_{eth} + m_{wat} = 150 \text{ g} \quad n_{eth} = m_{eth}/M_{eth} = 0.23 \text{ mol} \rightarrow m_{eth} = 0.23 \times 46 = 10.58 \text{ g}$$

$$m_w = 150 - 10.58 = 139.42 \text{ g} \quad n_w = 139.42/18 = 7.7 \text{ moles}$$

Solution

$$V_{eth} = \frac{\partial V_t}{\partial n_{eth}} = 0 + 2.32 + 2 \times 0.36 n_{eth}$$

$$V_{eth} = 2.32 + 2 \times 0.36 \times 0.23 = 2.485 \text{ ml/mol}$$

$V_{water} ?$

$$V_t = V_{eth} n_{eth} + V_{water} \times n_{water}$$

$$0.23 + 2.32 n_{eth} + 0.36 n_{eth}^2 = 2.485 \times 0.23 + V_{water} \times n_{water}$$

$$m_t = m_{eth} + m_{water} = 150 \text{ g}$$

$$n_{eth} = 0.23 \text{ mole} = m_{eth}/M_{eth}$$

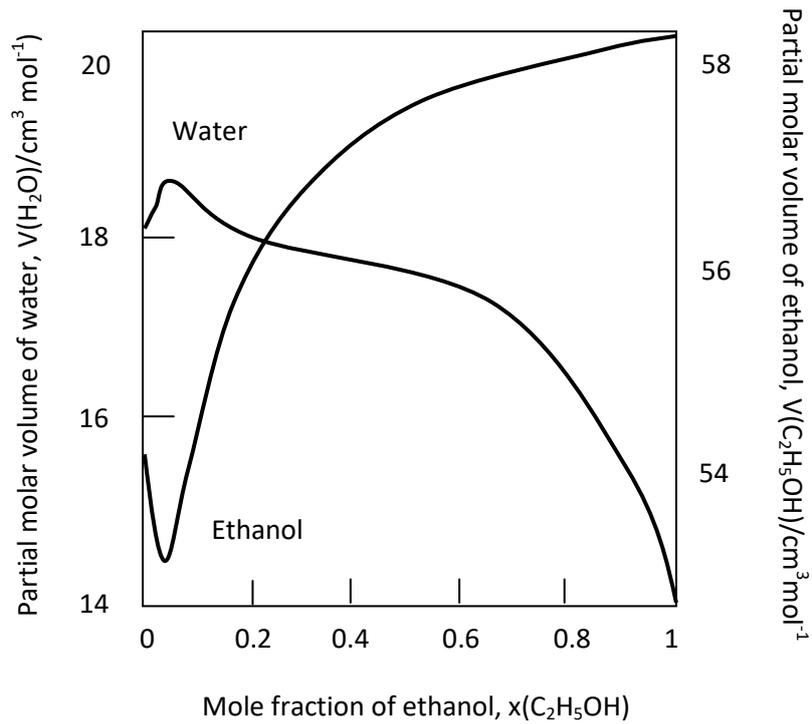
$$M_{eth} = C_2H_5OH = 2 \times 12 + 6 + 16 = 46 \text{ g/mol}$$

$$m_{eth} = 46 \times 0.23 = 10.58 \text{ g} \quad m_{water} = 150 \text{ g} - 10.58 \text{ g} = 139.42 \text{ g}$$

$$n_{water} = 139.42/18 = 7.746 \text{ moles}$$

$$0.23 + 2.32 \times 0.23 + 0.36 \times (0.23)^2 = 2.485 \times 0.23 + V_{water} \times 7.746$$

$$0.782 = 0.571 + 7.746 V_{water} \quad V_{water} = 0.211/7.746 = \underline{\underline{0.027 \text{ ml/mol}}}$$



B) Partial molar Gibbs energies

The concept of a partial molar quantity can be extended to any extensive state function. For a substance in a mixture, the chemical potential is defined as the partial molar Gibbs energy:

$$\mu_j = \left[\frac{\partial G}{\partial n_j} \right]_{P,T,n} \quad (2,4)$$

The total Gibbs energy of a binary mixture constituted of A and B components is

$$G = n_A \mu_A + n_B \mu_B \quad (2.5)$$

where μ_A and μ_B are the chemical potentials at the composition of the mixture.

$$G_t = a' + b'n_A + c'n_A^2 = n_A \mu_A + n_B \mu_B$$

$$\mu_A = \frac{\partial G_t}{\partial n_A} = 0 + b' + 2c'n_A$$

$$a' + b'n_A + c'n_A^2 = n_A(b' + 2c'n_A) + n_B \mu_B$$

$$\mu_B = \frac{\partial G_t}{\partial n_B}$$

The Gibbs energy of a mixture may change when these variables change, and, for a system of components A, B, etc.

the equation $dG = Vdp - SdT$ becomes

$$dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \dots \quad (2.6)$$

This expression is the fundamental equation of chemical thermodynamics. Its implication and consequences are explored and developed in this and the next chapters.

At constant pressure and temperature equation 5.6 simplifies to

$$dG = \mu_A dn_A + \mu_B dn_B + \dots \quad (2.7)$$

We saw in section 3.5e that under the same conditions $dG = dw_{\text{add,max}}$. Therefore, at constant temperature and pressure,

$$dw_{\text{add,max}} = \mu_A dn_A + \mu_B dn_B + \dots \quad (2.8)$$

That is, additional (non-expansion) work can arise from the changing composition of a system.

$$X_i = \left(\frac{\partial X_t}{\partial n_i} \right)_{T,P,n_B}$$

$$X_t = n_i X_i + n_j X_j$$

$$\mathbf{X} = \mathbf{V}, \mathbf{H}, \mathbf{S}, \mathbf{G}$$

C) The wider significance of the chemical potential

The chemical potential does not more than show G varies with composition.

Because $G = U + PV - TS$, and therefore $U = -PV + TS + G$, we can write a general infinitesimal change in U for a system of variable composition as

$$dU = -PdV - VdP + SdT + TdS + dG$$

$$dU = -PdV - VdP + SdT + TdS + (VdP - SdT + \mu_A dn_A + \mu_B dn_B + \dots)$$

$$dU = -PdV + SdT + \mu_A dn_A + \mu_B dn_B + \dots$$

This expression is the generalization of equation 3.46 (that $dU = TdS - PdV$) to systems in which the composition may change. It follows that, at constant volume and entropy,

$$dU = \mu_A dn_A + \mu_B dn_B + \dots \quad (2.9)$$

and hence that
$$\mu_j = \left[\frac{\partial U}{\partial n_j} \right]_{S,V,n} \quad (2.10)$$

Therefore, not only does the chemical potential show G changes when the composition changes, it also shows how the internal energy changes too (but under a different set of conditions). In the same way it is easy to deduce that

$$(a) \mu_j = \left[\frac{\partial H}{\partial n_j} \right]_{S,P,n} \quad ; \quad (b) \mu_j = \left[\frac{\partial A}{\partial n_j} \right]_{S,V,n}$$

Thus we see that the μ_j shows how all the extensive thermodynamic properties U, H, A, and G depend on the composition. This is why the chemical potential is so central to chemistry.

$$X_i = \frac{\partial X_T}{\partial n_i}$$

$$X_t = n_i X_i + n_j X_j$$

X: V, G, H, S, U and A

D) The Gibbs Duhem equation

$$dG = \mu_A dn_A + \mu_B dn_B + n_A d\mu_A + n_B d\mu_B \quad (2.11)$$

at constant temperature and pressure

$$n_A d\mu_A + n_B d\mu_B = 0$$

$$\sum n_j d\mu_j = 0$$

$$n_A d\mu_A = -n_B d\mu_B$$

$$d\mu_A = -n_B d\mu_B / n_A$$

$$\int_{\mu_{0A}}^{\mu_A} d\mu_A = n_B / n_A \int_{\mu_{0B}}^{\mu_B} d\mu_B$$

$$\mu_A - \mu_A^o = \frac{n_B}{n_A} \int_{\mu_{0B}}^{\mu_B} d\mu_B$$

This equation is special case of the Gibbs-Duhem equation

The significance of the Gibbs-Duhem equation is that the chemical potential of one component of a mixture cannot change independently of the chemical potentials of the other components.

If one partial molar quantity increases, then the other must decrease, with the two changes related by:

$$d\mu_B = \frac{n_A}{n_B} d\mu_A \quad (2.12)$$

Example

The experimental values of the partial molar volume of $K_2SO_4(aq)$ at 298 K are found to fit the expression

$$\mu_B = 32.280 + 18.216 x^{1/2}$$

where x is the numerical value of the mole number of K_2SO_4 . Use the Gibbs-Duhem equation to derive an equation for the molar volume of water in the solution. The molar volume of pure water at 298K is $18.079 \text{ cm}^3 \cdot \text{mol}^{-1}$.

Solution

Method

Let A denote H_2O the solvent, and B denote K_2SO_4 , the solute.

The Gibbs-Duhem equation for the partial molar volumes of two components is:

$n_A d\mu_A + n_B d\mu_B = 0$. This relation implies that $d\mu_A = - (n_B/n_A) d\mu_B$, and therefore that μ_A can be found by integration:

$$\mu_A = \int_0^{\mu_B} \frac{n_B}{n_A} d\mu_B$$

Exercise

Repeat the calculation for a solution containing A and B components for which:

$$V_B / (\text{cm}^3 \cdot \text{mol}^{-1}) = 6.218 + 5.146 n - 7.147 n^2$$

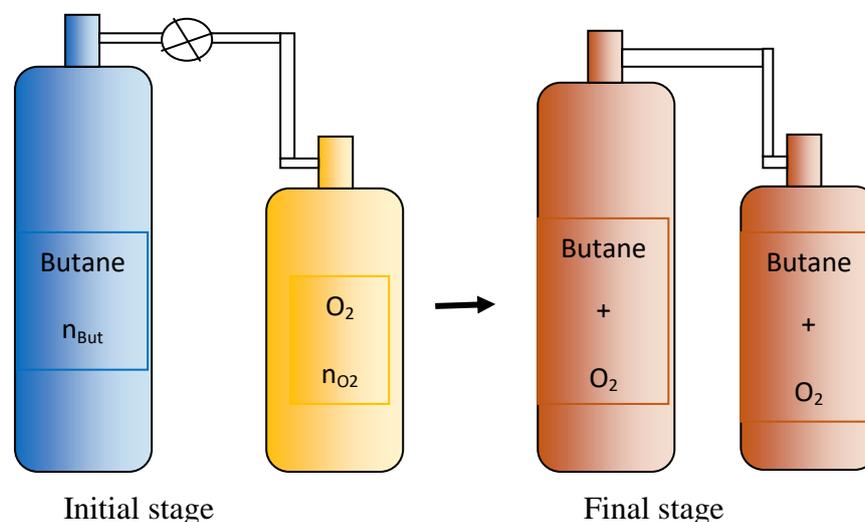
n is the mole number of A.

2.2 The thermodynamic of mixing

Definition

- The Gibbs energy of mixing is calculated by forming the difference of the Gibbs energies before and after mixing: the quantity is negative for perfect gases at the same pressure.
- The entropy of mixing of perfect gases initially at the same pressure is positive and the enthalpy of mixing is zero.

(A) The Gibbs energy of mixing of perfect gases



Determination of ΔG_M , ΔH_M and ΔS_M

$$\Delta G_M = G_f - G_i$$

$$\Delta H_M = H_f - H_i$$

$$\Delta S_M = S_f - S_i$$

$$\Delta G_M = \Delta H_M - T\Delta S_M \quad (\text{3th thermodynamic's law})$$

Two perfect gases (ideal) A and B in two containers have a chemical potential of A (n_A) and a chemical potential of B (n_B); both are at a temperature T and a pressure p. At this stage, the chemical potentials μ_A and μ_B have their pure values, which are obtained by applying the definition $\mu = G_m$ to:

$$\mu = \mu^o + RT \ln \frac{p}{p^o}$$

where μ^o is the standard chemical potential, the chemical potential of the pure gas at 1 bar. It will be much simpler notationally if we agree to let p denote the pressure relative to p^o ; that is, to replace p/p^o by p , for then we can write:

$$\mu = \mu^o + RT \ln p \quad \text{We can write the } G_i \text{ by:}$$

Initial

$$G_{A(i)} = \mu_A = \mu_A^o + n_A RT \ln P_{A(i)}$$

$$G_{B(i)} = \mu_B = \mu_B^o + n_B RT \ln P_{B(i)}$$

Final

$$G_{A(f)} = \mu_A = \mu_A^o + n_A RT \ln P_{A(f)}$$

$$G_{B(f)} = \mu_B = \mu_B^o + n_B RT \ln P_{B(f)}$$

According to the Dalton's Law

$$P_A = x_A P_T \quad x_A = P_A/P_T$$

$$P_B = x_B P_T \quad x_B = P_B/P_T$$

$$\Delta G_M = n_T RT [(x_A \ln x_A + x_B \ln x_B)]$$

$$\Delta G_M, \Delta H_M, \Delta S_M$$

$$\Delta G_M = n_T RT [(x_A \ln x_A + x_B \ln x_B)]$$

Because there is no attractions or repulsions between molecules A and molecules B
(Ideal gases)

This leads to $\Delta H_M = 0$

$$\Delta G_M = \Delta H_M - T\Delta S_M$$

$$\Delta G_M = 0 - T\Delta S_M$$

$$\Delta S_M = -\Delta G_M/T$$

$$\Delta S_M = -n_T R [(x_A \ln x_A + x_B \ln x_B)]$$

$$G_i = n_A \mu_A + n_B \mu_B = n_A (\mu_A^0 + RT \ln p) + n_B (\mu_B^0 + RT \ln p)$$

After mixing

$$G_f = n_A (\mu_A^0 + RT \ln p_A) + n_B (\mu_B^0 + RT \ln p_B)$$

$$\ln x - \ln y = \ln x/y$$

The difference $G_f - G_i$, the Gibbs energy of mixing, $\Delta_{mix}G$, is therefore:

$$\Delta G_{mix} = n_A RT \ln \frac{p_A}{p} + n_B RT \ln \frac{p_B}{p}$$

$$n_T = (n_A + n_B)$$

$$\Delta G_{mix} = \frac{n_A}{n_T} \times n_T RT \ln \frac{p_A}{p} + \frac{n_B}{n_T} \times n_T RT \ln \frac{p_B}{p}$$

$$x_A = n_A/n_T \quad ; \quad x_B = n_B/n_T$$

$$\Delta G_{mix} = x_A \times n_T RT \ln \frac{p_A}{p} + x_B \times n_T RT \ln \frac{p_B}{p}$$

Dalton's Law (gas mixture) $P_A = x_A P$ $x_A = P_A/P$ $x_B = P_B/P$

At this point we may replace n_j by x_j , where n is the total amount of A and B, and use the relation between partial pressure and mole fraction to write $p_j/p = x_j$ for each component, which gives:

$$\Delta G_{mix} = n_T RT (x_A \ln x_A + x_B \ln x_B)$$

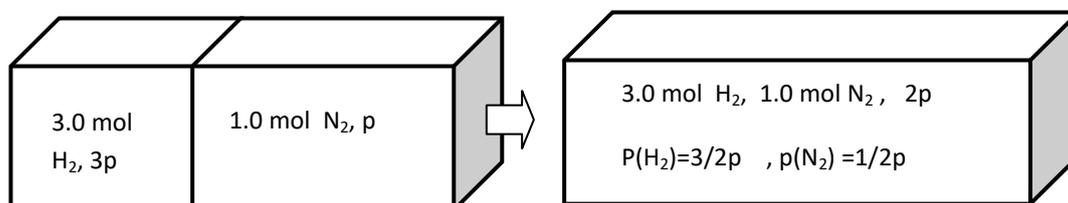
Because mole fractions are never greater than 1, the logarithms in this equation are negative, and $\Delta G_{mix} < 0$.

Example

Calculating a Gibbs energy of mixing

A container is divided into two equal compartments. One contains 3.0 mol of H₂(g) at 25°C; the other contains 1.0 mol of N₂(g) at 25°C. Calculate the Gibbs energy of mixing when the partition is removed. Assume perfect behaviour.

Answer



Initial state

$$P(\text{H}_2)V = 3RT; P(\text{N}_2)V = 1RT$$

$$P(\text{H}_2) = 3(RT/V); P(\text{N}_2) = 1(RT/V)$$

$$\text{If } P = RT/V \quad P(\text{H}_2) = 3P; P(\text{N}_2) = P$$

Final state

$$P(\text{H}_2) = 3(RT/2V) = 3/2(RT/V) = 3P/2$$

$$P(\text{N}_2) = 1(RT/2V) = 1P/2$$

$$\Delta G_M = RT[(n_A \ln(P_{A(f)}/P_{A(i)}) + n_B \ln(P_{B(f)}/P_{B(i)})]$$

$$\Delta G_M = 8.314 \times 298 [(3 \ln(3P/2/3P) + 1 \ln(P/2/P)]$$

$$\Delta G_M = 8.314 \times 298 [(3 \ln(1/2) + 1 \ln(1/2)]$$

$$\Delta G_M = 8.314 \times 298 [(3 \ln(1/2) + 1 \ln(1/2)]$$

$$2477.57 \times -4.0693 = 6868 \text{ J} = -6.868 \text{ KJ}$$

$$\Delta G_M < 0$$

$$\Delta H_M = 0$$

$$\Delta S_M = -\Delta G_M/T = 6.868/298 = 0.023 \text{ KJ/K} = 23 \text{ J/K}$$

$$\Delta S_M > 0$$

Given that the pressure of N₂ is p , the pressure of H₂ is $3p$; therefore, the initial Gibbs energy is:

$$G_i = (3.0 \text{ mol}) \left[\mu^0(\text{H}_2) + RT \ln 3p \right] + (1.0 \text{ mol}) \left[\mu^0(\text{N}_2) + RT \ln p \right]$$

When the partition is removed and each gas occupies twice the original volume, the partial pressure of N₂ falls to $1/2p$ and that H₂ falls to $3/2p$. Therefore, the Gibbs energy changes to:

$$G_f = (3.0\text{mol}) \left[\mu^o(H_2) + RT \ln \frac{3p}{2} \right] + (1.0\text{mol}) \left[\mu^o(N_2) + RT \ln \frac{p}{2} \right]$$

The Gibbs energy of mixing is the difference of these two quantities:

$$\Delta G_{mix} = (3.0\text{mol})RT \ln \frac{3/2p}{3p} + (1.0\text{mol})RT \ln \frac{p}{2p}$$

$$\begin{aligned} \Delta G_{mix} &= -(3.0\text{mol})RT \ln 2 - (1.0\text{mol})RT \ln 2 \\ &= -6.9\text{kJ} \end{aligned}$$

B) Other thermodynamic mixing functions

Because $\left(\frac{\partial G}{\partial T}\right)_{p,n} = -S$, for a mixture of perfect gas initially at the same pressure, the entropy of mixing,

$$\Delta S_{mix} = \left[\frac{\partial \Delta G_{mix}}{\partial T} \right]_{p,n_A,n_B} = -nR(x_A \ln x_A + x_B \ln x_B)$$

Because $\ln x < 0$, it follows that $\Delta S_{mix} > 0$

We can calculate the isothermal (constant temperature), isobaric (constant pressure) enthalpy of mixing, ΔH_{mix} , the enthalpy change accompanying mixing, of two perfect gases from $\Delta G = \Delta H - T\Delta S$

$$\Delta H_{mix} = 0$$

II.3 The chemical potential of liquids

Definition

a) **Raoult's law** provides a relation between the vapour pressure of a substance and its mole fraction in a mixture; it is the basis of the definition of an ideal solution.

b) Henry's law provides a relation between the vapour pressure of a solute and its mole fraction in a mixture; it is the basis of the definition of an ideal-dilute solution.

To discuss the equilibrium properties of liquid mixtures we need to know how the Gibbs energy of a liquid varies with composition. To calculate its value, we use the fact that, at equilibrium, the chemical potential of a substance present as a vapour must be equal to its chemical potential in the liquid.

(a) Ideal solutions

We shall denote quantities relating to pure substances by a superscript *, so the chemical potential of pure A is written μ_A^* and as $\mu_A^*(l)$ when we need to emphasize that A is a liquid. Because the vapour pressure of the pure liquid is p_A^* it follows from

$\mu = \mu^o + RT \ln \frac{p}{p^o}$ that the chemical potential of A in the vapour (perfect gas) is

$\mu_A = \mu_A^o + RT \ln p_A^*$. These two chemical potentials are equal at equilibrium, so we can write:

$$\mu_A = \mu_A^o + RT \ln p_A$$

Next, we combine these two equations to eliminate the standard chemical potential of the gas.

$$\mu_A = \mu_A^* - RT \ln p_A^* + RT \ln p_A = \mu_A^* + RT \ln \frac{p_A}{p_A^*}$$

According to the Raoult's law

$$p_A = x_A p_A^*$$

When we write equations that are valid only for ideal solutions, we shall label them with a superscript *

For an ideal solution

Raoult's law

$$P_A = X_A P_A^o ; P_B = X_B P_B^o ; P_T = P_A + P_B$$

$$G_i = (\mu_A^o + n_A RT \ln P_A^o) + (\mu_B^o + n_B RT \ln P_B^o)$$

$$G_f = (\mu_A^o + n_A RT \ln P_A) + (\mu_B^o + n_B RT \ln P_B)$$

$$\Delta G_M = G_f - G_i = (\mu_A^o + n_A RT \ln P_A) + (\mu_B^o + n_B RT \ln P_B) - (\mu_A^o + n_A RT \ln P_A^o) - (\mu_B^o + n_B RT \ln P_B^o)$$

$$\Delta G_M = n_A RT \ln P_A - n_A RT \ln P_A^o + n_B RT \ln P_B - n_B RT \ln P_B^o$$

$$\Delta G_M = [n_A RT (\ln P_A - \ln P_A^o)] + n_B RT (\ln P_B - \ln P_B^o)$$

$$\ln x - \ln y = \ln (x/y)$$

$$\Delta G_M = n_A RT [(\ln(P_A/P_A^o)) + n_B RT \ln(P_B/P_B^o)]$$

$$X_A = P_A/P_A^o ; X_B = P_B/P_B^o$$

$$\Delta G_M = n_A RT \ln x_A + n_B RT \ln x_B = RT [n_A \ln x_A + n_B \ln x_B]$$

$$n_T = n_A + n_B$$

$$\Delta G_M = RT [n_A \ln x_A + n_B \ln x_B] = RT (n_T)/(n_T) [n_A \ln x_A + n_B \ln x_B]$$

$$= n_T RT [(n_A/n_T) \ln x_A + (n_B/n_T) \ln x_B] \quad x_A = n_A/n_T ; x_B = n_B/n_T$$

$$\Delta G_M = n_T RT [x_A \ln x_A + x_B \ln x_B]$$

$$x_A < 1 ; \quad x_B < 1$$

$$\Delta G_M < 0$$

$$\Delta H_M = 0$$

$$\Delta G_M = \Delta H_M - T \Delta S_M$$

$$\Delta G_M = 0 - T \Delta S_M \quad \Delta S_M = -\Delta G_M / T = n_T R [x_A \ln x_A + x_B \ln x_B]$$

$$\Delta S_M = n_T R [x_A \ln x_A + x_B \ln x_B]$$

$$\text{Boltzman's Law} \quad S = -K \ln \Omega$$

$$\mu_A = \mu_A^* + RT \ln x_A$$

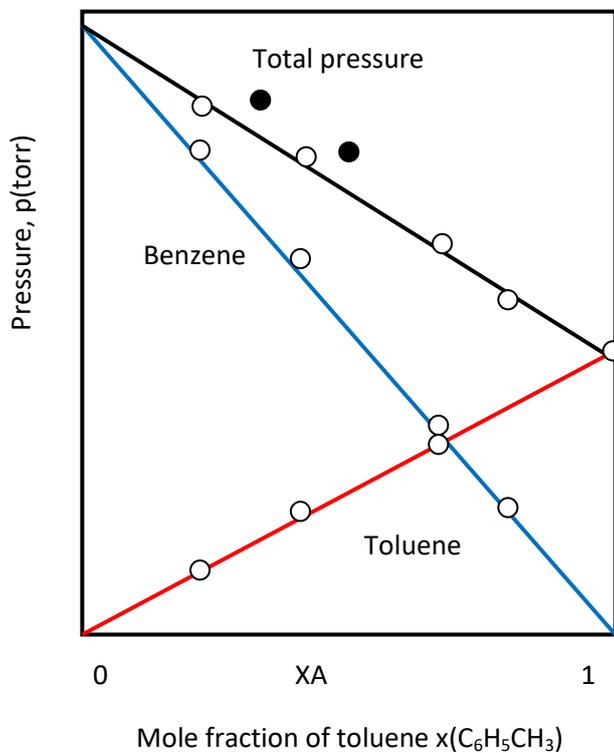


Fig. 1 Two similar liquids, in this case benzene and methylbenzene (toluene), behave almost ideally, and the variation of their vapour pressures with composition resembles that for an ideal solution.

Raoult's Law for real solutions

$$P_A = a_A P_A^o ; \quad P_B = a_B P_B^o \quad a_A = \gamma_A x_A \quad a_B = \gamma_B x_B$$

γ = activity coefficient

If $\gamma > 1$ repulsion between A and B; If $\gamma < 1$ attraction between A and B

If $\gamma = 1$ ideal no interaction between A and B

A) Real solution (Repulsion forces)

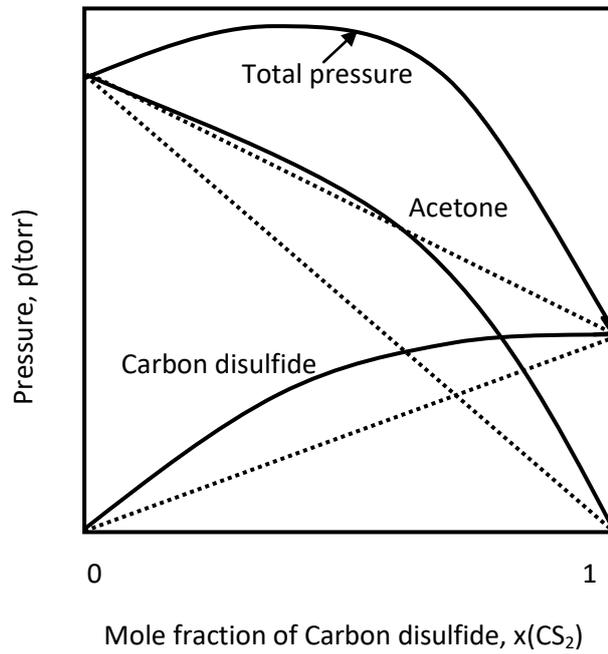


Fig. 2 Strong positive deviations from ideality are shown by dissimilar liquids.

B) *Real solution (Attraction forces)*

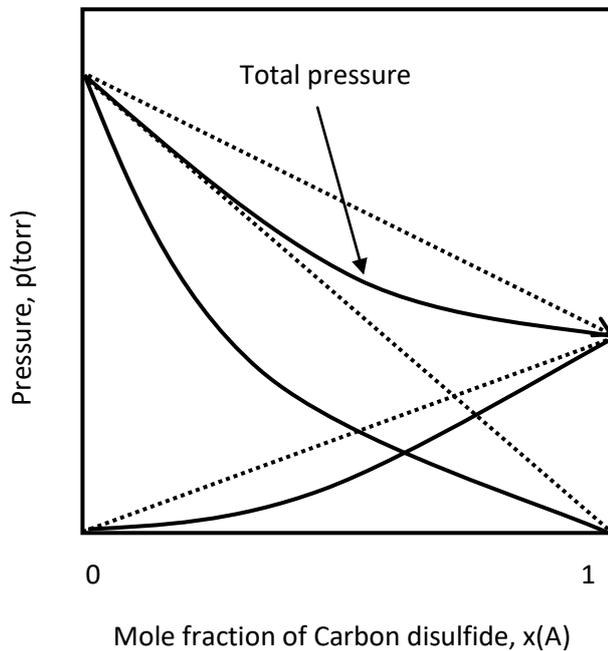


Fig. 2 Strong negative deviations from ideality are shown by dissimilar liquids.

A deviation from the ideality is observed in this previous diagram due to the interaction between CS_2 and Acetone. This interaction can be attraction or repulsion:

- A positive deviation indicating a repulsion between the different molecules
- A negative deviation indicating an attraction between the different molecules

In this case, the partial pressure of acetone becomes:

$$P_{acetone} = a_{acetone} \times P_{acetone}^* \quad \text{and} \quad P_{CS_2} = a_{CS_2} \times P_{CS_2}^*$$

where a_i is called activity of the constituent (i) in solution with $a_i = \gamma_i \times x_i$

$$a_{CS_2} = \gamma_{CS_2} \times x_{CS_2} \quad \text{and} \quad a_{acetone} = \gamma_{acetone} \times x_{acetone}$$

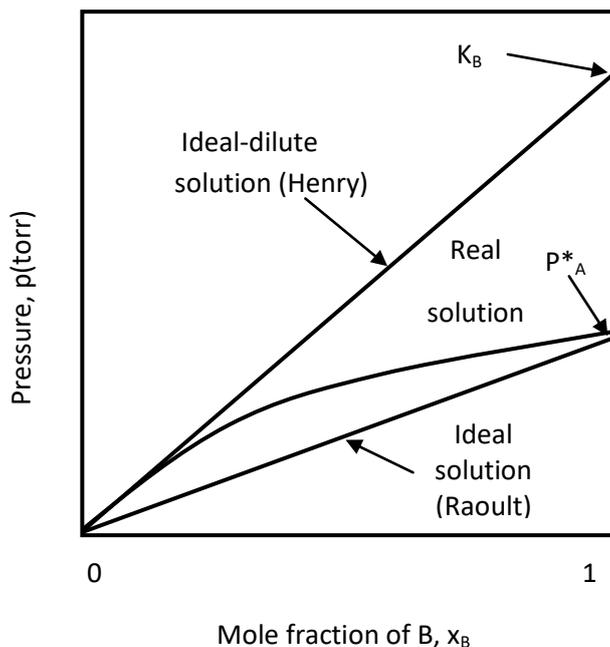


Fig. 3 When a component (the solvent) is nearly pure, it has a vapour pressure that is proportional to its mole fraction with a slope p_B^* (Raoult's law). When it is the minor component (the solute) its vapour pressure fraction, but the constant of proportionality is now K_B (Henry's law).

This important equation can be used as the definition of an ideal solution (so that it implies Raoult's law rather than stemming from it).

The molecular origin of Raoult's law is the effect of the solute on the entropy of the solution. In the pure solvent, the molecules have a certain disorder and corresponding entropy; the vapour pressure then represents the tendency of the system and its surroundings to reach a higher entropy. When a solute is present, the solution has a greater disorder than the pure solvent because we cannot be sure that a molecule chosen at random will be a solvent molecule. Because the entropy of the solution is higher than that of the pure solvent, the solution has a lower tendency to acquire an even higher entropy by the solvent vaporizing. In other words, the vapour pressure of the solvent in the solution is lower than that of the pure solvent.

(b) Ideal-dilute solutions

In ideal solutions the solute, as well as the solvent, obeys Raoult's law. However, Henry found experimentally that, for real solutions at low concentrations, although the vapour pressure of the solute is proportional to its mole fraction, the constant of proportionality is not the vapour pressure of the pure substance (Fig.3).

Henry's law is:

$$p_B = x_b K_B$$

Henry' law $P_A = x_A K_A$ K = Henry's constant

In this expression x_B is the mole fraction of the solute and K_B is an empirical constant chosen so that the plot of the vapour pressure of B against its mole fraction is tangent to the experimental curve at $x_B = 0$.

Table 1. Henry's law constants for gases in water at 298K

Substance (gas)	$K/\text{kPa.kg.mol}^{-1}$
CO ₂	3.01×10^3
H ₂	1.28×10^5
N ₂	1.56×10^5
O ₂	7.92×10^4

Example

The vapour pressures of each compound in a mixture of propanone (acetone, A) and trichloromethane (chloroforme, C) were measured at 35°C with the following results:

x_C	0	0.20	0.40	0.60	0.80	1.00
p_C/kPa	0	4.7	11	18.9	26.7	36.4
p_A/kPa	46.3	33.3	23.3	12.3	4.9	0

Confirm that the mixture conforms to Raoult's law for the component in large excess and to Henry's law for the minor component. Find the Henry's law constants.

Answer

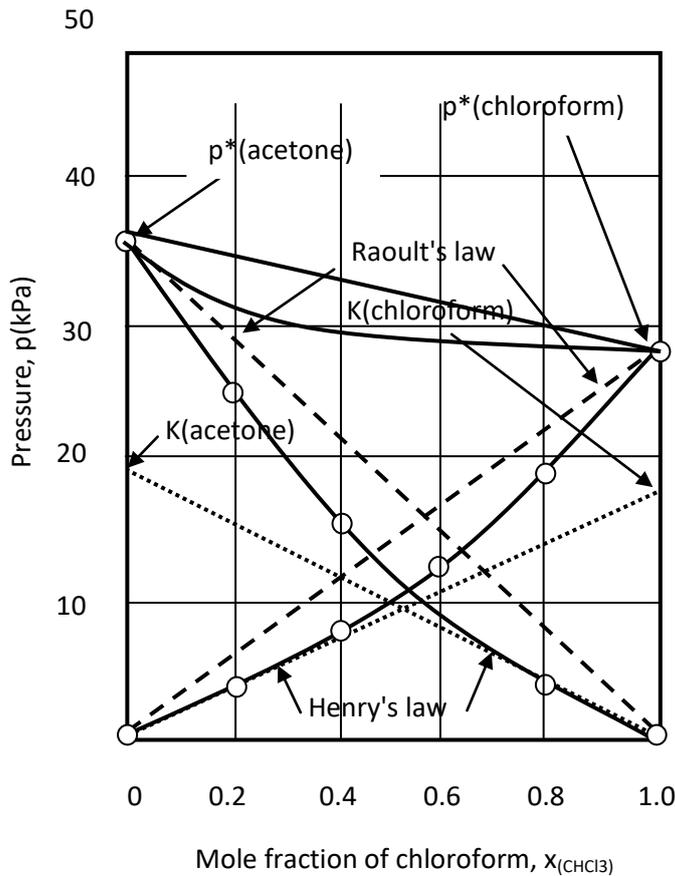


Fig. 4 The experimental partial vapour pressures of a mixture of chloroform and acetone. The values of K are obtained by extrapolating the dilute solution vapour pressures.

Figure 4.

The data are plotted in Fig 4 together with the Raoult's law lines Henry's law requires $K = 23.3$ kPa for propanone and $K = 22.0$ kPa for trichloromethane.

2.3 The properties of solutions

In this section we consider the thermodynamics of mixing of liquids. First, we consider the simple case of mixtures of liquids that mix to form an ideal solution.

5.3.1 Liquid mixtures

a) The Gibbs energy of mixing of two liquids to form an ideal solution is calculated in the same way as for two perfect gases. The enthalpy of mixing is zero and the Gibbs energy is due entirely to the entropy of mixing.

b) A regular solution is one in which the entropy of mixing is the same as for an ideal solution but the enthalpy of mixing is non-zero.

Ideal solutions

The Gibbs energy of mixing of two liquids to form an ideal solution is calculated in exactly the same way as for two gases. The total Gibbs energy before liquids are mixed is:

$$G_i = n_A \mu_A^* + n_B \mu_B^*$$

When they are mixed, the individual chemical potentials are given by $\mu_A = \mu_A^* + RT \ln x_A$ and the total Gibbs energy of mixing, the difference of these two quantities, is:

$$G_i = n_A[\mu_A^* + RT \ln x_A] + n_B[\mu_B^* + RT \ln x_B]$$

$$\Delta G_{mix} = nRT[x_A \ln x_A + x_B \ln x_B]$$

Where $n = n_A + n_B$. As for gases, it follows that the ideal entropy of mixing of two liquids is:

$$\Delta S_{mix} = -nR[x_A \ln x_A + x_B \ln x_B]$$

Because $\Delta H_{mix} = \Delta G_{mix} + T\Delta S_{mix} = 0$, the ideal enthalpy of mixing is zero.

The ideal volume of mixing, the change in volume on mixing, is also zero because it follows from $(\partial G / \partial p)_T = V$ that $\Delta V_{mix} = (\partial \Delta G_{mix} / \partial p)_T$ but ΔG_{mix} in $\Delta G_{mix} = nRT[x_A \ln x_A + x_B \ln x_B]$ is independent of pressure, so the derivative with respect to pressure is zero.

c) Excess functions and regular solutions

The thermodynamic properties of real solutions are expressed in terms of the excess functions, X^E , the difference between the observed thermodynamic function of mixing and the function for an ideal solution. The excess entropy, S^E , for example, is defined as:

$$S^E = \Delta S_{mix} - \Delta S_{mix}(\text{ideal})$$

The deviation of the excess energies from zero indicates the extent to which the solutions are nonideal. In this connection a useful model system is regular solution, a solution for which $H^E \neq 0$, but $S^E = 0$. We can think of a regular solution as one in which the two kinds of molecules are distributed randomly (as in an ideal solution) but have different energies of interactions with each other. To express this concept more quantitatively we can suppose that the excess enthalpy depends on composition as:

$$H^E = n\xi RTx_Ax_B$$

where ξ (ξ) is a dimensionless parameter that is a measure of the energy of AB interactions relative to that of the AA and BB interactions. If $\xi < 0$, mixing is exothermic and the solute-solvent interactions are more favorable than the solvent-solvent and solute-solute interactions. If $\xi > 0$, then the mixing is endothermic. Because the entropy of mixing has its ideal value for a regular solution, the excess Gibbs energy is equal to the excess enthalpy, and the Gibbs energy of mixing is:

$$\Delta G_{mix} = nRT[x_A \ln x_A + x_B \ln x_B + \xi x_A x_B]$$

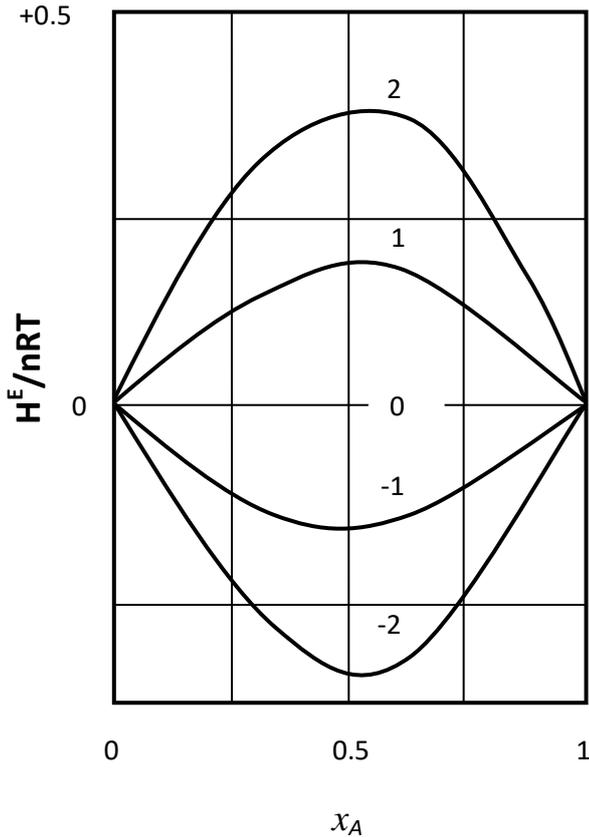


Fig. 5 The excess enthalpy according to a model in which it is proportional to $\xi x_A x_B$, for different values of the parameter ξ .

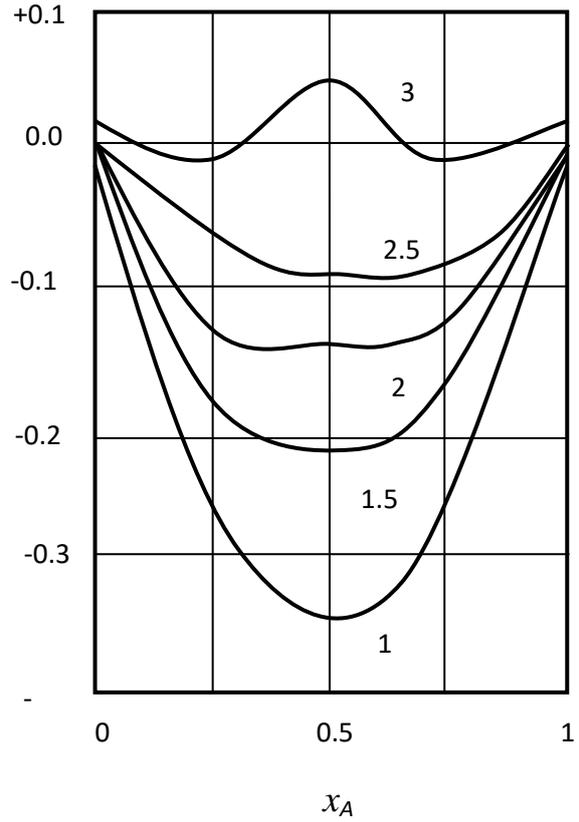


Fig. 6 The Gibbs energy of mixing for different values of the parameter ξ .

(A) The elevation of boiling point

The heterogeneous equilibrium of interest when considering boiling is between the solvent vapour and the solvent in solution at 1 atm. We denote the solvent by A and the solute by B. The equilibrium is established at a temperature for which

$$\mu_A^*(g) = \mu_A^*(l) + RT \ln x_A$$

We show in the following justification that this equation implies that the presence of a solute at a mole fraction x_B causes an increase in normal boiling point from T^* to $T^* + \Delta T$, where

$$\Delta T = K x_B = T_{eq} - T_i \quad K = \frac{RT^{*2}}{\Delta H_{vap}}$$

$$x_A = n_A / (n_A + n_B) = n_A / n_B$$

$$\Delta T = K \frac{n_{solute}}{m(kg)_{solvent}}$$

$$T_{eq} - T_{solvent} = K_{solvent} \times \frac{n_{solute}}{m_{solvent}(kg)}$$

$$T_{eq} - T_{solvent} = K_{solvent} \times \frac{n_{solute}}{m_{solvent}(g)10^3}$$

$$T_{eq} - T_{solvent} = K_{solvent} \times \frac{m_{solute}(g)}{M(solute)(g) \times m_{solvent}(g)10^3}$$

B) The depression of freezing point

The heterogeneous equilibrium of interest is between pure solid solvent A and the solution with solute present at a mole fraction x_B . At the freezing point, the chemical potentials of A in the two phases are equal:

$$\mu_A^*(s) = \mu_A^*(l) + RT \ln x_A$$

The only difference between this calculation and the last is the appearance of the solid's chemical potential in place of the vapour's. Therefore we can write the result directly from equation

$$\Delta T = K' x_B \quad K' = \frac{RT^{*2}}{\Delta H_{fus}}$$

Where ΔT is the freezing point depression, T^*-T , ΔH_{fus} is the enthalpy of fusion of the solvent. When the solution is diluted, the mole fraction is proportional to the molality of the solute, b , and it is common to write the last equation as

$$\Delta T = K_f \times b$$

$$T_{eq} - T_{solvent} = K'_{solvent} \times \frac{m_{solute}(g)}{M(solute)(g) \times m_{solvent}(g)10^3}$$

C) The solubility

In a saturated solution the chemical potential of pure solid solute, $\mu_B^*(s)$, and the chemical potential of B in solution, μ_B , are equal. Because the latter is

$$\mu_B = \mu_B^*(l) + RT \ln x_B \text{ we can write } \mu_B^*(s) = \mu_B^*(l) + RT \ln x_B$$

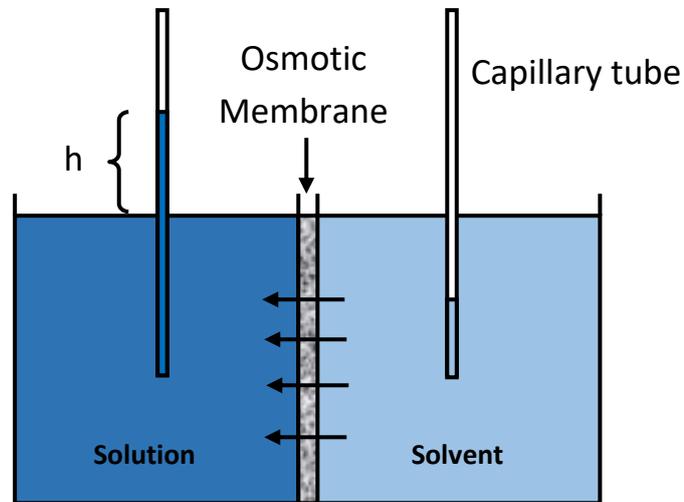
This expression is the same as the starting equation of the last section, except that the quantities refer to the solute B, not the solvent A. We now show in the following justification that:

$$\ln x_B = \frac{\Delta H_{fus}}{R} \left(\frac{1}{T_f} - \frac{1}{T} \right)$$

D) The Osmosis

The thermodynamic treatment of osmosis depends on noting that, at equilibrium, the chemical potential of the solvent must be the same on each side of the membrane. The chemical potential of the solvent is lowered by the solute, but is restored to its pure

value by the application of pressure. This equality implies that for dilute solutions the osmotic pressure is given by the Van'tHoff equation:



Osmosis equation: This equation is applicable only when the solution used is infinite diluted ($m_{\text{Solute}} \gg m_{\text{Solvent}}$)

$$\pi V = nRT \quad (\text{Osmose})$$

$$\pi = \frac{nRT}{V}$$

$$\pi = h \times g \times \rho$$

h: high in the capillary tube (cm)

g: gravitational force= 981 cm/s²

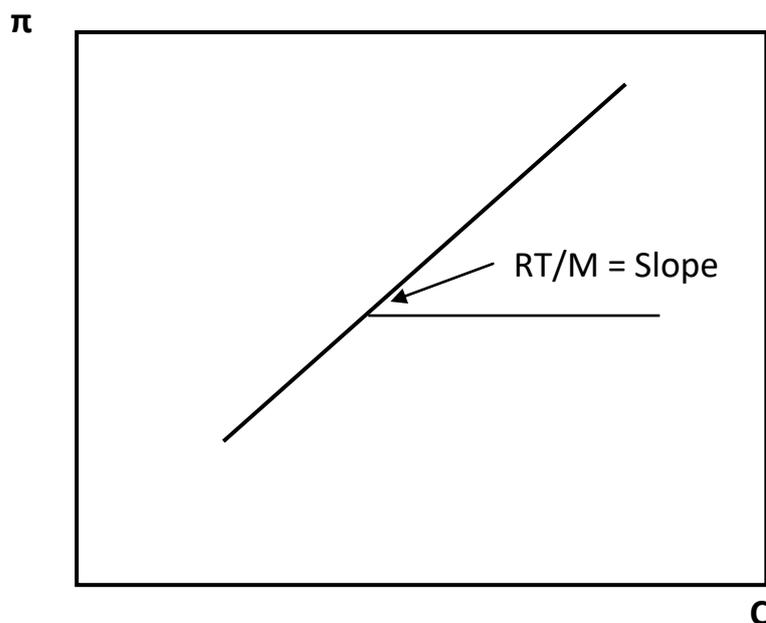
ρ : density of solution (g/cm³)

$$\pi = \frac{n(solute)RT}{V} = \frac{C}{M} RT$$

C: concentration of solute (g/cm³)

T: temperature (K)

R: gas constant= 8.314 J/K.mol = 8.314 kg·m²/s²K·mol



$$Pa = Kg/m^2$$

$$M\left(\frac{g}{mol}\right) = \frac{C\left(\frac{g}{cm^3}\right) \times R\left(\frac{g}{cm^2 \times K \times mol}\right) T(k)}{h(cm) \times g\left(\frac{g}{cm^2}\right) \times d\left(\frac{g}{cm^3}\right)}$$

Example

The osmotic pressures of solutions of poly(vinylchloride), PVC, in cyclohexanone at 298K are given below. The pressures are expressed in terms of the heights of solution (of mass density $\rho = 0.980 \text{ g.cm}^{-3}$) in balance with the osmotic pressure.

Determine the molar mass of the polymer.

$c/(\text{g.dm}^{-3})$	1.00	2.00	4.00	7.00	9.00
h/cm	0.28	0.71	2.01	5.10	8.00

Answer

$c/(\text{g}\cdot\text{dm}^{-3})$	1.00	2.00	4.00	7.00	9.00
h/cm	0.28	0.71	2.01	5.10	8.00
$(h/c)/(\text{cm}\cdot\text{g}^{-1}\cdot\text{dm}^3)$	0.28	0.36	0.503	0.729	0.889

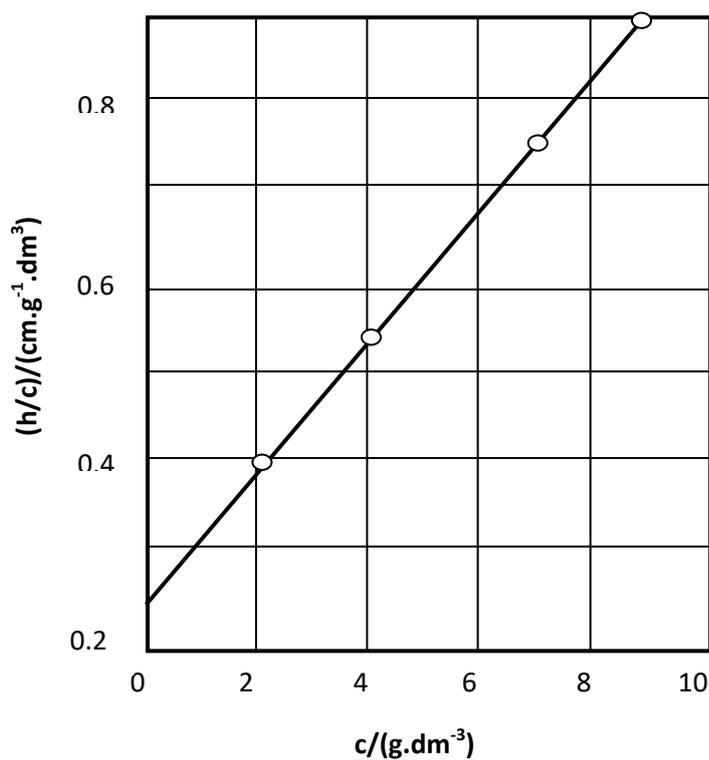


Fig. 7 The plot involved in the determination of molar mass by osmometry. The molar mass is calculated from the intercept at $c = 0$.

$$\frac{C}{M}RT = h \times g \times d$$

$$h/c = RT/g \times d \times M$$

The points are plotted in figure 7. The intercept is at 0.21. Therefore,

$$M = \frac{RT}{\rho \times g} \times \frac{1}{0.21 \text{ cm g}^{-1} \text{ dm}^3}$$

$$M = \frac{(8.3145 \text{ JK}^{-1} \text{ mol}^{-1})}{(980 \text{ kg m}^{-1}) \times (9.81 \text{ ms}^{-2})} \times \frac{298 \text{ K}}{2.1 \times 10^{-3} \text{ m}^4 \text{ kg}^{-1}} = 1.2 \times 10^2 \text{ kg} \cdot \text{mol}^{-1}$$

$$M = 1200000 \text{ g/mol}$$

3. PHASE DIAGRAMS OF BINARY SYSTEMS

3.1 Vapour pressure diagrams

Raoult's law is used to calculate the total vapour pressure of a binary system of two volatile liquids.

- The composition of the vapor in equilibrium with a binary mixture is calculated by using Dalton's law.
- The compositions of the vapour and the liquid phase in equilibrium are located at each end of a tie line.
- The lever rule is used to deduce the relative abundances of each phase in equilibrium.

The partial pressures of the components of an ideal solution of two volatile liquids are related to the composition of the liquid mixture by Raoult's law

$$p_A = x_A p_A^* \quad \text{and} \quad p_B = x_B p_B^* \quad (5.6.1)$$

where p_A^* is the vapour pressure of pure A and p_B^* that of pure B. The total vapor pressure p of the mixture is therefore

$$p = p_A + p_B = x_A p_A^* + x_B p_B^* = p_B^* + (p_A^* - p_B^*)x_A \quad (5.6.2)$$

This expression shows that the total vapour pressure (at some fixed temperature) changes linearly with the composition from p_B^* to p_A^* as x_A changes from 0 to 1.

3.1.1 The composition of the vapor

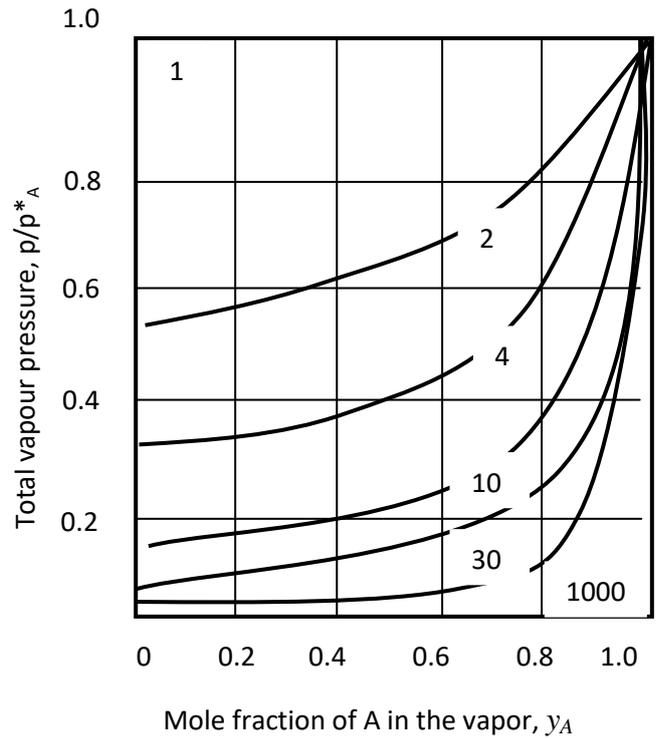
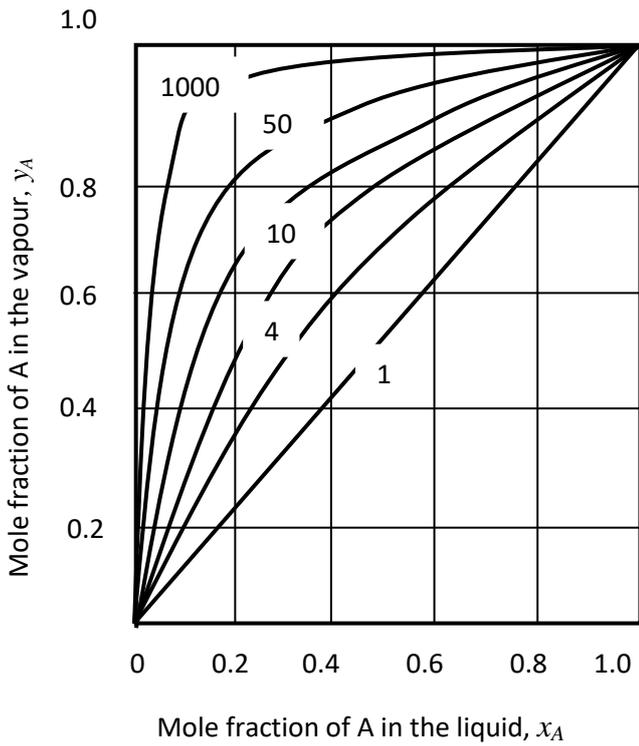
The composition of the liquid and vapour that are in mutual equilibrium are not necessarily the same. Common sense suggests that the vapour should be richer in the more volatile component. This expectation can be confirmed as follows. The partial pressures of the components are given by the Dalton's equation.

$$y_A = \frac{p_A}{p} \quad ; \quad y_B = \frac{p_B}{p} \quad (5.6.3) \quad p_A = x_A p_T \quad p_B = x_B p_T$$

y_A and y_B are the mole fractions in the gas.

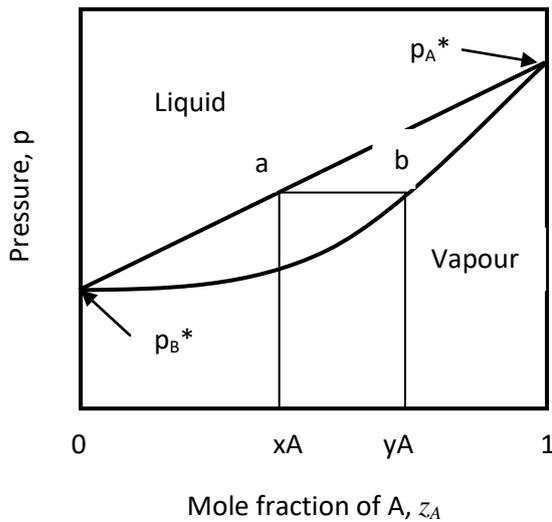
Provided the mixture is ideal, the partial pressures and the total pressure may be expressed in terms of the mole fractions in the liquid by using: $p_A = x_A p_A^*$ and $p_B = x_B p_B^*$ and $p = p_A + p_B = x_A p_A^* + x_B p_B^* = p_B^* + (p_A^* - p_B^*)x_A$ which gives:

$$y_A = \frac{x_A p_A^*}{p_B^* + (p_A^* - p_B^*)x_A} \quad \text{and} \quad y_A = 1 - y_B \quad (5.6.4)$$



The mole fraction of A in the vapour of binary ideal solution expressed in terms of its mole fraction in the liquid, calculated using eqn (5.6.4) for various values of P_A^*/P_B^* with A more volatile than B. In all cases the vapour is richer than the liquid in A.

The dependence of the vapour pressure of the same system as in the side figure, but expressed in terms of the mole fraction of A in the vapour by using eqn (5.6.5). Individual curves are labeled with the value of P_A^*/P_B^* .



The dependence of the total vapour pressure of an ideal solution on the mole fraction of A in the entire system.

A point between the two lines corresponds to both liquid and vapour being present; outside that region there is only one phase present. The mole fraction of A is denoted z_A , as explained below.

We can also relate the total vapour pressure to the composition of the vapour:

$$p = \frac{p_A^* p_B^*}{p_A^* + (p_B^* - p_A^*) y_A} \quad (5.6.5)$$

This expression is plotted in the middle figure.

3.1.2 Temperature-composition diagrams

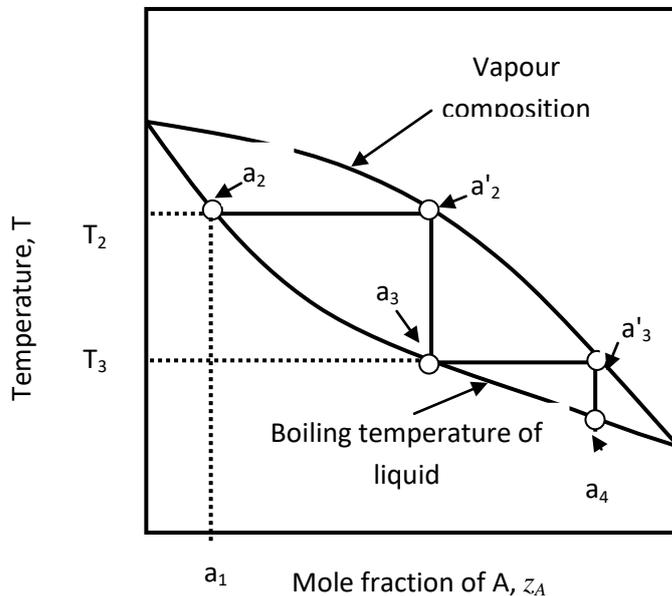
- a) a phase diagram can be used to discuss the process of fractional distillation.
- b) Depending on the relative strengths of the intermolecular forces, high- or low-boiling azeotropes may be formed.
- c) The vapour pressure of a system composed of immiscible liquids is the sum of the vapour pressures of the pure liquids.
- d) A phase diagram may be used to discuss the distillation of partially miscible liquids.

To discuss distillation we need a temperature-composition diagram, a phase diagram in which the boundaries show the composition of the phases that are in equilibrium at various temperatures (and a given pressure, typically 1 atm). An example is shown in this figure.

Xethanol	1	0.80	0.60	0.50	0.30	0.20	0
T _{boiling}	87	67	60	70	80	90	100
T _{vaporization}	87	70	80	90	95	97	100

A) Liquid-Vapor binary diagram

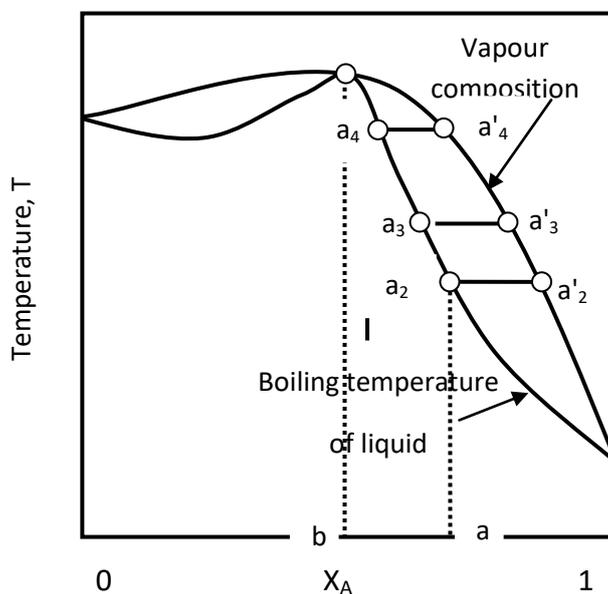
Phase diagram Liq-Vap using the reduction of pressure



The temperature-composition diagram corresponding to an ideal mixture with the component A more volatile than component B. Successive boiling and condensations of a liquid originally of composition a_1 lead to a condensate that is pure A. The separation-technique is called fractional distillation.

(a) Azeotropes

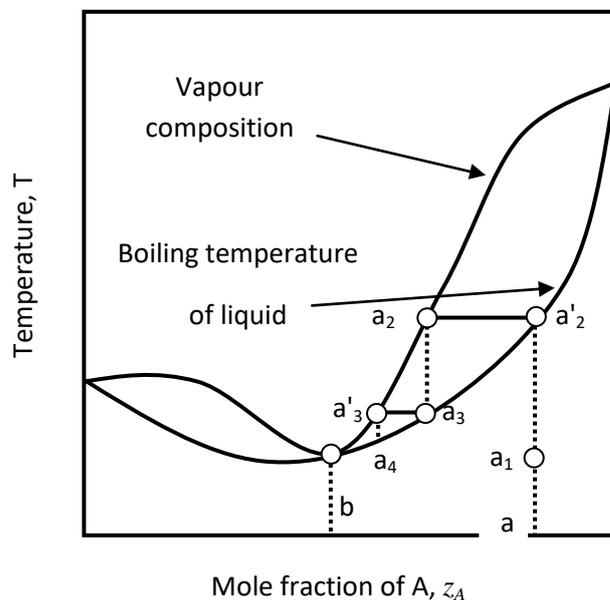
Although many liquids have temperature-composition phase diagrams resembling the ideal version in the precedent figure, in a number of important cases there are marked deviations. A maximum in the phase diagram (figure below) may occur when the favourable interactions between A and B molecules reduce the vapour pressure of the mixture below the ideal value: in effect, the A-B interactions stabilize the liquid. In such cases the excess Gibbs energy, G^E , is negative (more favourable to mixing than ideal). Examples of this behaviour include trichloromethane/propanone and nitric acid/water mixtures. Phase diagrams showing a minimum (figure) indicate that the mixture is destabilized relative to the ideal solution, A-B interactions then being unfavourable. For such mixtures G^E is positive (less favourable to mixing than ideal), and there may be contributions from both enthalpy and entropy effects. Examples include dioxane/water and ethanol/water mixtures.



A high-boiling azeotrope. When the liquid of composition a is distilled, the composition of the remaining liquid changes towards b but no further.

The system shown in the figure below is also azeotropic, but shows its azeotropy in a different way. Suppose we start with a mixture of composition a_1 , and follow the changes in the composition of the vapour that raises through a fractionating column.

The mixture boils at a_2 to give a vapour of composition a'_2 . This vapour condenses in the column to a liquid of the same composition (a_3). That liquid reaches equilibrium with its vapour at a'_3 , which condenses higher up the tube to give a liquid of the same composition, which we now call a_4 . The fractionation therefore shifts the vapour towards the azeotropic composition at b , but not beyond, and the azeotropic vapour emerges from the top of the column. An example is ethanol/water, which boils unchanged when the water content is 4 per cent by mass and the temperature is 78°C .



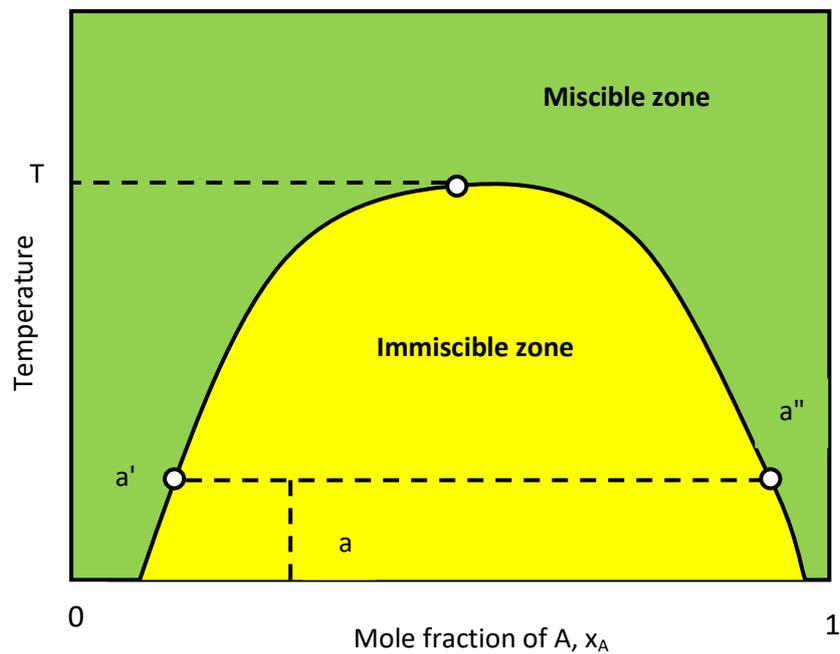
A low-boiling azeotrope. When the mixture at a is fractionally distilled, the vapour in equilibrium in the fractionating column moves towards b and then remains unchanged

B) Liquid-liquid phase diagrams

- a) Phase separation of partially miscible liquids may occur when the temperature is below the upper critical solution temperature or above the lower critical solution temperature.
- b) The upper critical solution temperature is the highest temperature at which phase separation occurs.
- c) The outcome of a distillation of a low-boiling azeotrope depends on whether the liquids become fully miscible before they boil or boiling occurs before mixing is complete.

Phase separation

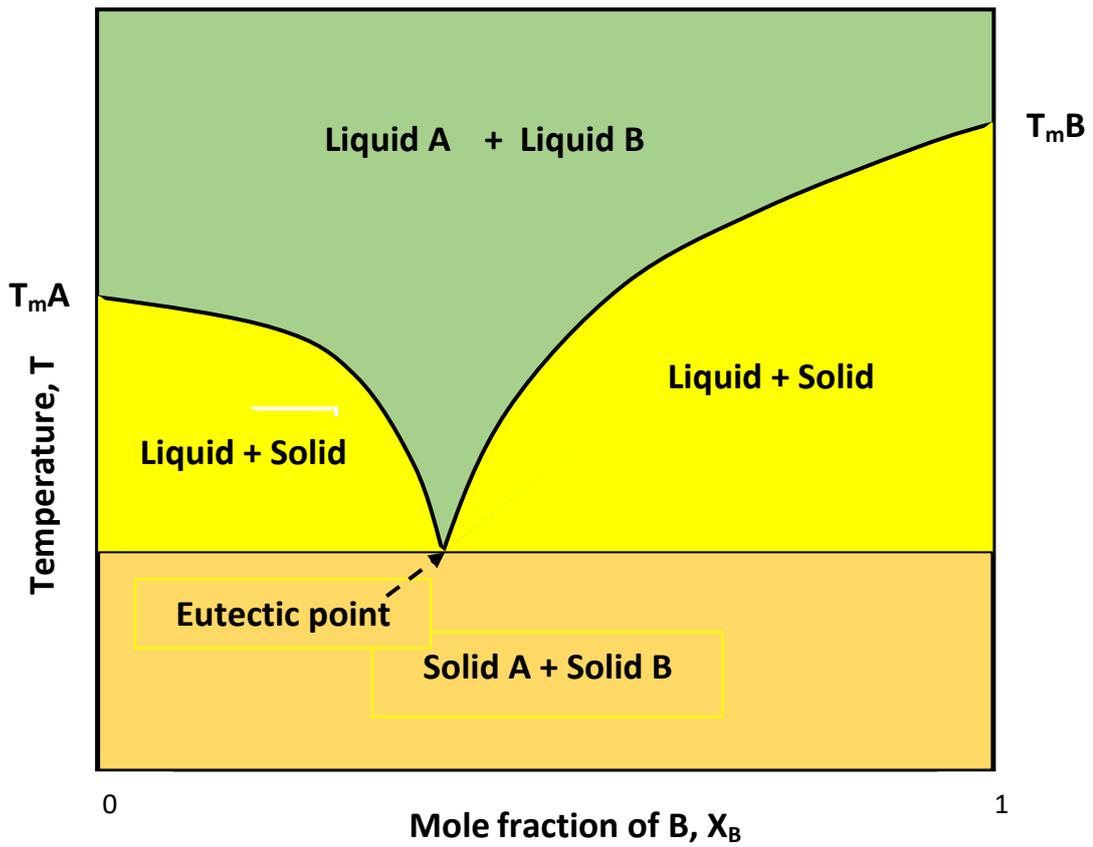
Suppose a small amount of a liquid B is added to a sample of another liquid A at a temperature T' . Liquid B dissolves completely, and the binary system remains a single phase. As more B is added, a stage comes at which no more dissolves. The sample now consists of two phases in equilibrium with each other, the most abundant one consisting of A saturated with B, the minor one a trace of B saturated with A. In the temperature-composition diagram drawn below, the composition of the former is represented by the point a' and that of the latter by the point a'' . The relative abundances of the two phases are given by the level rule.



C) Liquid-Solid phase diagrams

- A phase diagram summarizes the temperature-composition properties of a binary system with solid and liquid phases; at the eutectic composition the liquid phase solidifies without change of composition.
- The phase equilibria of binary systems in which the components react may also be summarized by a phase diagram.
- In some cases, a solid compound does not survive melting.

X_A	0	0.2	0.4	0.7	1.0
T_{fusion}	100	80	50	70	80

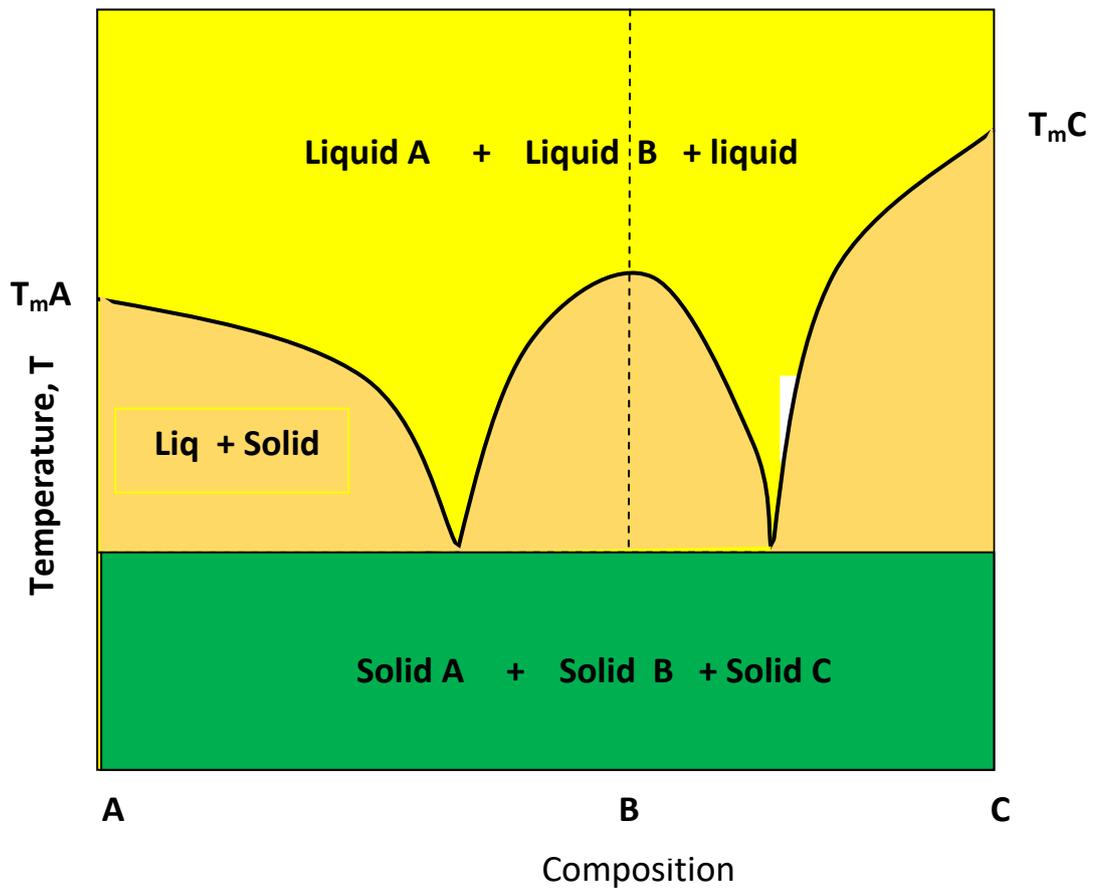


Eutectic (X, Temperature) point

Eutectics

At certain temperature called “eutectic temperature” the two components in certain composition called also “eutectic composition” in the mixture has the same melting temperature.

A ternary mixture A, B and C can also contain two eutectic points in which at certain composition the three component have the same melting temperature.



$$\ln x_A = \frac{\Delta H_{fusion}}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

Exercise 1

What is the boiling temperature of pure ethanol in the ethanol/water liquid-vapor system. What are the azeotropic temperature and composition of this system. What is the temperature proposed to separate this mixture when the composition is 0.5?

$$P_T = P_A + P_B = P_A^0 X_A + P_B^0 X_B$$

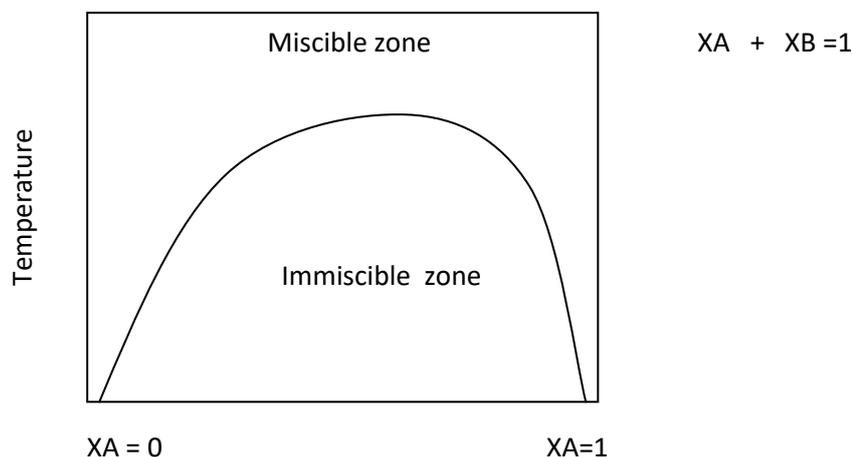
$P_{ethanol}^0$?

Azeotropic composition?

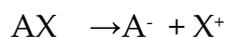
Pressure to separate the mixture ?

Liquid-liquid diagram

Exercise. Put the different zones in the liquid-liquid diagram. What is the necessary temperature used to separate this mixture at 0.5 composition?



4. The ionic solutions (electrolytes)



$\text{Li}^+ \text{Na}^+ \text{K}^+ \dots$ Column I (alkaline)

$\text{Ca}^{2+}, \text{Mn}^{2+}, \dots$ Column II (earth alkaline)

$\text{F}^-, \text{Cl}^-, \text{Br}^-, \dots$ Column VII (halogens)

Electrolyte $\text{CaCl}_2 \rightarrow \text{Ca}^{2+} + 2\text{Cl}^-$

SO_4^{2-} anion sulfate; CO_3^{2-} carbonate

$\text{Na}_2\text{SO}_4 \rightarrow 2\text{Na}^+ + \text{SO}_4^{2-}$

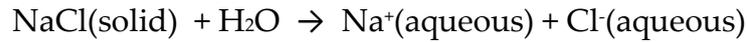
$\text{NH}_4^+ \text{Cl}^-$

$\text{NH}_4\text{Cl}(\text{s}) + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{Cl}(\text{aqueous}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{Cl}^-(\text{aq})$

The ionic or electrolyte solutions when they are in polar solvents like water or sometimes alcohols dissociate giving ions (cations and anions).

A strong electrolyte will dissociate completely as sodium chloride (NaCl).

H₂O : amphotere (acid, base)



A weak electrolyte will only dissociate partially as acetic acid (CH₃COOH).



The presence of the charged ions causes the electrolyte solution to deviate much more from ideal solution behavior than a non-electrolyte solution does.

This is the case even at very low electrolyte concentrations. The reason is that the ions interact with electrostatic forces which are of much longer range than those involved in the interaction of neutral molecules. This effect is stronger the greater the charge on the ions.

For a proper description of electrolyte solutions not only the short range energetic interactions but also the long range electrostatic interactions have to be considered. Another basic difference between electrolyte and non-electrolyte solutions is the constraint of electro-neutrality on electrolyte solutions. Because of this constraint, a system consisting of water and two ions is a binary system: The concentrations of the two ions cannot be chosen independently so the system has two independent components.

Consider a salt, S, which dissociates in water giving cations, ν_C , and anions, ν_A , with ionic charges Z_C and Z_A , respectively.

$$S = \nu_C C^{Z_C} + \nu_A A^{Z_A} \quad (1)$$

Table 1. Salt dissociation

S	C	Z_C	ν_C	A	Z_A	ν_A
NaCl	Na ⁺	1	1	Cl ⁻	-1	1
Na ₂ SO ₄	Na ⁺	1	2	SO ₄ ²⁻	-2	1
CaCl ₂	Ca ²⁺	2	1	Cl ⁻	-1	2

The eletro-neutrality requirement gives for salt S:

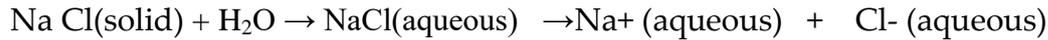
$$0 = \nu_C Z_C + \nu_A Z_A \quad (2)$$

In general the electro-neutrality of a multi components solution containing n_i moles of ion i with the charge Z_i relative to a hydrogen ion can be expressed as:

$$\sum_i n_i \times Z_i = 0 \quad (3)$$

Sodium chloride is often described as a 1-1 salt, sodium sulfate as a 1-2 salt, calcium chloride as a 2-1 salt, and calcium sulfate as a 2-2 salt, based on the values of the ionic charges.

Solubility:

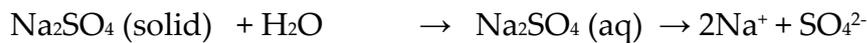


$$K_s = [\text{Na}^+][\text{Cl}^-] \quad K_s: \text{Solubility constant}$$

$[\text{Na}^+]$: solubility of $\text{Na}^+ = s$; $[\text{Cl}^-]$: solubility of $\text{Cl}^- = s$

Solubility : concentration of ion in water at saturation (equilibrium)

$$K_s = s^2 \quad s = \sqrt{K_s} \quad (\text{mol/L})$$



$$K_s = [\text{Na}^+]^2[\text{SO}_4^{2-}] = (2s)^2(s) = 4 \times s^3 \quad s = \sqrt[3]{\frac{K_s}{4}}$$

$$K_s = A \exp(-\Delta G/RT)$$

Concentration

For the description of electrolyte solutions the most common concentration unit is the molality. The molality unit is very often used in the presentation of experimental data, while the mole fraction unit most often is used in thermodynamic models for electrolytes. The molarity unit is also often used, but is dependent on temperature and to a certain extent also on pressure. It is not a practical unit because the density needs to be known in order to convert molarity units to molality units or mole fraction units.

The molality m_i of an ion i is the number of moles n_i , of the ion per kg water in the liquid phase:

$$m_i = \frac{n_i}{n_w \times M_w} \left(\frac{\text{mol}}{\text{kg.water}} \right) \quad (4) \quad n = m/M$$

The amount of water in the solution is here calculated as the product of n_w , the number of moles of water and M_w , the molar mass of water in kg/mol.

The molarity C_i of an ion i is the number of moles of the ion per liter solution:

$$C_i = \frac{n_i}{V_{solution}} \left(\frac{mol}{liter(solution)} \right) \quad (5)$$

If the volume of solute is negligible $C_i \approx \frac{n_i}{V_{solvent}} \left(\frac{mol}{liter(solvent)} \right)$

The volume of the solution, $V_{solution}$, is related to its mass and its density:

$$d_{solution} = \frac{n_w M_w + \sum n_i M_i}{V_{solution}} \quad (6)$$

If the density of the solution $d_{solution}$ is given in *kg/liter* and the molar masses of water and ions are given in *kg/mol*, the volume of the solution will be calculated in liter.

From equation (4), it can be seen that the molality concentration unit is only dependent on the amount of the relevant solute and the amount of solvent. The mole fraction unit and the molarity units on the other hand are also dependent on the amount of other solutes present. In addition, the molarity unit is also dependent on temperature and pressure because the density of the solution depends on temperature and pressure.

Example 1: A solution containing 6 mol of sodium chloride and one kg of water is a 6 molal solution of sodium chloride. The molality of the sodium ion in the solution is 6. The molar mass of water is 18.02 gram/mol, and the number of mol water in one kg water can therefore be calculated as 1000/18.02. The molality of the chloride ion in the solution is also 6. What is the mole fraction of the sodium ion?

Solution

$$x_{Na^+} = \frac{n_{Na^+}}{n_{Na^+} + n_{Cl^-} + n_{H_2O}} = \frac{6}{6 + 6 + \frac{1000}{18.02}} = 0.0889$$

The mole fraction of the chloride ion is also 0.0889. The mole fraction of water is:

$$x_w = \frac{1000/18.02}{6 + 6 + 1000/18.02} = 0.8222$$

Sometimes the composition of an electrolyte solution is given in terms of the amounts of water and salts instead of water and ions. If this approach is used, the composition of the same solution can be described by the mole fraction of sodium chloride:

$$x_{NaCl} = \frac{n_{NaCl}}{n_{NaCl} + n_{H_2O}} = \frac{6}{6 + 1000/18.02} = 0.0975$$

The mole fraction of water is $1 - 0.0975 = 0.9025$ when this approach is used. The density of this solution is 1.1942 kg/liter at 25 °C and 1 bar.

The volume of the solution can be calculated from equation (6):

$$V_{\text{Solution}} = \frac{n_w M_w + n_{\text{Na}^+} + n_{\text{Cl}^-} M_{\text{Cl}^-}}{1.1942} = \frac{1.000 + 6.0 \times 0.02299 + 6.0 \times 0.035453}{1.1942} = 1.1310 \text{ Liter}$$

The molarity of the sodium ion, the chloride ion and of sodium chloride in the solution is:

$$C_{\text{Na}^+} = C_{\text{Cl}^-} = C_{\text{NaCl}} = \frac{6}{1.1310} = 5.305 \text{ mol/Liter}$$

At 100 °C and 1 bar, the density of the same sodium chloride solution is 1.1490 kg/liter. The volume of the solution is 1.1755 liter and the molarity of solution chloride is 5.104 mol/Liter.

For a salt S the molarity is:

$$m_S = \frac{n_S}{n^S M_w} \quad (7)$$

If the salt dissociates into ν_C cations and ν_A anions the molality of the cation C is:

$$m_C = \frac{\gamma_C n_S}{n_w M_w} = \gamma_C m_S \quad (8)$$

The molality of the anion A is:

$$m_A = \frac{\gamma_A n_S}{n_w M_w} = \gamma_A m_S \quad (9)$$

The molality of the salt can therefore be expressed either in terms of the cation molality or in terms of the anion molality:

$$m_S = \frac{m_C}{\gamma_C} \quad \text{or} \quad m_S = \frac{m_A}{\gamma_A} \quad (10)$$

Most thermodynamic models use the traditional mole fraction scale:

$$x_i = \frac{n_i}{\sum n_j} \quad (11)$$

The summation in the denominator is over all solute and solvent species. A relation between the molality unit and the mole fraction unit can be derived as follows:

$$x_i = \frac{n_i}{\sum n_j} = \frac{n_i}{\sum n_j} \times \frac{m_w M_w}{n_w M_w} = m_i \times x_w \times M_w \quad (12)$$

M_w is the molar mass of water given in kg/mol.

The molarity unit is related to the mole fraction unit by:

$$x_i = \frac{n_i}{\sum n_j} = \frac{n_i}{\sum n_j} \times \frac{V_{\text{Solution}}}{V_{\text{Solution}}} = \frac{c_i V_{\text{Solution}}}{\sum n_j} \quad (13)$$

A large number of different concentration units are used to present experimental data for electrolytes. These include:

1. Mass percent
2. Molality
3. Mole fraction (water, ions, and non electrolytes)
4. Mass of salt per mass of H₂O
5. Mass of salt per volume solution
6. Mole salt per volume of solution
7. Mole salt per mass of solution
8. Jänecke coordinates (Charge fraction + gram H₂O per mole salts)
9. Mass percent solvent (salt free) + molality of salt
10. Mass percent solvent(salt free) + mass of salt per mass of mixed solvent
11. Mole percent solvent(salt free) + molality salt

One reason why molality is a popular unit for salt solutions is that the concentrations in molality units practical numbers, often between 0 and 20 for most salts, for most salts, while the concentrations in mole fraction units are very small as indicated in figure 2.1: The figures show the phase diagram of the ternary system NaCl-KCl-H₂O using these two different concentration units. The lines in the phase diagrams mark concentrations saturated with either NaCl or KCl. At 25°C, the solubility of NaCl is 6.15 mol/kg water, 0.0997 salt mole fraction, or 26.4 mass percent. The corresponding numbers for KCl are 4.79 mol/kg water, 0.0795 salt mole fraction, or 20.7 mass percent.

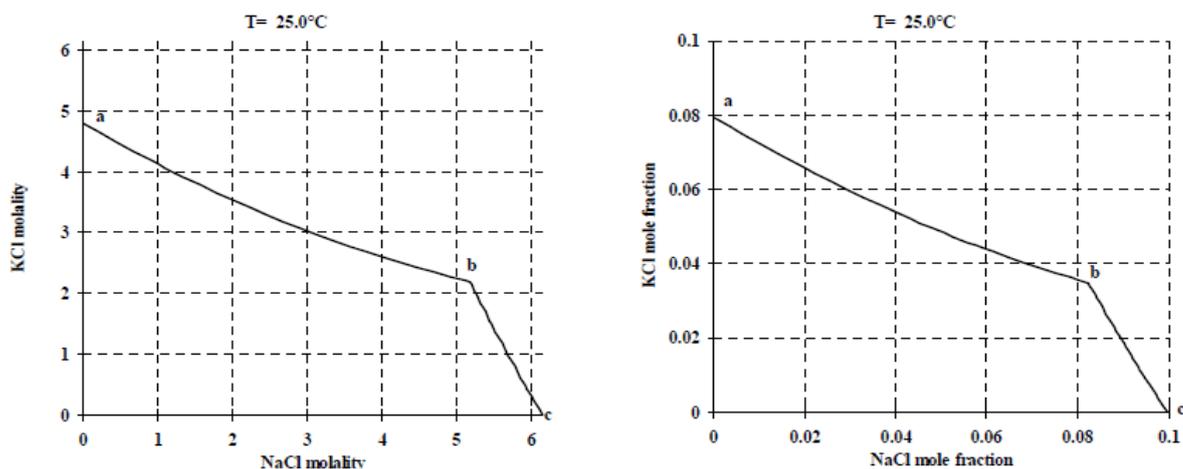


Figure 2.1: Phase diagram for the NaCl-KCl-H₂O system using molality as concentration unit (left) and salt mole fraction (right). The phase diagram consists of two curves. On the curve a - b solid potassium chloride is in equilibrium with saturated solutions. On b - c solid sodium chloride is in equilibrium with saturated solutions. In the point b both solid salts are in equilibrium with a saturated solution.

4.1 Ideal ionic solutions

4.1.1 Definition

An ideal solution can be defined as a solution in which the molar Gibbs energy of species i is calculated as:

$$G_i^{id} = G_i^o + RT \ln x_i \quad (14)$$

R is the gas constant, T is the absolute temperature in Kelvin, and x_i is the mole fraction of component i . Based on the definition of the ideal solution, the properties of real solutions can be calculated by the sum of two terms: an ideal term and an excess term. Equation (14) defines the ideal term of the Gibbs energy and is therefore given the superscript id . G_i^o is the molar standard state Gibbs energy and is a function of temperature and pressure.

If there is only one component, the mole fraction x_i of component i is equal to one. The term $RT \ln x_i$ then becomes zero, and the Gibbs energy of i is equal to the standard state Gibbs energy of i at the temperature and pressure. Therefore this standard state is often called the “*pure component standard state*”.

An alternative definition of the ideal solution is based on the molality scale:

$$G_i^{id,m} = G_i^m + RT \ln(m_i) \quad (14)$$

The ideal solution Gibbs energy calculated from equation (13) is different from the one calculated from equation (14). The latter is therefore marked with superscript m . G_i^m is the value of the molar standard state Gibbs energy on the molality scale and is a function of temperature and pressure.

The entropy of component i is related to the Gibbs energy through the fundamental thermodynamic relation:

$$S_i = \left(\frac{\partial G_i}{\partial T} \right)_{P,x} \quad (15) \quad dG = dH - d(TS) = dH - SdT \quad (\text{if } S \text{ constant})$$

$$dG = -SdT \quad S = -dG/dT$$

The entropy of component i in an ideal solution can be calculated from equation (13) using the relation in (14):

$$S_i^{id} = - \left[\frac{\partial G_i^{id}}{\partial T} \right] = - \left[\frac{\partial G_i^o}{\partial T} \right] = -R \ln x_i = S_i^o - R \ln x_i \quad (16)$$

S_i^o is the molar standard state entropy of component i and is a function of temperature and pressure.

Through the fundamental thermodynamic relation $G_i = H_i - TS_i$, the enthalpy of component i in an ideal solution can be calculated from equations (13) and (15):

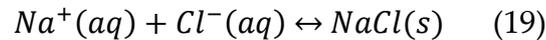
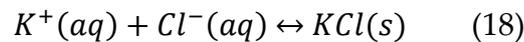
$$H_i^{id} = G_i + TS_i = G_i^o + RT \ln x_i + TS_i^o - R \ln x_i \quad (17)$$

$$= G_i^o + TS_i^o = H_i^o$$

H_i^o , pressure. The Gibbs energy and the entropy of a component in an ideal solution both depend on the composition of the solution according to equation (13) and (15). According to equation (17), the enthalpy of a component in an ideal solution is not dependent on the composition.

Example 2

We will calculate the phase diagram assuming ideal solution behavior. The phase diagram consists of two equilibrium curves. On one curve solid potassium chloride is in equilibrium with a saturated solution. On the other curve solid sodium chloride is in equilibrium with a saturated solution. The two equilibria can be expressed as:



The brackets (s) indicate solid, crystalline phase, the brackets (aq) indicate solutes in aqueous solution. Equilibrium is attained when there is no Gibbs energy change for a pair of ions that choose to go from the crystalline phase to the aqueous phase or vice versa. The equilibria we consider in this example are heterogeneous, involving two solid phases and a liquid phase. The solid phases are pure, homogeneous phases, not mixtures. Even in point b in Figure 2.1 where two solid salts are in equilibrium with the same liquid, the two solid salts will form crystals of pure NaCl and of pure KCl. In other systems, for example mixtures of ammonium and potassium salts, there is a tendency to form mixed crystals, solid solutions, due to the similarity of the two cations. The Gibbs energy of the pure solid salts can be found in thermodynamic tables. Also the Gibbs energy of the aqueous ions can be found in such tables. Table 5.2 contains the values necessary to calculate the phase diagram in Figure 2.1.

The Gibbs energy of each component in the molality based ideal solution can be expressed using equation (14):

$$G_{K^+(aq)}^{id,m} = \Delta_f G_{K^+(aq)}^m + RT \ln m_{K^+} \quad (20)$$

$$G_{Cl^-(aq)}^{id,m} = \Delta_f G_{Cl^-(aq)}^m + RT \ln m_{Cl^-} \quad (21)$$

$$G_{KCl(s)} = \Delta_f G_{KCl(s)} \quad (22)$$

$$G_{NaCl(s)} = \Delta_f G_{NaCl(s)} \quad (23)$$

Table 5.2: Standard state properties of ions and salts at 25°C. The values for ions are based on the molality concentration scale.

Compound	$\Delta_f G$ kJ/mol	$\Delta_f H$ kJ/mol	C_p kJ/mol/K
KCl(s)	-409.140	-436.744	0.0513
NaCl(s)	-384.138	-411.153	0.05050
K ₂ SO ₄ (s)	-1321.37	-1437.79	0.13146
AgCl(s)	-109.789	-127.068	0.05079
H ⁺ (aq)	0	0	0
K ⁺ (aq)	-283.270	-252.380	0.0218
Na ⁺ (aq)	-261.905	-240.120	0.0464
Cl ⁻ (aq)	-131.228	-167.159	-0.1364
SO ₄ ²⁻ (aq)	-744.530	-909.270	-0.293

All the Gibbs energies used are Gibbs energies of *formation* as indicated by the subscript *f*. The Gibbs energies of formation refer to the same standard state: The natural state of the elements at 25°C and 1 bar. The values therefore allow us to calculate the Gibbs energy change by reactions among these compounds.

The condition for equilibrium of potassium and chloride ions with solid potassium chloride is that the Gibbs energy is identical in the two phases, which can be expressed as:

$$G_{K^+(aq)}^{id,m} + G_{Cl^-(aq)}^{id,m} = G_{KCl(s)} \quad (24)$$

or

$$\Delta_f G_{K^+(aq)}^m + RT \ln m_{K^+} + \Delta_f G_{Cl^-(aq)}^m + RT \ln m_{Cl^-} = \Delta G_{KCl(s)} \quad (25)$$

A corresponding expression for sodium chloride could also be written. By inserting numbers from Table 5.2, the following expression is obtained for potassium chloride:

$$-283270 + RT \ln m_{K^+} - 131228 + RT \ln m_{Cl^-} = -409140 \quad (26)$$

The equation can be modified to

$$m_{K^+} m_{Cl^-} = \exp\left(\frac{5358}{RT}\right) = \exp\left(\frac{5358}{8.314 \times 298.15}\right) = 8.6843 \quad (27)$$

By a similar method the corresponding equation for the equilibrium of sodium chloride can be derived as:

$$m_{Na^+}m_{Cl^-} = \exp\left(\frac{8995}{RT}\right) = 37.6655 \quad (28)$$

The curve for KCl solubility can now be calculated at fixed concentrations of NaCl by using equation (27). Because the NaCl concentration is fixed, the molality of Cl⁻ can be calculated as the molality of NaCl plus the molality of K⁺. The molality of K⁺ therefore is the only unknown. The curve for NaCl solubility can be calculated at fixed concentrations of KCl by using equation (28) in a similar manner. The point b from Figure 2.1 can be calculated by solving equations (27) and (28) simultaneously.

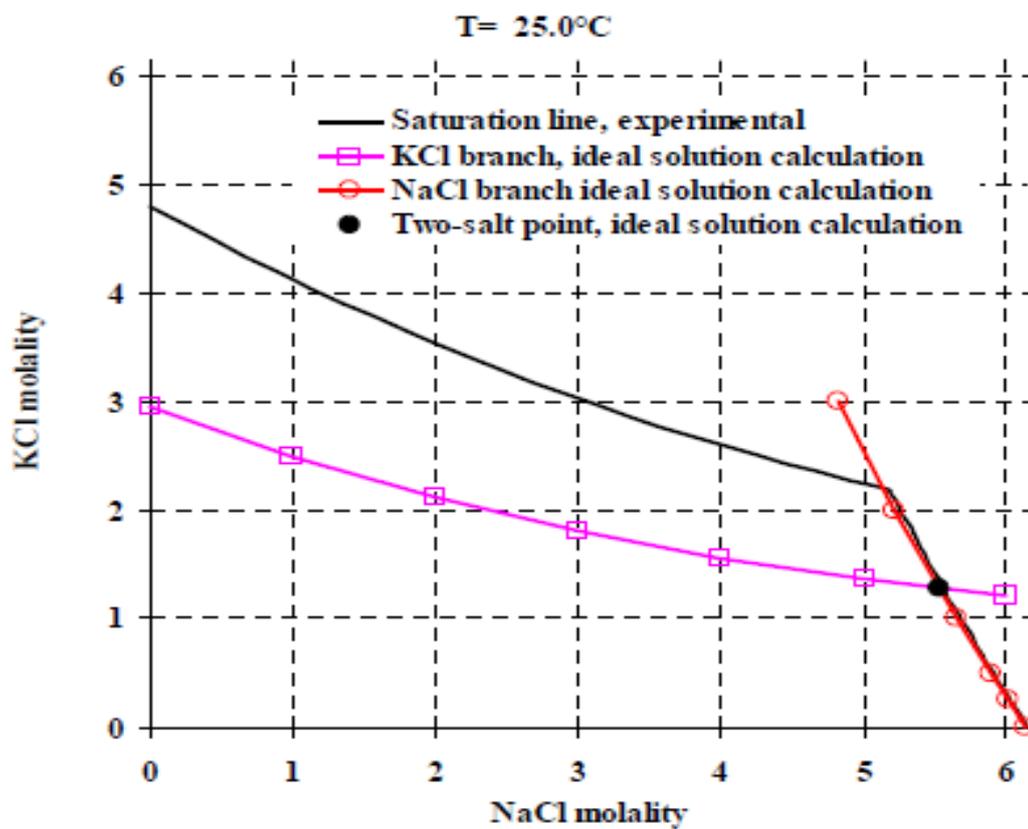


Figure 3.1: Phase diagram for the KCl-NaCl-H₂O system calculated assuming ideal solution behavior.

The result of the calculation is shown in Figure 3.1. The calculated solubility of sodium chloride is very close to the actual solubility of sodium chloride. For potassium chloride on the other hand, the calculated solubility is much lower than the actual solubility of potassium chloride. This indicates that one of these apparently similar salts has ideal solution behavior while the other deviates strongly from ideal behavior. This is a coincidence caused by the fact that the mean molal activity coefficient of sodium chloride has values near 1 at concentrations near saturation of NaCl at room temperature.

Obviously, the ideal solution assumption gives results that deviate significantly from the experimental value of the solubility in this system. In order to make this kind of calculations correct, it is very important to use a thermodynamic model that takes the deviation from ideality into account.

Exercise 3.1

In Example 3.1, the solid-liquid phase diagram of the ternary system KCl – NaCl – H₂O system at 25°C was calculated, assuming ideal solution behavior and using molality as concentration scale. Derive the corresponding equations necessary for calculating the same phase diagram using mole fraction as the concentration scale, and calculate the phase diagram.

The Gibbs energies of formation for the ions based on the mole fraction scale are given in Table 3.2.

Table 3.2: Standard state Gibbs energy of formation of ions at 25°C. The values are based on the mole fraction concentration scale

	Na ⁺	K ⁺	Cl ⁻
$\Delta_f G$ kJ/mol	-251.949	-273.314	-121.272

4.1.2 Colligative properties

Colligative properties are properties that according to physical chemistry textbooks are independent of the type of species in the solution but are dependent on the amount of species. As it will be shown here, these colligative properties are not independent of the type of species. On the contrary, they are strongly depending on the type of species. The colligative properties are freezing point depression and boiling point elevation. Vapor pressure lowering and osmotic pressure are usually mentioned separately as colligative properties but these two latter properties are so closely related to the boiling point elevation that they don't need to be discussed separately.

In a freezing point depression experiment, the temperature at which solid solvent (ice) is in equilibrium with a solution is determined. This temperature is lower than the freezing point of pure water. In a boiling point elevation experiment, the temperature at which solvent vapor (steam) is in equilibrium with the solution is determined. At atmospheric pressure, this boiling point is higher than the normal boiling point of pure water.

These phenomena can be understood by considering equations (13), and (14). According to these equations, the Gibbs energy of an ideal solution depends on

the composition of the solution in addition to temperature and pressure. Ice and steam are two pure phases. The Gibbs energies of pure phases depend only on temperature and pressure. At equilibrium between solution and ice or solution and steam, the Gibbs energy of water in solution is identical to the Gibbs energy of ice or that of steam respectively. By varying the composition, it will therefore be possible to find a range of temperatures and pressures at which there is equilibrium between an ideal solution and the pure phases, ice and steam respectively.

The equilibria between solutions and pure phases can be expressed:

- For freezing point depression as:

$$\Delta_f G_w^o(T, P) + RT \ln x_w = \Delta_f G_{ice}^o(T, P) \quad (29)$$

- For boiling point elevation as

$$\Delta_f G_w^o(T, P) + RT \ln x_w = \Delta_f G_{stream}^o(T, P) \quad (30)$$

The left hand sides of the equations (29, 30) express the Gibbs energies of ideal solutions as functions of composition, temperature and pressure. The right hand sides of the expressions give the Gibbs energies of the pure phases as functions of temperature and pressure. By varying the water mole fractions it is possible to determine a range of temperatures and pressures at which these equilibria can be established.

The expression for the equilibrium between aqueous solution and ice, equation (29) is plotted in figure 3.2 together with experimentally measured freezing point depressions. The pressure was held constant at 1 bar. The freezing point temperatures were calculated at a number of water mole fractions, using equation (29). The water mole fractions were converted to mol solute per kg water. The experimental data marked in Figure 3.2 show a significant difference between real electrolyte solutions and ideal solution behavior. The data also show a significant difference between the freezing point depressions caused by different electrolytes.

Apparently, sodium chloride solutions are closer to ideal solution behavior than magnesium chloride solutions are. A solution containing 5.08 moles NaCl per kg water freezes at -21.7°C. Assuming full dissociation such a solution contains 10.16 mol solutes (Na⁺ and Cl⁻ ions) per kg water. This solution is called a eutectic solution because it is the sodium chloride solution with the lowest possible freezing point. A eutectic solution of magnesium chloride contains 2.73 moles magnesium chloride and freezes at -33.6°C. If full dissociation is assumed, this solution contains 8.19 mol of solutes (Mg²⁺ and Cl⁻ ions). This eutectic

solution is therefore more dilute than the eutectic sodium chloride solution. It would be expected that the more concentrated solution would have a lower freezing point.

Magnesium sulfate solutions have higher freezing points than ideal solutions have. The same is the case for sodium sulfate solutions but the positive deviation for sodium sulfate solutions is lower than for magnesium sulfate solutions. The experimental data for sodium sulfate solutions are not shown in Figure 3.2. The eutectic solution of sodium sulfate only contains 0.84 mol solutes per kg water.

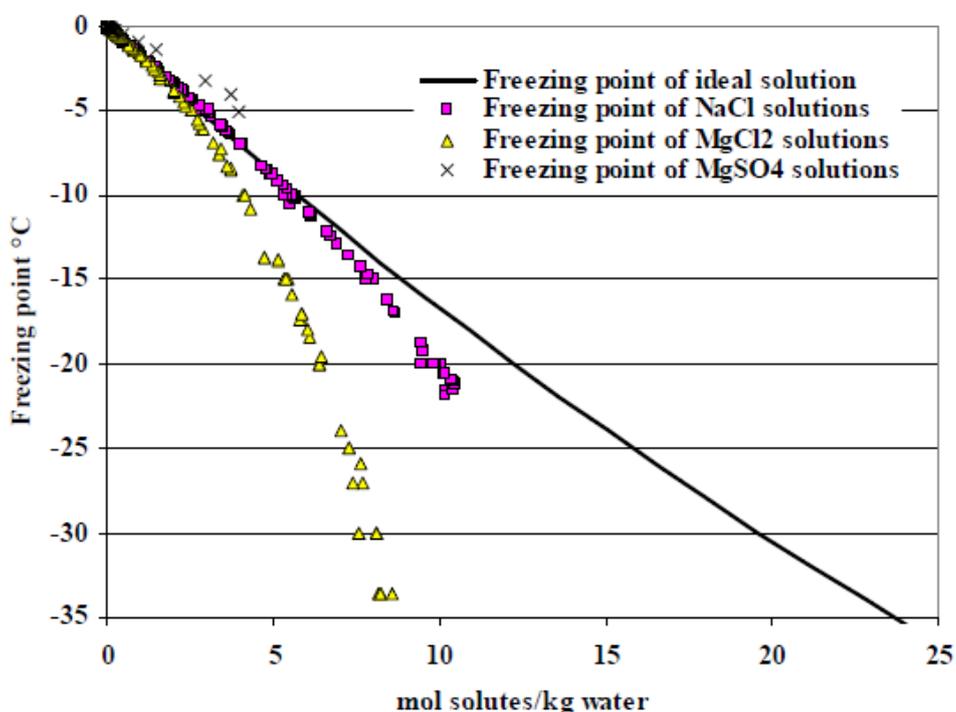


Figure 3.2: The theoretical freezing point depression of an ideal solution compared to measured freezing point depressions of sodium chloride, magnesium chloride, and magnesium sulfate solutions.

Exercise 3.2

Calculate the boiling point elevation of an ideal solution of solutes in water at 1 atm pressure. Find the appropriate Gibbs energies as a function of temperature and pressure on the internet or in steam tables. Alternatively, you can use the relation $G = H - TS$ to calculate Gibbs energies in the relevant temperature range, based on table values at 100°C and 1 atm. Compare the results with the experimental data from Hakuta given in Table 3.3. Plot the results in a graph similar to Figure 3.2.

Table 3.3: Experimental measurements of the boiling point of electrolyte solutions at 1 atm.

NaCl		Na ₂ SO ₄		MgCl ₂	
Boiling point	mass percent	Boiling point	Mass percent	Boiling point	Mass percent
100.151	0.956	100.082	1.004	100.125	0.976
100.308	1.944	100.163	2.019	100.264	2.007
100.471	2.916	100.239	2.999	100.411	3.032
100.648	3.948	100.319	4.006	100.568	4.025
100.821	4.898	100.396	5.038	100.734	5.032
100.996	5.851	100.478	6.096	100.927	6.055
101.198	6.938	100.555	7.103	101.065	6.749
101.453	8.158	100.637	8.101	101.327	7.972
101.675	9.158	100.714	9.056	101.535	8.868
101.9	10.245	100.802	10.162	101.805	9.89
102.17	11.246	100.886	11.188	102.119	10.994
102.41	12.264	100.971	12.179	102.405	11.905
102.694	13.346	101.053	13.134	102.74	12.872
102.955	14.35	101.138	14.178	103.131	13.915
103.249	15.362	101.228	15.174	103.594	15.116

4.2 Chemical potential and activity coefficients

4.2.1 Chemical potential

The chemical potential of a species i is the partial molar derivative of the total Gibbs energy G , enthalpy H , Helmholtz energy A , or internal energy U of substance i

$$\mu_i = \left[\frac{\partial G}{\partial n_i} \right]_{T,P,n_j} = \left[\frac{\partial H}{\partial n_i} \right]_{S,P,n_j} = \left[\frac{\partial A}{\partial n_i} \right]_{T,V,n_j} = \left[\frac{\partial U}{\partial n_i} \right]_{S,V,n_j} \quad (31)$$

In equation (31), n_i is the amount of component i , T is the temperature, P is the pressure, S is the entropy, and V is the volume.

Matter flows spontaneously from a region of high chemical potential to a region of low chemical potential just like electric current flows from a region of high electric potential to a region of low electric potential and mass flows from a position of high gravitational potential to a position of low gravitational potential. The chemical potential can therefore be used to determine whether or

not a system is in equilibrium. When the system is in equilibrium, the chemical potential of each substance will be the same in all phases of the system.

The chemical potential of a species in its standard state is identical to its molar standard state Gibbs energy. Equation (14) can therefore be rewritten:

$$\mu_i^{id} = \mu_i^o + A = \pi r^2 R T L n_i \quad (32)$$

4.2.2 Excess chemical potentials for real solutions

It was shown in chapter 3 that aqueous salt solutions deviate significantly from ideal solution behavior. In order to describe phase equilibria of electrolyte solutions it is therefore necessary to introduce a correction for the deviation from ideal solution behavior. The difference between the chemical potential of a real solution and that of an ideal solution is called the excess chemical potential. The excess chemical potential for component i is:

$$\mu_i^{ex} = R T L n \gamma_i \quad (33)$$

γ_i is the activity coefficient of component i . The activity coefficient is a function of composition, temperature and pressure. By including this excess term, the chemical potential of component i in a real solution is expressed as:

$$\mu_i = \mu_i^{id} + \mu_i^{ex} \quad (34)$$

$$\mu_i = \mu_i^o + R T L n x_i + R T L n \gamma_i \quad (35)$$

$$\mu_i = \mu_i^o + R T L n (x_i \gamma_i) \quad (36)$$

The chemical potential of water in an aqueous solution can be calculated from the definition in equation (31) and expressed through an equation of the form given in equations (34-36):

$$\mu_w = \left(\frac{\partial G}{\partial n_w} \right)_{P, T, n_i, x_w} = \mu_w^o + R T L n (x_w \gamma_w) \quad (37)$$

As shown in chapter 3, dilute solutions are exhibiting ideal solution behavior. In the limit of $x_w \rightarrow 1$ it follows that $\gamma_w = 1$ and the excess chemical potential vanishes. The excess term is only relevant for mixtures. The standard state chemical potential of water, μ_w^o is identical to the molar Gibbs energy of pure liquid water at temperature T and pressure P .

5. Thermodynamic models for electrolyte solutions

Thermodynamic models for electrolyte solutions are developed in order to be able to mathematically describe the properties and the phase behavior of solutions. For the chemical industry it is very valuable to be able to optimize processes for the production of chemicals. Electrolyte solutions are involved in

many processes and it is therefore important to have good models for the description of electrolyte properties.

In order to properly model electrolyte systems, all different types of interactions: ion-ion, ion-dipole, dipole-dipole, molecule-molecule should be taken into account. The potential energy caused by ion-ion interactions is proportional to the inverse separation distance; $1/r$. Electrostatic ion-ion interactions therefore have an effect over a relatively long distance and are called long range interactions. The potential energy caused by molecule-molecule interactions is proportional to the sixth power of the inverse separation distance, $1/r^6$. These interactions are therefore called short-range interactions. The potential energy of ion-dipole interactions is proportional to $1/r^2$ and the potential energy of dipole-dipole interactions is proportional to $1/r^3$. These interactions could be called intermediate range interactions.

Models are structured with terms representing only long range and intermediate/short range interactions.

5.1 Electrostatic interactions

5.1.1 Debye-Hückel theory

The first really successful model for the electrostatic interactions between ions in aqueous electrolyte systems was developed in 1923 by P. Debye and E. Hückel. This author described the thermodynamics of ideal solutions of charged ions. As mentioned above, the electrostatic interactions between charged ions only represent the long range interactions in such solutions and not the short range interactions. The interactions between ions and water are not described by the Debye-Hückel model, which has led people to describe this model as a “dielectric continuum model”. In this model, the solvent only plays a role due to its relative permittivity (dielectric constant) and its density. The Debye-Hückel model can therefore not stand alone as a model for electrolyte solutions. It only represents some of the electrostatic interactions and should be combined with a term for short and intermediate range interactions in order to fully describe the properties of concentrated electrolyte solutions.

In the Debye-Hückel theory, the electrostatic force that a positive ion exerts on a negative through the solvent medium is expressed through Coulombs law:

$$F = \frac{1}{4\pi\epsilon_0\epsilon_r} \times \frac{e^2}{r^2} \quad (38)$$

e is the electronic charge = 1.60206×10^{-19} C

ϵ_0 is the permittivity in vacuum = 8.8542×10^{-12} C² J⁻¹ m⁻¹

ϵ_r is the dielectric constant (relative permittivity) of the solvent (unitless). The value of the relative permittivity of water is 78.4 at 298.15K

r is the distance between the ions (meter).

Poisson's equation gives a relationship between the charge density ($\rho_i \text{ Cm}^{-3}$) around ion i and the electrical potential ($\psi_i \text{ J/C}$) for a sphere with radius r around ion i :

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) = \frac{\rho_i}{\epsilon_0 \epsilon_r} \quad (39)$$

Due to the charges, the ions are not distributed evenly or randomly in the solution. Near a cation, anions tend to be in excess, near an anion, cations tend to be in excess. An ion j has an electrical potential energy of $z_j e \psi$ if it is in the distance r from the ion i . Debye and Hückel assumed the distribution of the ions in the solution to be a Boltzmann distribution. This assumption gives another relation between the charge density and the electrical potential:

$$\rho_i = e N_A \sum_{\text{all ions}} \frac{n_j z_j}{nV} \exp\left(\frac{z_j e \psi_i}{kT}\right) \quad (40)$$

n_j is the mol number of component j , z_j is the charge of component j , N_A is Avogadro's number = $6.023 \times 10^{23} \text{ mol}^{-1}$, k is the Boltzmann's constant = $1.381 \times 10^{-23} \text{ JK}^{-1}$, and T is the temperature in Kelvin, V is the molar volume of the solution.

Debye and Hückel combined the Poisson equation and the Boltzmann equation thereby eliminating the charge density. The resulting Poisson-Boltzmann equation was solved for the electrical potential ψ_i . Debye and Hückel finally arrived at an excess Helmholtz function for an ideal solution of charged ions. It sounds like a contradiction to have an excess Helmholtz function for an ideal solution of charged ions. Ideal solutions do not have excess terms. But as mentioned before, this excess Helmholtz function only takes the non-ideality caused by the electrostatic interactions into account and does not deal with the traditional non-ideality, caused by short range forces. The molar excess Helmholtz function for the electrostatic interactions can be expressed by the equation:

$$\frac{A^E}{RT} = -\frac{1}{3} \sum x_i z_i^2 s k \chi(k a_i) \quad (41)$$

The term s is defined by:

$$s = \frac{e^2}{4\pi\epsilon_0\epsilon_r kT} \quad (42)$$

The distance of closest approach to the ion i was given the symbol a_i , (a for "annäherungsabstand"). The distance of closest approach is a parameter for the radius of ion i , not its diameter. It is expected that a_i is larger than the radius of the ion, because the ions are thought to be surrounded by water that gives the ions a larger radius than the bare ion. The product " κa_i " is dimensionless and κ

is therefore a reciprocal length. $1/\kappa$ is a characteristic length called the screening length. The screening length provides a good first estimate of the distance beyond which Coulomb interactions can be essentially ignored, as well as the size of the region near a point charge where opposite-charge counter-ions can be found. The expression for κ is:

$$\kappa = \left(\frac{e^2 N_A}{\epsilon_0 \epsilon_r k T} \times \frac{\sum n_i z_i^2}{n V} \right)^{1/2} \quad (43)$$

The function χ is given by:

$$\chi(x) = \frac{3}{x^3} \left(\frac{3}{2} + \ln(1-x) - 2(1+x) + \frac{1}{2}(1+x)^2 \right) \quad (44)$$

Apparently, the Helmholtz function of Debye and Hückel (41) has not been used by those who have developed models for electrolyte solutions. Actually this equation is usually not even mentioned. Instead, a number of simplifications of the Debye-Hückel equation have been used for model development and are often mentioned in text books.