Part 1: Equilibrium

7. Simple mixtures

Bilingual Program

7. Simple mixtures

The chapter begins by developing the concept of chemical potential to show that it is a particular of a class of partial molar quantities. Then it explores how the chemical potential of a substance is used to describe the physical properties of mixture. The underlying principle is that at equilibrium the chemical potential of a species is the same in every phase.

7. Simple mixtures

The thermodynamic description of mixtures

7.1 Partial molar quantities ▶

7.2 The thermodynamics of mixing

7.3 The chemical potentials of liquid

The properties of solutions

7.4 Liquid mixtures

7.5 Colligative properties

Activities

7.6 The solvent activity

7.7 The solute activity

7.1 Partial molar quantities

1) Partial molar volume

When the composition of the mixture is changed by the addition of dn_A of A and dn_B of B, the total volume of the mixture changes by

$$\mathrm{d}V = \left(\frac{\partial V}{\partial n_A}\right)_{p,T,n_B} \mathrm{d}n_A + \left(\frac{\partial V}{\partial n_B}\right)_{p,T,n_A} \mathrm{d}n_B$$

$$\mathrm{d}V = V_A \mathrm{d}n_A + V_B \mathrm{d}n_B$$

V_A and V_B are the partial molar volumes, they vary with composition.

7.1 Partial molar quantities

Once the partial molar volumes of the two components of a mixture at the composition (and *T*) of interest are known, we can state the total volume, *V*, of the mixture by using

$$V = n_{\mathrm{A}}V_{\mathrm{A}} + n_{\mathrm{B}}V_{\mathrm{B}}$$

7.1 Partial molar quantities

- The determination of partial molar volume

With particular values of the parameters *A*, *B*, and *C*, then the partial molar volume of A at any composition could be obtained from

$$V_{\mathrm{J}} = \left(\frac{\partial V}{\partial n_{\mathrm{J}}}\right)_{p,T,n'}$$

$$V_{\mathrm{A}} = \left(\frac{\partial V}{\partial n_{\mathrm{A}}}\right)_{p,T,n_B} = B + 2Cn_{\mathrm{A}}$$

7.1 Partial molar quantities

The determination of partial molar volume

The partial molar volume of the second component is obtained from

$$V = n_A V_A + n_B V_B$$

$$V_B = \frac{V - n_A V_A}{n_B} = \frac{A - (n_A^2 + 1)C}{n_B}$$

7.1 Partial molar quantities

The determination of partial molar volume

The molar volume: the volume that 1 mol substance occupies, which is always positive.

The partial molar volume: the contribution of 1 mol of a component to the volume of the mixture at a specific *T* and *p*, which may be positive or negative.

7.1 Partial molar quantities

Partial molar quantities

The concept of a partial molar quantity can be extended to any extensive state function. Let *X* denote any extensive properties of a system that contains *K* components

$$X = X(T, p, n_1, n_2 \cdots n_K)$$

The change in *X* When d*T*, d*p*, dn_i

$$\mathrm{d}X = \left(\frac{\partial X}{\partial T}\right)_{p,n_\mathrm{j}} \mathrm{d}T + \left(\frac{\partial X}{\partial p}\right)_{T,n_\mathrm{j}} \mathrm{d}p + \sum_{i=1}^{K}\left(\frac{\partial X}{\partial n_\mathrm{i}}\right)_{T,p,n_{j\neq i}} \mathrm{d}n_\mathrm{i}$$

7.1 Partial molar quantities

Partial molar quantities

Definition $$X_i \overset{\text{def}}{=} \left(\frac{\partial X}{\partial n_i}\right)_{T,p,n_{j\neq i}}$$

X **and** n_i **are extensive properties, and they are independent of the total quantities in systems;**

however, the partial molar quantities, X_i **, is intensive property.**

$$X = n_1 X_1 + n_2 X_2 \cdots + n_\mathrm{K} X_\mathrm{K} = \sum_{i=1}^{\mathrm{K}} n_i X_i$$

7.1 Partial molar quantities

2) Partial molar Gibbs energies

For a pure substance

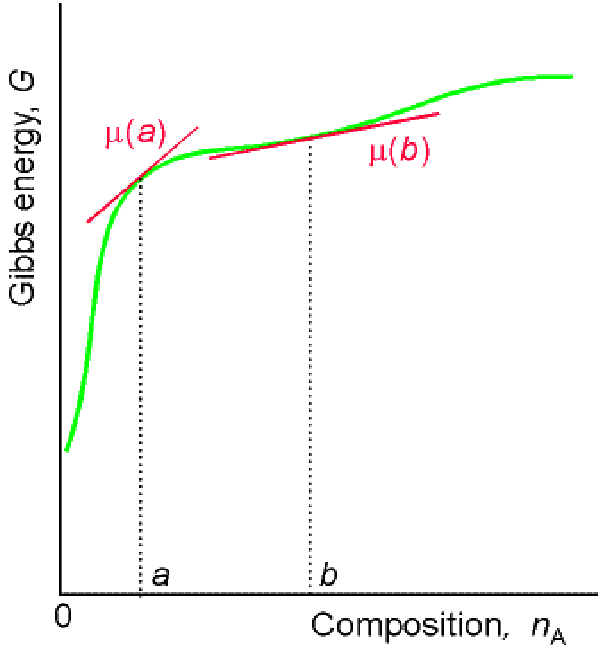
$$\mu = G_{\mathrm{m}} = \left(\frac{\partial G}{\partial n}\right)_{p,T}$$

For a substance in a mixture

$$\mu_{\mathrm{J}} = \left(\frac{\partial G}{\partial n_{\mathrm{J}}}\right)_{p,T,n'}$$

7.1 Partial molar quantities

2) Partial molar Gibbs energies



$$\mu_J = \left(\frac{\partial G}{\partial n_J}\right)_{p,T,n'}$$

The chemical potential of a substance is the slope of the total Gibbs energy of a mixture with respect to the amount of substance of interest. In general, the chemical potential varies with composition.

The total Gibbs energy of binary mixture is

$$G = n_A\mu_A + n_B\mu_B$$

7.1 Partial molar quantities

2) Partial molar Gibbs energies

In an open system of constant composition, the Gibbs energy depends on the n_i, p, and T. Thus, G may change when p, T, and the n_i. And $dG=Vdp-SdT$ becomes:

$$\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T + \mu_A \mathrm{d}n_A + \mu_B \mathrm{d}n_B + \cdots$$

At constant p and T:

$$\mathrm{d}G = \mu_A \mathrm{d}n_A + \mu_B \mathrm{d}n_B + \cdots$$

7.1 Partial molar quantities

2) Partial molar Gibbs energies

$$\mathrm{d}w_{\mathrm{e,max}} = \mathrm{d}G = \mu_{\mathrm{A}}\mathrm{d}n_{\mathrm{A}} + \mu_{\mathrm{B}}\mathrm{d}n_{\mathrm{B}} + \cdots$$

Non-expansion work can arise from the changing composition of a system.

7.1 Partial molar quantities

3) The wider significance of the chemical potential

Since $G=U+pV-TS$,

$$\mathrm{d}U=-p\mathrm{d}V-V\mathrm{d}p+S\mathrm{d}T+T\mathrm{d}S+\mathrm{d}G$$

$$=-p\mathrm{d}V-V\mathrm{d}p+S\mathrm{d}T+T\mathrm{d}S+(V\mathrm{d}p-S\mathrm{d}T+\mu_\mathrm{A}\mathrm{d}n_\mathrm{A}+\mu_\mathrm{B}\mathrm{d}n_\mathrm{B}+\cdots)$$

The generalization equation (that d$U = T$dS –pdV) to systems in which the composition may change:

$$\underline{\mathrm{d}U=-p\mathrm{d}V+T\mathrm{d}S+\mu_\mathrm{A}\mathrm{d}n_\mathrm{A}+\mu_\mathrm{B}\mathrm{d}n_\mathrm{B}+\cdots}$$

7.1 Partial molar quantities

3) The wider significance of the chemical potential

$$\mathrm{d}U = -p\mathrm{d}V + T\mathrm{d}S + \mu_\mathrm{A}\mathrm{d}n_\mathrm{A} + \mu_\mathrm{B}\mathrm{d}n_\mathrm{B} + \cdots$$

It follows that, at constant volume and entropy:

$$\mathrm{d}U = \mu_\mathrm{A}\mathrm{d}n_\mathrm{A} + \mu_\mathrm{B}\mathrm{d}n_\mathrm{B} + \cdots$$

$$\mu_\mathrm{J} = \left(\frac{\partial U}{\partial n_\mathrm{J}}\right)_{S,V,n'}$$

7.1 Partial molar quantities

3) The wider significance of the chemical potential

The relations of μ_J with *G, U, H, A* are as followings:

$$\mu_J = \left(\frac{\partial G}{\partial n_J}\right)_{p,T,n'} \qquad \mu_J = \left(\frac{\partial U}{\partial n_J}\right)_{S,V,n'}$$

$$\mu_J = \left(\frac{\partial H}{\partial n_J}\right)_{S,p,n'} \qquad \mu_J = \left(\frac{\partial A}{\partial n_J}\right)_{T,V,n'}$$

When the composition changes, not only does μ_J show how *G* changes, it also shows how *U*, *H*, and *A* change too (but under a different set of conditions).

7.1 Partial molar quantities

4) The Gibbs-Duhem equation

The total Gibbs energy of a mixture depends on μ_J and n, for a binary mixture:

$$G = n_A\mu_A + n_B\mu_B$$

$$dG = \mu_A dn_A + \mu_B dn_B + n_A d\mu_A + n_B d\mu_B$$

At constant p and T:

$$dG = \mu_A dn_A + \mu_B dn_B + \cdots$$ **It implies that**

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

This equation is a case of the Gibbs-Duhem equation.

7.1 Partial molar quantities

4) The Gibbs-Duhem equation

$$\sum_J n_\mathrm{J} \mathrm{d}\mu_J = 0$$

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.

In general $$\sum_J n_\mathrm{J} \mathrm{d}X_J = 0$$

7.1 Partial molar quantities

4) The Gibbs-Duhem equation

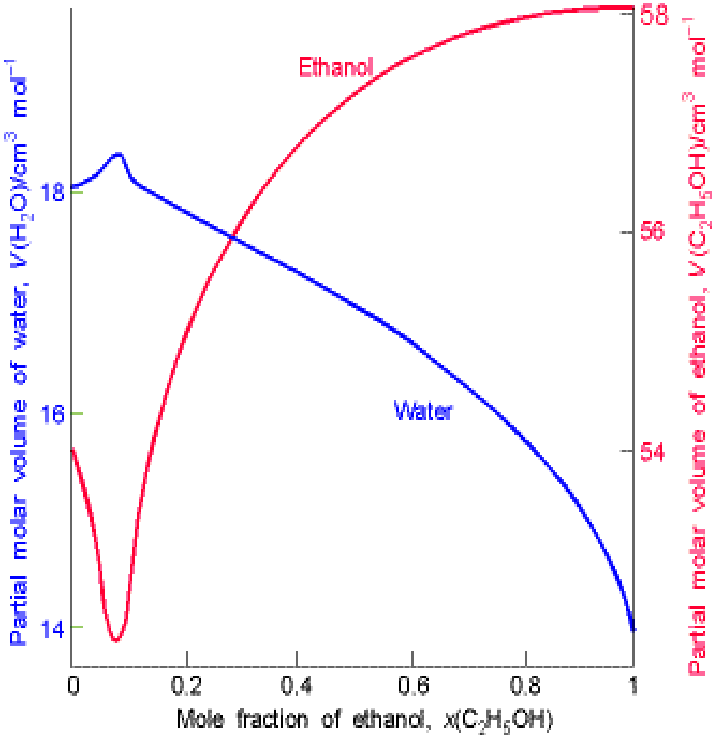
In a binary mixture, if one partial molar quantity increases, the other must decrease:

$$\mathrm{d}\mu_B = -\frac{n_A}{n_A}\mathrm{d}\mu_A$$

This is true for all partial molar quantities.

7.1 Partial molar quantities

4) The Gibbs-Duhem equation



The partial molar volumes of water and ethanol at 25°C.

Where V_{water} increases, V_{ethanol} decreases. Moreover, a small change in V_A corresponds to a large change in V_B if n_A / n_B is large, but the opposite is true when this ratio is small.

Example

Using the Gibbs-Duhem equation

The experimental value of the partial molar volume of K_2S0_4(aq) at 298 K is given by the expression

$$V_{K_2S0_4}/(\mathrm{cm^3 mol^{-1}}) = 32.280 + 18.216b^{1/2}$$

where *b* is the numerical value of the molality of K_2S0_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 298 K is 18.079 $\mathrm{cm^3 mol^{-1}}$

Example

Method: Let A denote K_2S0_4 and B denote H_2O, the solvent. The Gibbs-Duhem equation for the partial molar volumes of two components is

$$\sum_J n_J \mathrm{d}X_J = 0 \qquad n_A \mathrm{d}X_A + n_B \mathrm{d}X_B = 0$$

this relation implies that

$$\mathrm{d}V_B = -\frac{n_A}{n_B}\mathrm{d}V_A \quad \Longrightarrow \quad V_B = V_B^* - \int \frac{n_A}{n_B}\mathrm{d}V_A$$

Change the variable V_A to the molality b, and integrate the right-hand side between $b = 0$ (pure B) and the molality of interest.

Example

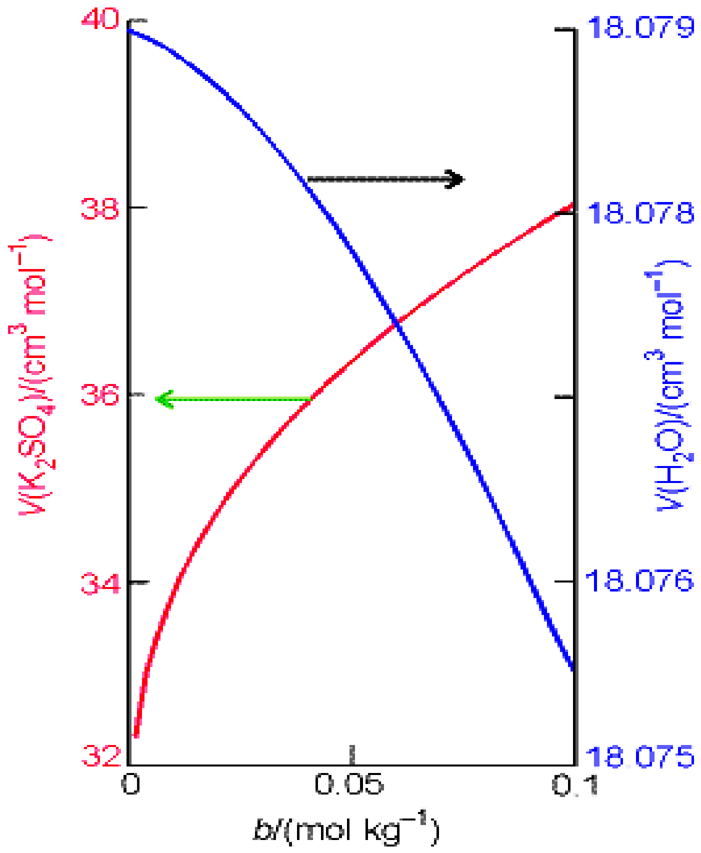
Answer: **It follows from the information in the question, that, with A = K_2S0_4, and $V_A = 32.280 + 18.216b^{1/2}$**

$$\frac{\mathrm{d}V_A}{\mathrm{d}b} = 9.108\, b^{-1/2}$$

$$V_B = V_B^* - \int \frac{n_A}{n_B}\mathrm{d}V_A \Rightarrow V_B = V_B^* - 9.108\int \frac{n_A}{n_A} b^{-1/2}\mathrm{d}b$$

$$b = \frac{n_A}{n_B M_B},$$ **where b is the molar mass of water**

Example



The partial molar volumes of the components of an aqueous solution of potassium sulfate.

$$V_\mathrm{B} = V_B^* - 9.108\,M_\mathrm{B}\int b^{1/2}\mathrm{d}b$$

$$= V_B^* - \frac{2}{3}(9.108\ \ M_\mathrm{B}\,b^{3/2})$$

$$V_\mathrm{B} = V_B^* - \frac{2}{3}(9.108\ M_\mathrm{B}\,b^{3/2})$$

By substituting the data

$$V_\mathrm{B}/(\mathrm{cm^3 mol^{-1}}) = 18.079 - 0.1094\,b^{3/2}$$

7. Simple mixtures

The thermodynamic description of mixtures

7.1 Partial molar quantities

7.2 The thermodynamics of mixing ▶

7.3 The chemical potentials of liquid

The properties of solutions

7.4 Liquid mixtures

7.5 Colligative properties

Activities

7.6 The solvent activity

7.7 The solute activity

版权所有：华东理工大学物理化学教研室

上一页 下一页 节首

7.2 The thermodynamics of mixing

The dependence of the Gibbs energy of a mixture on its composition is given and we know that at constant *T* and *p* systems tend towards a lower Gibbs energy. This is the link we need in order to apply thermodynamics to the discussion of spontaneous changes of composition, as in the mixing of two substances.

7.2 The thermodynamics of mixing

1) The Gibbs energy of mixing

Let the amounts of two perfect gases in the two containers be n_A and n_B; both are at a temperature T and a pressure p. At this stage, the Gibbs energy of the total system is

$$G_\mathrm{i} = n_\mathrm{A}\mu_A + n_\mathrm{B}\mu_B$$

$$= n_\mathrm{A}\left\{\mu_\mathrm{A}^{\ominus} + RT\ln\left(\frac{p}{p^{\ominus}}\right)\right\} + n_\mathrm{B}\left\{\mu_\mathrm{B}^{\ominus} + RT\ln\left(\frac{p}{p^{\ominus}}\right)\right\}$$

7.2 The thermodynamics of mixing

1) The Gibbs energy of mixing

To replace $p/p^{\ominus}$ by p, before mixing, the total Gibbs energy is

$$G_{\mathrm{i}} = n_{\mathrm{A}}\left\{\mu_{\mathrm{A}}^{\ominus} + RT\ln p\right\} + n_{\mathrm{B}}\left\{\mu_{\mathrm{B}}^{\ominus} + RT\ln p\right\}$$

After mixing, the partial pressures of the gases are p_{A} and p_{B}, with $p_{\mathrm{A}} + p_{\mathrm{B}} = p$. The total Gibbs energy changes to

$$G_{\mathrm{f}} = n_{\mathrm{A}}\left\{\mu_{\mathrm{A}}^{\ominus} + RT\ln p_{\mathrm{A}}\right\} + n_{\mathrm{B}}\left\{\mu_{\mathrm{B}}^{\ominus} + RT\ln p_{\mathrm{B}}\right\}$$

7.2 The thermodynamics of mixing

1) The Gibbs energy of mixing

The Gibbs energy of mixing, $\Delta_{\text{mix}}G$, is

$$\Delta_{\text{mix}}G = G_{\text{f}} - G_{\text{i}}$$

$$= n_{\text{A}}\left\{\mu_{\text{A}}^{\ominus} + RT\ln p_{\text{A}}\right\} + n_{\text{B}}\left\{\mu_{\text{B}}^{\ominus} + RT\ln p_{\text{B}}\right\}$$

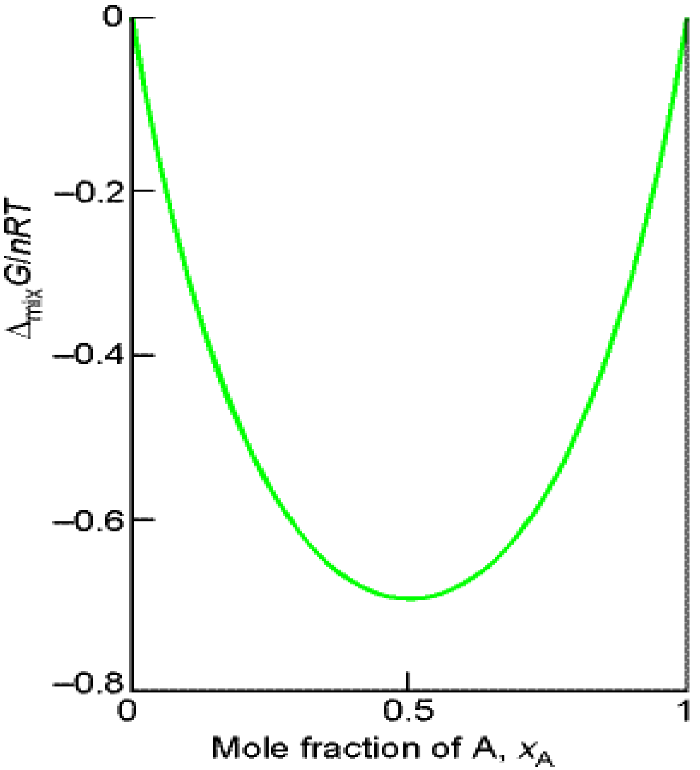
$$-\left(n_{\text{A}}\left\{\mu_{\text{A}}^{\ominus} + RT\ln p\right\} + n_{\text{B}}\left\{\mu_{\text{B}}^{\ominus} + RT\ln p\right\}\right)$$

$$\Delta_{\text{mix}}G = n_{\text{A}}RT\ln\left(\frac{p_{\text{A}}}{p}\right) + n_{\text{B}}RT\ln\left(\frac{p_{\text{B}}}{p}\right)$$

7.2 The thermodynamics of mixing

1) The Gibbs energy of mixing

At this point we may replace n_J by x_J and use Dalton's law to write $p_J/p = x_J$ for each component, which gives



$$\Delta_{mix}G = nRT(x_A \ln x_A + x_B \ln x_B)$$

Because $x_J \ngtr 1$, $\ln x_J < 0$, and $\Delta_{mix}G < 0$. The negative $\Delta_{mix}G$ confirms perfect gases mix spontaneously in all proportions. And $\Delta_{mix}G$ is directly proportional to the T but is independent of the total pressure.

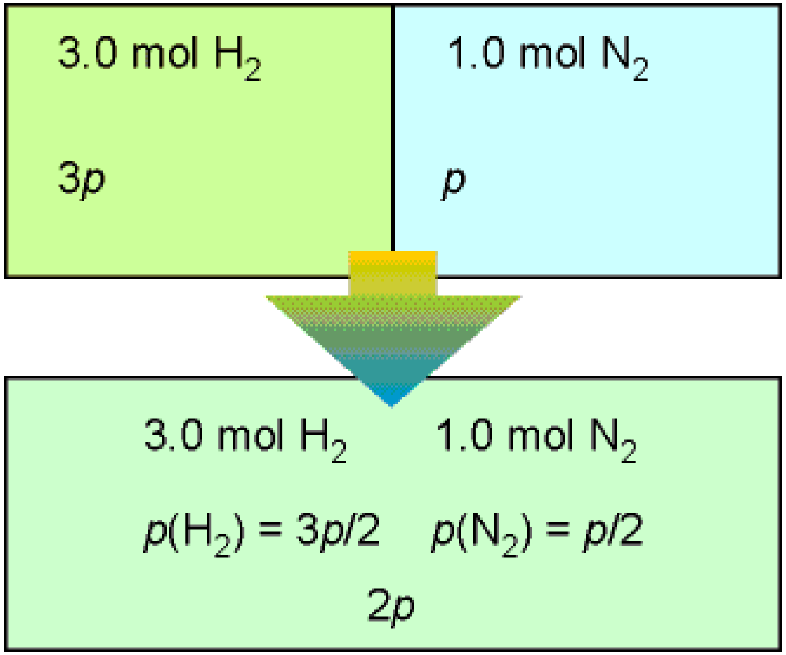
Example

Calculating a Gibbs energy of mixing

A container is divided into two equal compartments. One contains 3.0 mol H_2 at 25 ℃; the other contains 1.0 mol N_3 at 25 ℃. Calculate the Gibbs energy of mixing when the partition is removed. Assume perfect behavior.

Example

Method: We proceed by calculating the initial Gibbs energy from the chemical potentials. To do so, we need the pressure of each gas. Write the pressure of nitrogen as *p*; then the pressure of hydrogen as a multiple of *p* can be found from the gas laws. Next, calculate the Gibbs energy for the system when the partition is removed. The volume of each gas doubles, so its partial pressure falls by a factor of 2.



Example

Answer: Given that the pressure of N_2 is p, the pressure of H_2 is $3p$; therefore, the initial Gibbs energy is

$$G_1 = n_A\left\{\mu_A^\ominus + RT\ln p\right\} + n_B\left\{\mu_B^\ominus + RT\ln p\right\}$$

$$= (3.00\,\text{mol})\left\{\mu_A^\ominus(H_2) + RT\ln 3p\right\} + (1.00\,\text{mol})\left\{\mu_B^\ominus(N_2) + RT\ln p\right\}$$

The partial pressure of N_2 falls to $\frac{1}{2}p$ and that of H_2 falls to $\frac{3}{2}p$. Therefore, the Gibbs energy changes to

$$G_2 = (3.00\text{mol})\left\{\mu_A^\ominus(H_2) + RT\ln\tfrac{3}{2}p\right\} + (1.00\text{mol})\left\{\mu_B^\ominus((N_2) + RT\ln\tfrac{1}{2}p\right\}$$

Example

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

$$\Delta_{\text{mix}}G = (3.00\text{mol})RT\ln\frac{\frac{3}{2}p}{3p} + (1.00\text{mol})RT\ln\frac{\frac{1}{2}p}{p}$$

$$= -(4.00\text{mol})RT\ln 2 = -6.9\text{kJ}$$

In this example, the value of $\Delta_{\text{mix}}G$ is the sum of two contributions: the mixing itself, and the changes in pressure of the two gases to their final pressure, 2*p*. When two gases mix at the same pressure, the change of Gibbs energy is only from mixing, that is −5.6 kJ.

7.2 The thermodynamics of mixing

2) Other thermodynamic mixing functions

- **The entropy of mixing for a mixture of perfect gases**

Because $(\partial G/\partial T)_{p,n} = -S$

$$\Delta_{\text{mix}} S = -\left(\frac{\partial \Delta_{\text{mix}} G}{\partial T}\right)_{p,n_A,n_B}$$

$$= -nR(x_A \ln x_A + x_B \ln x_B)$$

Because ln$x$ < 0, it follows that $\Delta_{\text{mix}} S > 0$ for all compositions

7.2 The thermodynamics of mixing

2) Other thermodynamic mixing functions

- **The enthalpy of mixing for a mixture of perfect gases**

The isothermal, isobaric enthalpy of mixing, $\Delta_{\mathrm{mix}}H$, of two perfect gases may be found from $\Delta G = \Delta H - T\Delta S$

$$\Delta_{\mathrm{mix}}H = 0$$

The enthalpy of mixing is zero, as we should expect for a system in which there are no interactions between the molecules forming the gaseous mixture. It follows that the whole of the driving force for mixing comes from the increase in entropy of the system, because the entropy of the surroundings is unchanged.

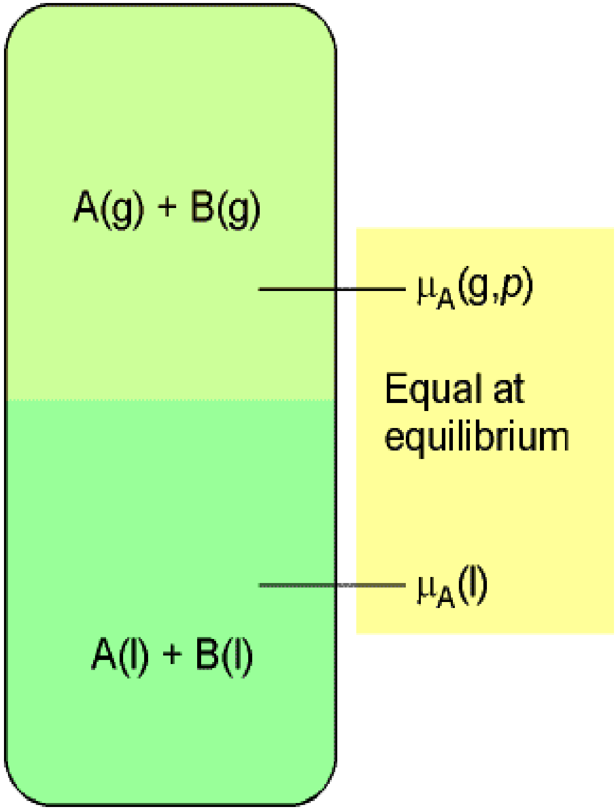
7. Simple mixtures

The thermodynamic description of mixtures

The properties of solutions

Activities

7.3 The chemical potentials of liquids



To discuss the equilibrium properties of liquid mixtures we need to know how the chemical potential of a liquid varies with its 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.

7.3 The chemical potentials of liquids

1) Raoult's Law

The French chemist Francois Raoult found that the ratio of the partial vapour pressure of each component to its vapour pressure as a pure liquid, p_A/p^*_A, is approximately equal to the mole fraction of A in the liquid mixture. That is

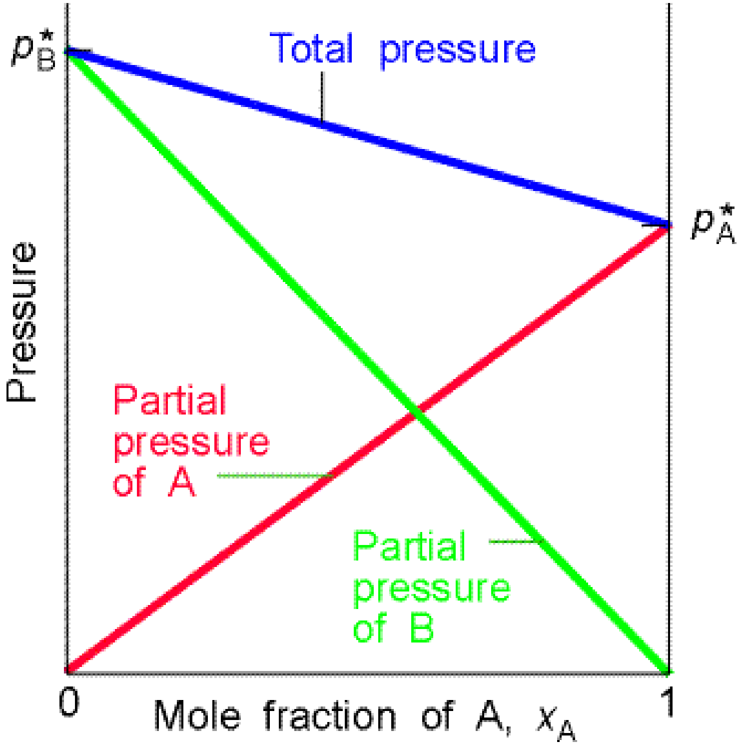
$$p_A = x_A p_A^*$$

This expression is called Raoult's law

Quantities relating to pure substances are denoted by a superscript * in the following discussions.

7.3 The chemical potentials of liquids

1) Raoult's Law



$$p_A = x_A p_A^*$$

The total vapour pressure and the two partial vapour pressures of an ideal binary mixture are proportional to the mole fractions of the components.

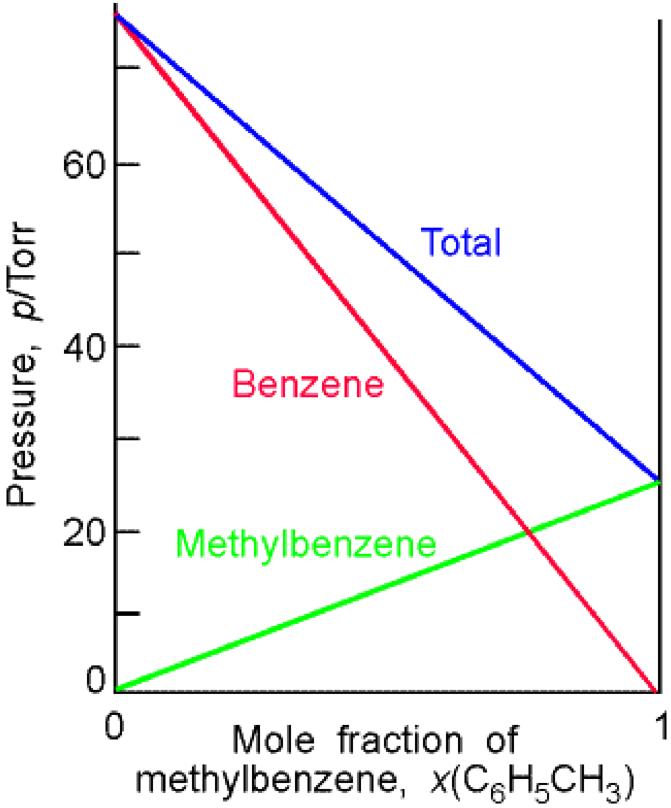
For a binary mixture:

$$x_A + x_B = 1$$

$$p_A^* - p_A = p_A^* x_B$$

7.3 The chemical potentials of liquids

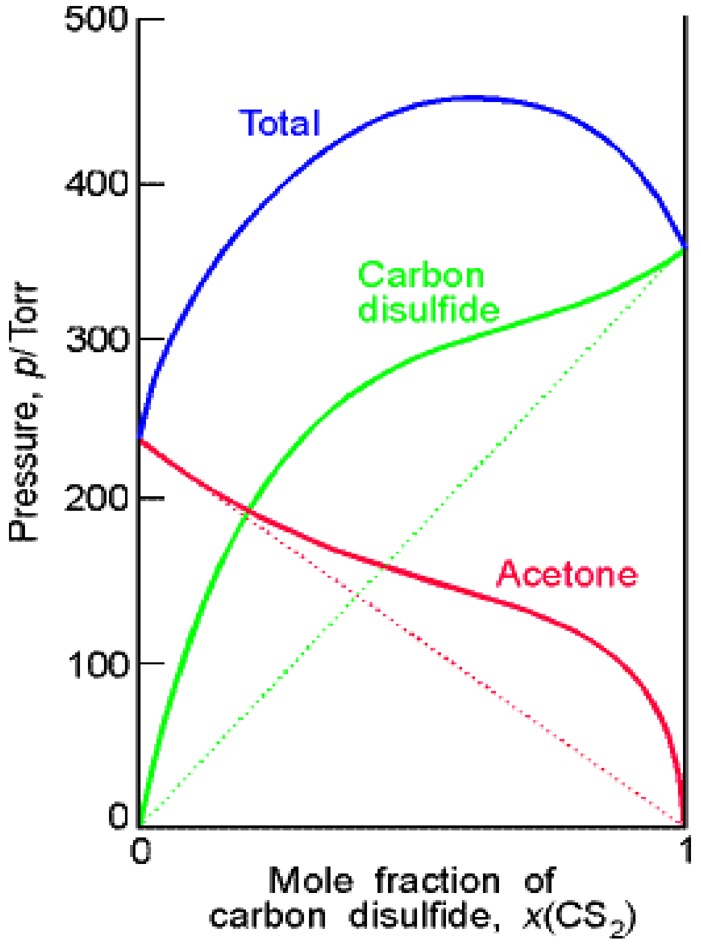
1) Raoult's Law − Definition for Ideal solutions



$$p_A = x_A p_A^*$$

Mixtures that obey the Raoult's law throughout the composition range from pure A to pure B are called ideal solutions.

7.3 The chemical potentials of liquids



Some mixtures obey Raoult's law very well, especially when the components are structurally similar.

But some mixtures do not obey Raoult's law; and strong deviations from ideality are shown by dissimilar liquids, e.g. carbon disulfide and acetone.

7.3 The chemical potentials of liquids

2) Henry's law

Henry found 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:

$$p_B = x_B K_B$$

where x_B is the mole fraction of the solute and K_B is an empirical constant, the tangent to the experimental curve of plot of the vapour pressure of B against its mole fraction at $x_B = 0$.

7.3 The chemical potentials of liquids

2) Henry's law- ideal dilute solutions

$$p_B = x_B K_B$$

Mixtures for which the solute obeys Henry's law and the solvent obeys Raoult's law are called ideal-dilute solutions.

7.3 The chemical potentials of liquids

3) Chemical potential for ideal mixtures

For a pure substance:

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,p} = \mu^{\ominus} + RT\ln\left(\frac{p}{p^{\ominus}}\right)$$

Because the vapour pressure of the pure liquid is p^*_{A}, it follows that

$$\mu^*_{\mathrm{A}} = \mu^{\ominus} + RT\ln\left(\frac{p^*_{\mathrm{A}}}{p^{\ominus}}\right) = \mu^{\ominus} + RT\ln p^*_{\mathrm{A}}$$

Where p^*_{A} is the relative pressure, $p^*_{\mathrm{A}}/p^{\theta}$

7.3 The chemical potentials of liquids

1) ideal solutions –The chemical potential

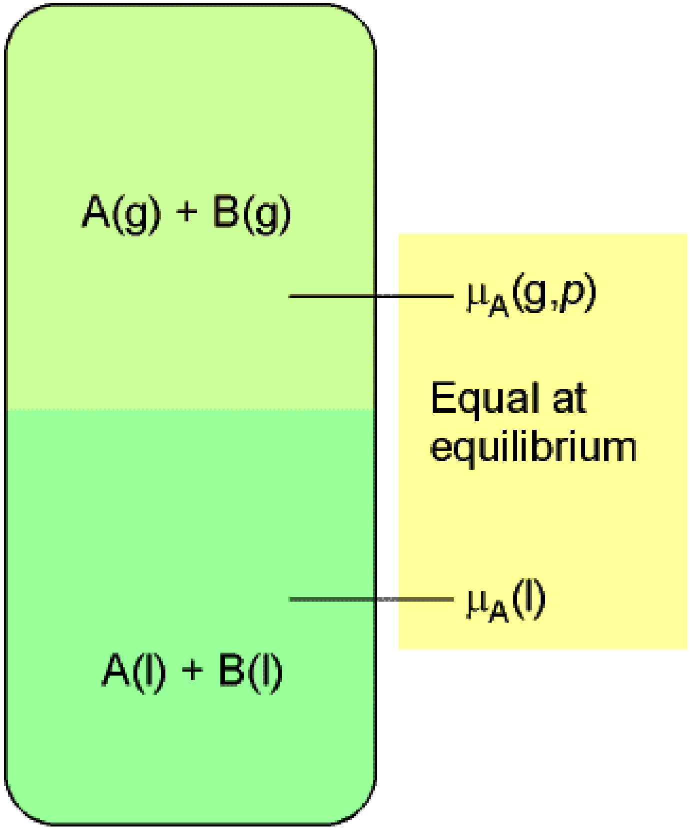
If another substance, a solute, is also present in the liquid, the chemical potential of *A* in the liquid is μ_A and its vapour pressure is p_A, in this case

$$\mu_A = \mu^{\ominus} + RT\ln\left(\frac{p_A}{p^{\ominus}}\right) = \mu^{\ominus} + RT\ln p_A$$

Where p_A is the relative pressure, p_A / p^{θ}

7.3 The chemical potentials of liquids

1) ideal solutions –The chemical potential



$$\mu_A^* = \mu^\ominus + RT\ln p_A^*$$

$$\mu_A = \mu^\ominus + RT\ln p_A$$

At equilibrium

$$\mu_A = (\mu_A^* - RT\ln p_A^*) + RT\ln p_A$$

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

7.3 The chemical potentials of liquids

1) ideal solutions –The chemical potential

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

It shows a relation between the ratio of vapour pressures and the composition of the liquid.

According to Raoult’s law $p_A = x_A p_A^*$

$$\underline{\mu_A = \mu_A^* + RT\ln x_A}$$

This important equation can be used as the definition of an ideal solution.

Example

Investigating the validity of Raoult's and Henry's laws

The vapour pressures of each component in a mixture of acetone(A) and chloroform(C) were measured at 35 ℃ with the following results:

x_C	0	0.20	0.40	0.60	0.80	1
p_C/Torr	0	35	82	142	219	293
p_A/Torr	347	270	185	102	37	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.

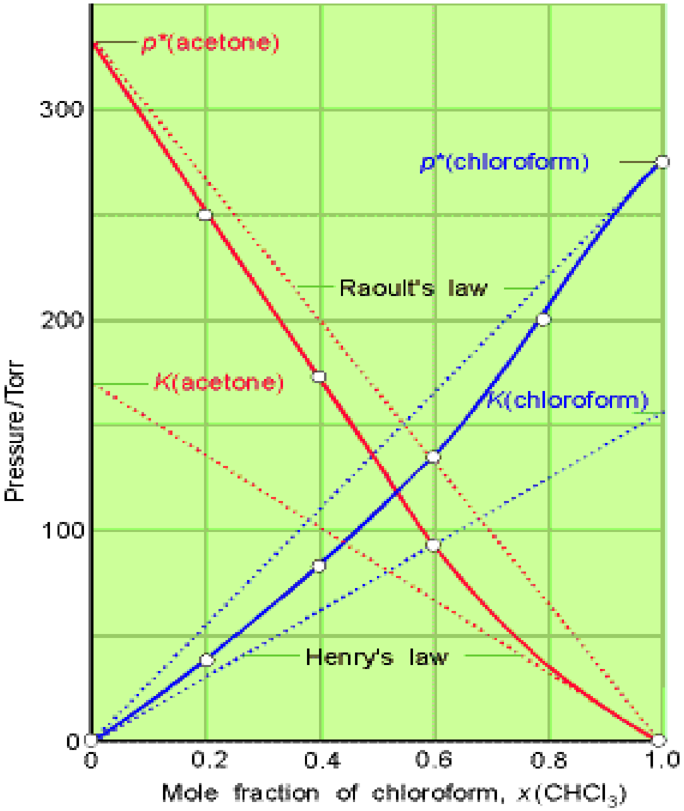
Example

Method: Both Raoult's and Henry's laws are statements about the form of the graph of partial vapour pressure against mole fraction. Therefore, plot the partial vapour pressures against mole fraction.

Raoult's law is tested by comparing the data with the straight line $p_J = x_J p^*_J$ for each component in the region in which it is in excess (and acting as the solvent).

Henry's law is tested by finding a straight line $p_J = x_J K_J$ that is tangent to each partial vapour pressure at low x, where the component can be treated as the solute.

Example



The experimental partial vapour pressures of a mixture of chloroform and acetone.

Answer: The data are plotted in the Figure together with the Raoult's law lines..

Henry's law requires
$K = 175$ Torr for acetone and
$K = 165$ Torr for chloroform

Example

Using Henry's law

Estimate the molar solubility (the solubility in moles per liter) of oxygen in water at 25 ℃ and a partial pressure of 160 Torr, its partial pressure in the atmosphere at sea level.

Example

Method: The mole fraction of solute is given by Henry's law as $x = p/K$, where p is the partial pressure of the gaseous solute. All we need do is to calculate the mole fraction that corresponds to the stated partial pressure, and then interpret that mole fraction as a molar concentration. For the latter part of the calculation, we calculate the amount of O_2 dissolved in 1.00 kg of water (which corresponds to about 1.00 L water). The solution is dilute, so the expressions for the mole fraction can be simplified.

Example

Answer: Because the amount of O_2 dissolved is small, its mole fraction is

$$x(\mathrm{O_2}) = \frac{n(\mathrm{O_2})}{n(\mathrm{O_2}) + n(\mathrm{H_2O})} \approx \frac{n(\mathrm{O_2})}{n(\mathrm{H_2O})}$$

since $p_\mathrm{B} = x_\mathrm{B} K_\mathrm{B}$ ⬇

$$n(\mathrm{O_2}) \approx x(\mathrm{O_2})n(\mathrm{H_2O}) = \frac{p(\mathrm{O_2})n(\mathrm{H_2O})}{K}$$

$$\approx \frac{(160\,\mathrm{Torr}) \times (55.5\,\mathrm{mol})}{3.33 \times 10^{7}\,\mathrm{Torr}} = 2.69 \times 10^{-4}\,\mathrm{mol}$$

The molality of the saturated solution is therefore 2.69×10^{-4} molkg^{-1}, corresponding to a molar concentration of approximately 2.7×10^{-4} mol L^{-1}

7. Simple mixtures

The thermodynamic description of mixtures

7.1 Partial molar quantities

7.2 The thermodynamics of mixing

7.3 The chemical potentials of liquid

The properties of solutions

7.4 Liquid mixtures ▶

7.5 Colligative properties

Activities

7.6 The solvent activity

7.7 The solute activity

版权所有：华东理工大学物理化学教研室

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. In this way, we identify the thermodynamic consequences of molecules of one species mingling randomly with molecules of the second species. The calculation provides a background for discussing the deviations from ideal behavior exhibited by real solutions

7.4 Liquid mixtures

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

$$G_{\mathrm{i}} = n_{\mathrm{A}}\mu_A^* + n_{\mathrm{B}}\mu_B^*$$

when they are mixed, the individual chemical potential is

$$\mu_i = \mu_i^* + RT\ln x_i$$

and the total Gibbs energy is

$$G_{\mathrm{f}} = n_{\mathrm{A}}\left\{\mu_{\mathrm{A}}^* + RT\ln x_{\mathrm{A}}\right\} + n_{\mathrm{B}}\left\{\mu_{\mathrm{B}}^* + RT\ln x_{\mathrm{B}}\right\}$$

7.4 Liquid mixtures

The Gibbs energy of mixing, $\Delta_{\text{mix}}G$, is

$$\Delta_{\text{mix}}G = G_{\text{f}} - G_{\text{i}}$$

$$\Delta_{\text{mix}}G = nRT\ \{x_{\text{A}} \ln x_{\text{A}} + x_{\text{B}} \ln x_{\text{B}}\}$$

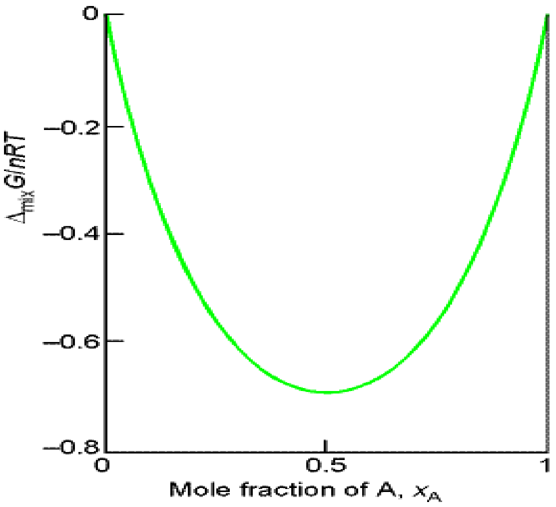
Because $(\partial G/\partial T)_{p,n} = -S$

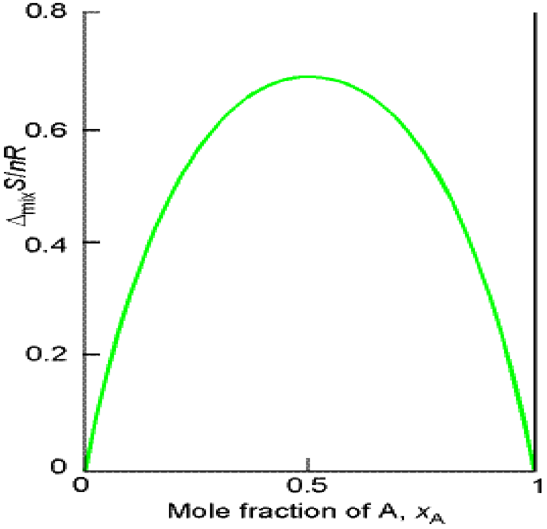
It follows that the ideal entropy and enthalpy of mixing of two liquids is

$$\Delta_{\text{mix}}S = -nR(x_{\text{A}} \ln x_{\text{A}} + x_{\text{B}} \ln x_{\text{B}})$$

$$\Delta_{\text{mix}}H = 0$$

7.4 Liquid mixtures





The variation of the Gibbs energy of mixing with composition is the same as that already depicted for gases (above); the same is true of the entropy of mixing (below). and all the conclusions drawn there are valid here: the driving force for mixing is the increasing entropy of the system as the molecules mingle, and the enthalpy of mixing is zero.

7.4 Liquid mixtures

It should be noted that solution ideality means something different from gas perfection. In a perfect gas there are no interactions between molecules. In ideal solutions there are interactions, but the average A-B interactions in the mixture are the same as the average A-A and B-B interactions in the pure liquids.

7.4 Liquid mixtures

□ The regular solution

Real solutions are composed of particles for which A-A, A-B, and B-B interactions are all different. Not only may there be an enthalpy change when liquids mix,but there may also be an additional contribution to the entropy arising from the way in which the molecules of one type might cluster together instead of mingling freely with the others.

7.4 Liquid mixtures

□ The excess functions

The difference between the observed thermodynamic function (extensive) of mixing and the function for an ideal solution is defined as the excess functions, X^{E}

$$X^{E} \xrightarrow{\text{def}} X - X^{id}$$

$$X^{E} = \Delta_{\mathrm{mix}} X - \Delta_{\mathrm{mix}} X^{id}$$

7.4 Liquid mixtures

□ The excess functions

The thermodynamic properties of real solutions may be expressed in terms of the excess functions, X^{E}. Deviations of the excess functions from zero indicate the extent to which the solutions are nonideal.

$$G^{E} = \Delta_{\text{mix}} G - \Delta_{\text{mix}} G^{id}$$

$$S^{E} = \Delta_{\text{mix}} S - \Delta_{\text{mix}} S^{id}$$

7.4 Liquid mixtures

□ The regular solution

$$H^E \neq 0 \qquad S^E = 0$$

A regular solution can be thought of 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.

7. Simple mixtures

The thermodynamic description of mixtures

The properties of solutions

Activities

7.5 Colligative properties

1) The common features of colligative properties

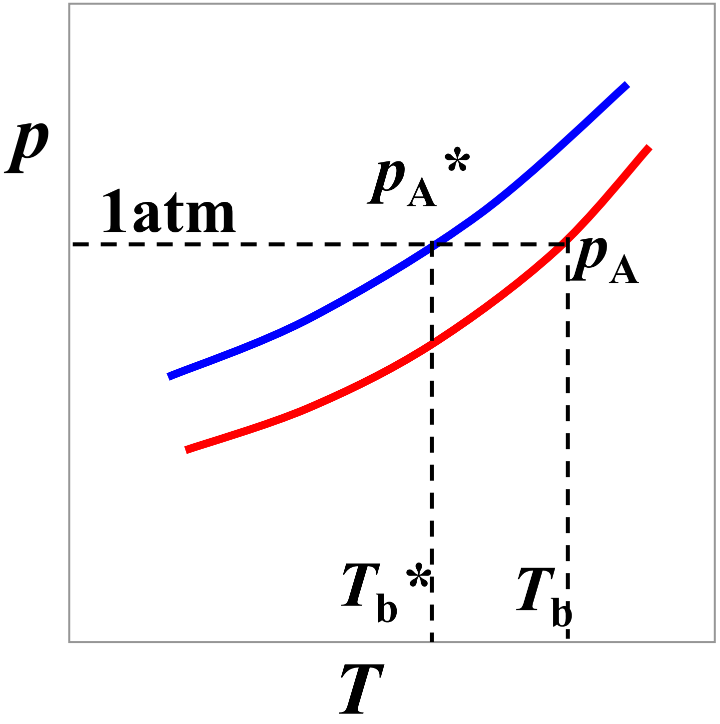
In dilute solutions, some properties depend only on the number of solute particles present, not their identity. They are called colligative properties.

Some of these properties are as followings:

The elevation of boiling point
The depression of freezing point
Solubility and osmotic properties

7.5 Colligative properties

2) The elevation of boiling point



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

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

7.5 Colligative properties

2) The elevation of boiling point

The presence of a solute at a mole fraction x_B causes an increase in normal boiling point from T^* to $T^*+\Delta T$

$$\Delta T = Kx_B \qquad K = \frac{RT^{*2}}{\Delta_{vap}H}$$

Because the equation make no reference to the identity of the solute, only to its mole fraction, we conclude that the elevation of boiling point is a colligative property. The value of ΔT does depend on the properties of the solvent.

7.5 Colligative properties

2) The elevation of boiling point

For practical applications, we note that the mole fraction of B is proportional to its molality, *b*, in dilute solutions, then

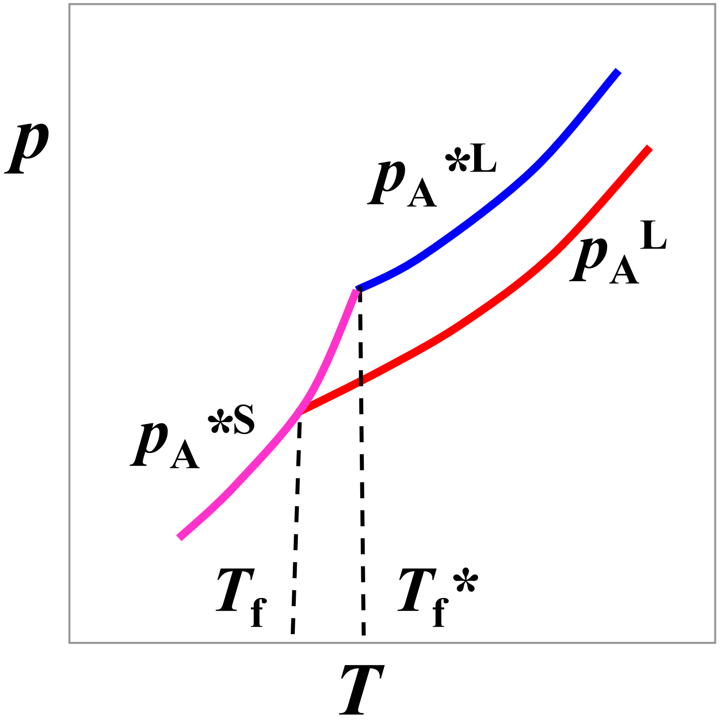
$$\Delta T = K_b b$$

K_b is the empirical constant of the solvent

7.5 Colligative properties

3) The depression of freezing point

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



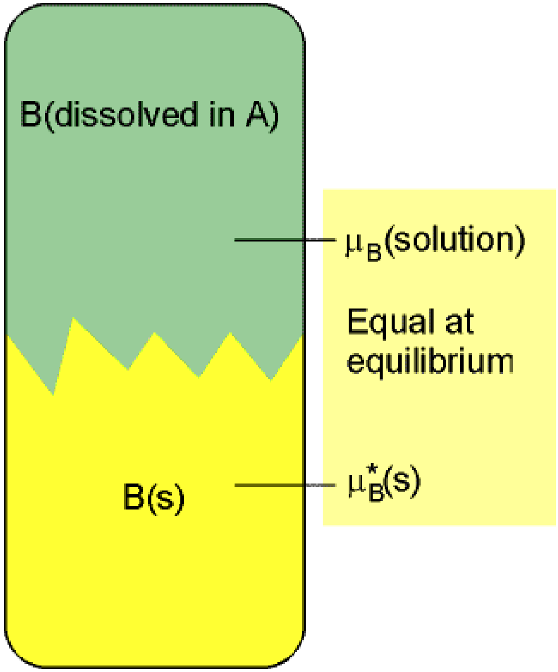
$$\Delta T = K' x_B$$

$$K' = \frac{RT^{*2}}{\Delta_{fus}H}$$

where ΔT is the freezing point depression, $\Delta_{fus}H$ is the enthalpy of fusion of the solvent.

7.5 Colligative properties

4) Solubility



When a solid solute is left in contact with a solvent, it dissolves until the solution is saturated. Saturation is a state of equilibrium, with the undissolved solute in equilibrium $\mu_B{}^*(s)$, and the chemical potential of B in solution, $\mu_B(l)$, are equal

The heterogeneous equilibrium involved in the calculation of the solubility is between pure solid B and B in the solution.

$$\mu_B^*(s) = \mu_B(l) = \mu_B^*(l) + RT\ln x_B$$

7.5 Colligative properties

4) Solubility

To find the mole fraction of B in solution at equilibrium when the temperature is *T*:

$$\ln x_B = \frac{\mu_B^*(\mathrm{s}) - \mu_B^*(\mathrm{l})}{RT} = -\frac{\Delta_{\mathrm{fus}} G}{RT}$$

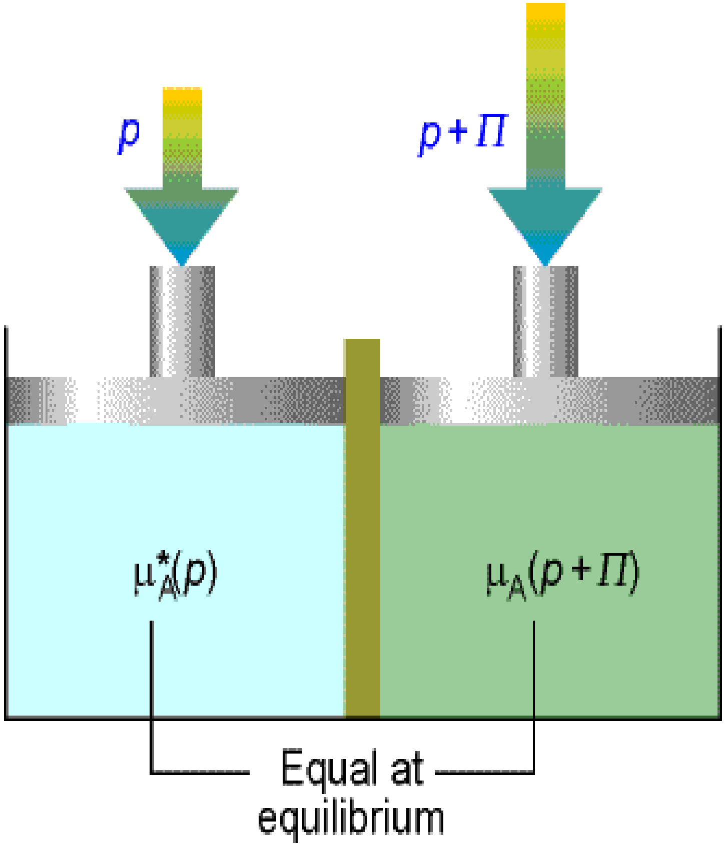
$$= -\frac{\Delta_{\mathrm{fus}} H}{RT} + \frac{\Delta_{\mathrm{fus}} S}{R}$$

At the melting point of the solute, T^*, we know that $\Delta_{\mathrm{fus}} G = 0$, consequently,

$$\ln x_B = -\frac{\Delta_{\mathrm{fus}} H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

7.5 Colligative properties

5) Osmosis



The osmotic pressure, Π,

The phenomenon of osmosis is the spontaneous passage of a pure solvent into a solution separated from it by a semipermeable membrane, a membrane permeable to the solvent but not to the solute. The osmotic pressure, Π, is the pressure that must be applied to the solution to stop the influx of solvent.

7.5 Colligative properties

5) Osmosis

For dilute solutions

$$\underline{\Pi = [\mathrm{B}]RT} \qquad [\mathrm{B}] = \frac{n_\mathrm{B}}{V}$$

[B] is the molar concentration of the solute.

The above equation is called vant't Hoff equation.

7. Simple mixtures

The thermodynamic description of mixtures

7.1 Partial molar quantities

7.2 The thermodynamics of mixing

7.3 The chemical potentials of liquid

The properties of solutions

7.4 Liquid mixtures

7.5 Colligative properties

Activities

7.6 The solvent activity ▶

7.7 The solute activity

Activities

Now we see how to adjust the expressions developed earlier in the chapter to take into account deviations from ideal behaviour. In Section 5.4 we saw how the fugacity was introduced to take into account the effects of gas imperfections in a manner that resulted in the least upset of the form of equations. Here we see how the expressions encountered in the treatment of ideal solutions can also be preserved almost intact by introducing the concept of activity.

7.6 The solvent activity

The general form of the chemical potential of a real or ideal solvent

$$\mu_A = \mu_A^* + RT\ln\left(\frac{p_A}{p_A^*}\right)$$

Raoult's law $$\mu_A = \mu_A^* + RT\ln x_A$$

When the solution does not obey Raoult's law the equation can be preserved as

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

7.6 The solvent activity

□ **The activity, a_A**

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

The quantity a_A is the activity of A, a kind of 'effective' mole fraction, just as the fugacity is an effective pressure.

Because $\mu_A = \mu_A^* + RT\ln(\frac{p_A}{p_A^*})$ is true for both real and ideal solutions,

$$a_A = \frac{p_A}{p_A^*}$$

7.6 The solvent activity

□ The activity coefficient, γ_A

Because all solvents obey Raoult's law increasingly closely as the concentration of solute approaches zero, the activity of the solvent approaches the mole fraction as $x_A \to 1$

$$a_A \to x_A \text{ as } x_A \to 1$$

$$a_A = \gamma_A x_A \quad \gamma_A \to 1 \text{ as } x_A \to 1$$

$$\gamma_A = \frac{a_A}{x_A}$$

γ_A is called the **activity coefficient**

7.6 The solvent activity

□ **The activity coefficient, γ_A**

$$a_A \to x_A \text{ as } x_A \to 1$$

$$a_A = \gamma_A x_A \quad \gamma_A \to 1 \text{ as } x_A \to 1$$

At all temperatures and pressures, the chemical potential of the solvent is then

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

The standard state of the solvent, the pure liquid solvent at 1 bar, is established when x_A=1

7. Simple mixtures

The thermodynamic description of mixtures

7.1 Partial molar quantities
7.2 The thermodynamics of mixing
7.3 The chemical potentials of liquid

The properties of solutions

7.4 Liquid mixtures
7.5 Colligative properties

Activities

7.6 The solvent activity
7.7 The solute activity ▶

7.7 The solute activity

1). Ideal-dilute solutions

A solute B that satisfies Henry's law has a vapour pressure given by $p_B = K_B x_B$, where K_B is an empirical constant. In this case, the chemical potential of B is

$$\mu_B = \mu_B^* + RT\ln\left(\frac{p_B}{p_B^*}\right) = \underline{\mu_B^* + RT\ln\left(\frac{K_B}{p_B^*}\right)} + RT\ln x_B$$

The new standard chemical potential is

$$\mu_B^+ = \mu_B^* + RT\ \ln\left(\frac{K_B}{p_B^*}\right)$$

It follows that $\mu_B = \mu_B^+ + RT\ln x_B$

7.7 The solute activity

2). Real solutes

When permit deviations from ideal-dilute, Henry's law behaviour. For the solute, introduce a_B in place of x_B

$$\mu_B = \mu_B^{+} + RT\ln x_B \quad \Rightarrow \quad \mu_B = \mu_B^{+} + RT\ln a_B$$

The standard state remains unchanged, and all the deviations from ideality are captured in the activity a_B. The value of the activity at any concentration can be obtained in the same way as for the solvent, but here

$$a_B = \frac{p_B}{K_B}$$

7.7 The solute activity

2). Real solutes

$$a_B = \gamma_B x_B$$

All the deviations from ideality are captured in the activity coefficient $\gamma_{B.}$ Because the solute obeys Henry's law as $x_B \rightarrow 0$, it follows that

$$a_B \rightarrow x_B \text{ and } \gamma_B \rightarrow 1 \qquad \text{as } x_B \rightarrow 0$$

At all temperatures and pressures. Deviations of the solute from ideality disappear as zero concentration is approached.

7.7 The solute activity

3). Activities in terms of molalities

In dilute solutions the amount of solute is much less than that of solvent

$$n_B << n_A \quad \Rightarrow \quad x_B \approx n_B / n_A$$

Because n_B is proportional to the molality b_B, so $x_B = \dfrac{\kappa b_B}{b^\theta}$

where $b^\theta = 1$ mol kg^{-1} and κ is a dimensionless constant.

For an ideal-dilute solution it follows that

$$\mu_B = \mu_B^+ + RT\ \ln \kappa + RT\ \ln\left(\frac{b_B}{b_B^\theta}\right)$$

When replace b/b^θ by b

$$\mu_B = \underline{\mu_B^+ + RT\ \ln \kappa} + RT\ \ln b_B$$

7.7 The solute activity

$$\mu_B = \underline{\mu_B^{+} + RT\ \ln \kappa} + RT\ \ln b_B$$

Let $\mu_B^{\ominus} = \mu_B^{+} + RT \ln \kappa$ be a new standard chemical potential

then $\mu_B = \mu_B^{\ominus} + RT\ \ln b_B$

μ_B^{θ} is defined as the chemical potential of the solute when the molality of B is equal to b^{θ} (at 1 mol kg^{-1}).

The deviations from ideality by introducing a dimensionless activity, a_B a dimensionless activity coefficient γ_B

$$a_B = \gamma_B \frac{b_B}{b^{\theta}} \qquad \text{where } \gamma_B \to 1 \quad \text{as } b_B \to 0$$

Summary on activities

Component	Basis	Standard state	Chemical potential	Limits
Solvent	Raoult	Pure solvent	$\mu = \mu^* + RT\ln a$	
			$\mu^* = \mu^\ominus + RT\ln(\frac{p_A^*}{p^\ominus})$	$\gamma \to 1$ as $x \to 1$
			$a=p/p^*$ and $a = \gamma x$	Pure solvent
Solute	Henry	1) A hypothetical state of pure solute	$\mu = \mu^+ + RT\ln a$ $\mu^+ = \mu^* + RT\ln(\frac{K_B}{p_B^*})$	
			$a=p/K$ and $a = \gamma x$	$\gamma \to 1$ as $x \to 0$
		2) A hypothetical state of solute at molality b^θ	$\mu = \mu^\ominus + RT\ln a$ $\mu^\ominus = \mu^+ + RT\ln \kappa$	
			$a= \gamma b/b^\theta$ $x_B = \frac{\kappa b_B}{b^\theta}$	$\gamma \to 1$ as $b \to 0$

Example

Measuring activity

Use the information in Example 7.3 to calculate the activity and activity coefficient of chloroform in acetone at 25 ℃, treating it first as a solvent and then as a solute.

The vapour pressures of each component in a mixture of acetone(A) and chloroform(C) were measured at 35 ℃ with the following results:

$K_B = 165\ \text{Torr}$

x_C	0	0.20	0.40	0.60	0.80	1
p_C/Torr	0	35	82	142	219	293
p_A/Torr	347	270	185	102	37	0

Example

x_C	0	0.20	0.40	0.60	0.80	1
p_C/Torr	0	35	82	142	219	293

Method: For the activity of chloroform as a solvent

$a_A = p_A / p_A^*$	0	0.12	0.28	0.49	0.75	1.00

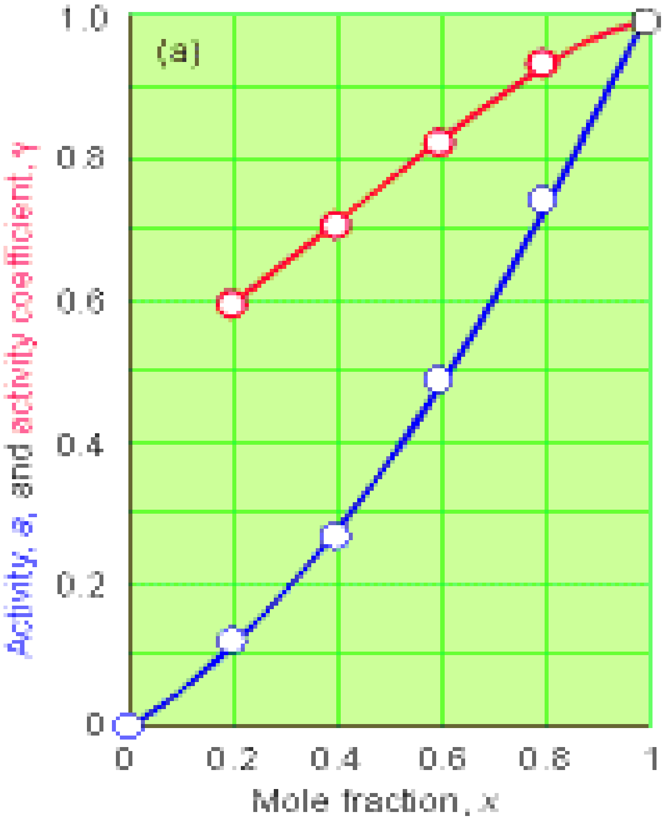
$$\gamma_A = a_A / x_A$$

For its activity as a solute (the Henry's law activity):

$a_B = p_B / K_B$	0	0.21	0.50	0.86	1.33	1.78

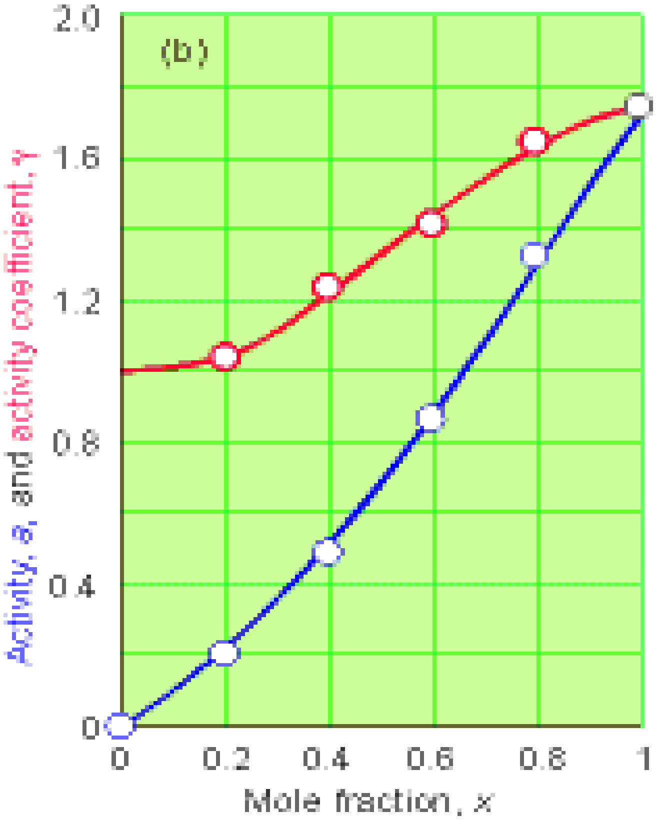
$$\gamma_B = a_B / x_B$$

Example



$\gamma \to 1$ as $x \to 1$

the Raoult's law case



$\gamma \to 1$ as $x \to 0$

the Henry's law case

Part 1: Equilibrium

1. The properties of gases
2. The First Law: the concepts
3. The First Law: the machinery
4. The Second Law: the concepts
5. The Second Law: the machinery
6. Physical transformations of pure substances
7. Simple mixtures
8. Phase diagrams
9. Chemical equilibrium
10. Electrochemistry