Lecture Contents

5. Simple mixtures

The properties of solutions

5.4 Liquid mixtures

5.5 Colligative properties

Activities

***Fugacity - Gases**

5.6 The solvent activity

5.7 The solute activity

5.8 The activities of regular solutions

5.9 The activities of ions in solution

The properties of solutions

5.4 Liquid mixtures

(a) Ideal solutions

The total Gibbs energy before mixing, $G_i = n_A \mu_A^* + n_B \mu_B^*$

After mixing, $G_f = n_A \{\mu_A^* + RT \ln x_A\} + n_B \{\mu_B^* + RT \ln x_B\}$

The Gibbs energy of mixing, $\Delta_{mix}G = G_f - G_i$, $\Delta_{mix}G = nRT\{x_A \ln x_A + x_B \ln x_B\}$

As for gases, the ideal entropy of mixing of two liquids $\Delta_{mix}S = -nR\{x_A \ln x_A + x_B \ln x_B\}$

The difference between perfect gas and ideal solution

- **perfect gas : no interactions between molecules**
- **ideal solution : avg. A-B interactions in the mixture = avg. A-A or B-B interaction in the pure liquids**

Real solutions

- **A-A, A-B, and B-B interactions : all different**
- **Not only changes in enthalpy and volume, but also additional contribution to S (due to clustering)**

If $\Delta H > 0$ (large) or $\Delta S < 0$,

- **$\Delta_{mix}G > 0$: separation is spontaneous (liquids may be immiscible)**
- **Partially miscible liquids : miscible only over a certain range of compositions**

5.4 Liquid mixtures

(b) Excess functions and regular solutions

Excess function, X^E :

= difference between the observed thermodynamic function of mixing and the function of an ideal solution

Excess entropy : $S^E = \Delta_{mix}S - \Delta_{mix}S^{ideal}$

where $\Delta_{mix}S^{ideal} = -nR\{x_A \ln x_A + x_B \ln x_B\}$

Regular solution : $H^E \neq 0$ but $S^E = 0$

Supposing excess enthalpy, $H^E = n\beta RTx_Ax_B$

where β is a dimensionless parameter(See Fig. 5.19)

- if $\beta < 0$: mixing is exothermic
- if $\beta > 0$: mixing is endothermic

Excess Gibbs energy of mixing

$$\Delta_{mix}G = nRT\{x_A \ln x_A + x_B \ln x_B + \beta x_Ax_B\}$$

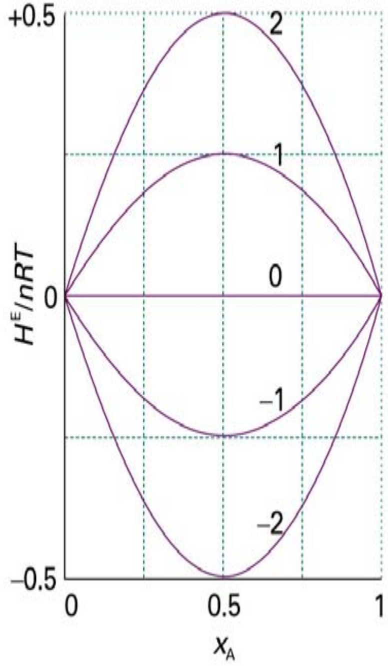


Fig. 5.19 The excess enthalpy according to a model in which it is proportional to βx_Ax_B, for different values of the parameter β.

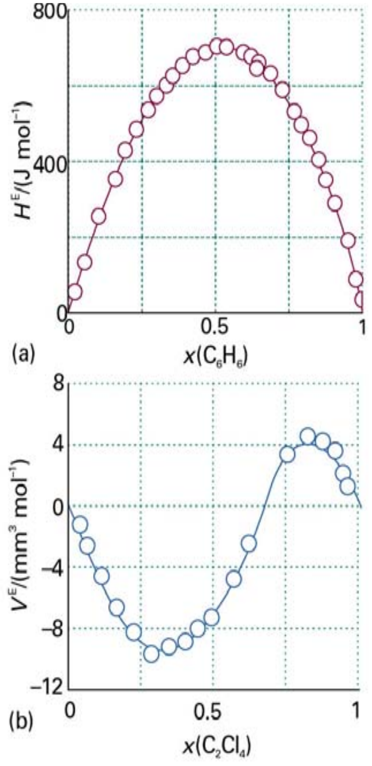


Fig. 5.18 Experimental excess functions at 25°C. (a) H^E for benzene/cyclohexane; this graph shows that the mixing is endothermic (because $\Delta_{mix}H = 0$ for an ideal solution). (b) The excess volume, V^E, for tetrachloroethene/cyclopentane; this graph shows that there is a contraction at low tetrachloroethane mole fractions, but an expansion at high mole fractions (because $\Delta_{mix}V = 0$ for an ideal mixture).

5.4 Liquid mixtures

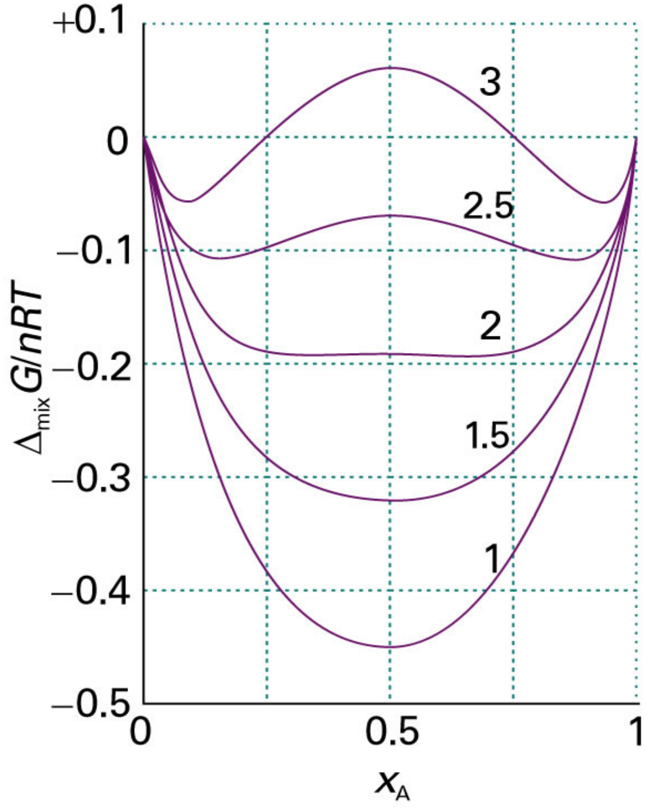


Fig. 5.20 The Gibbs energy of mixing for different values of the parameter β.

If β > 2, the graph shows two minima separated by a maximum, implying that the system will separate spontaneously into two phases (a reduction in Gibbs energy!!!)

5.5 Colligative properties

Colligative ('depending only on the collection) properties e.g.) the lowering of vapour pressure, the elevation of boiling point, the depression of freezing point, and osmotic pressure arising from the presence of a solute

Basic assumption: non-volatile solute and no dissolution of solute in the solid solvent

(a) The common features of colligative properties

For an ideal-dilute solution, (no direct influence of the solute on the chemical potential of the solvent vapour and the solid solvent)

$$\mu_A^* \xrightarrow{\text{reduction}} \mu_A^* + RT\ln x_A$$

→ higher T_b and lower T_f (see Fig. 5.21)

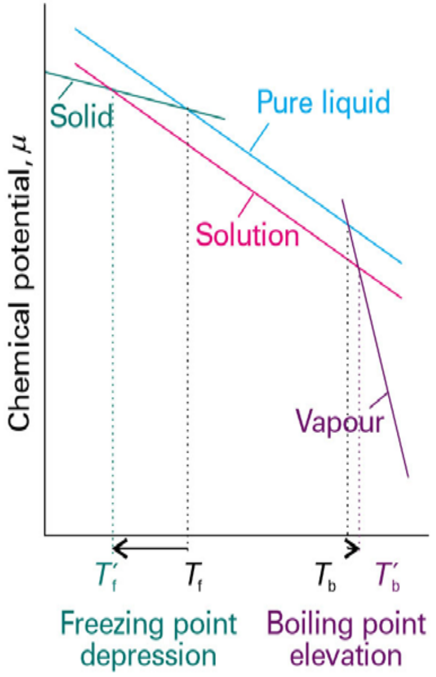


Fig. 5.21 The chemical potential of a solvent in the presence of a solute. The lowering of the liquid's chemical potential has a greater effect on the freezing point than on the boiling point because of the angles at which the lines intersect.

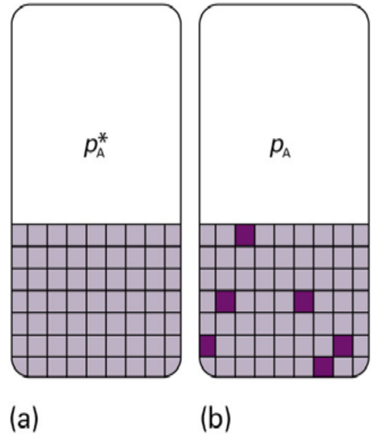


Fig. 5.22 The vapour pressure of a pure liquid represents a balance between the increase in disorder arising from vaporization and the decrease in disorder of the surroundings. (a) Here the structure of the liquid is represented highly schematically by the grid of squares. (b) When solute (the dark squares) is present, the disorder of the condensed phase is higher than that of the pure liquid, and there is a decreased tendency to acquire the disorder characteristic of the vapour.

Molecular Interpretation 5.2

When a solute is present, an additional contribution to the entropy of the liquid, even in an ideal solution. -> weaker tendency to form the gas (see Fig. 5.22), leading to a lower vapour pressure and hence a higher boiling point. Similarly, a lower freezing point due to enhanced molecular randomness of the solution.

5.5 Colligative properties

(b) The elevation of boiling point

When solvent (A) and solute (B) are present at 1atm, (Fig. 5.23)

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

The presence of the solute *B* with x_B causes boiling point ↑

$(T^* \rightarrow T^* + \Delta T)$

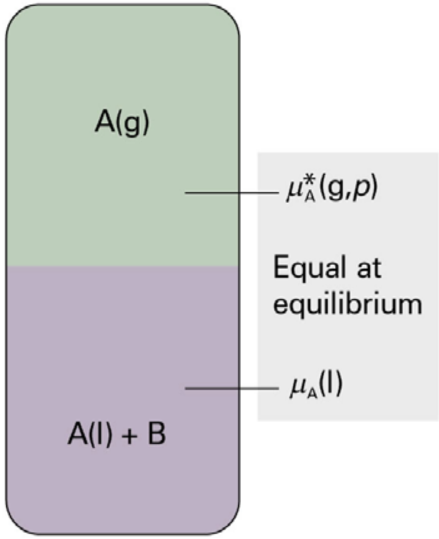


Fig. 5.23 The heterogeneous equilibrium involved in the calculation of the elevation of boiling point is between A in the pure vapour and A in the mixture, A being the solvent and B an involatile solute.

Justification 5.1

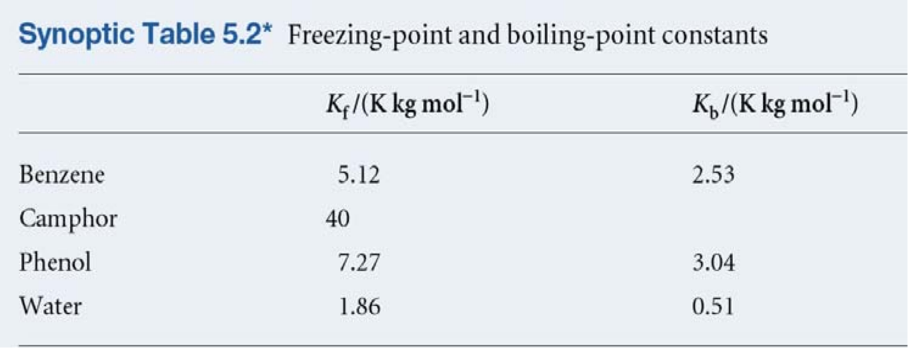
$$\ln x_A = \frac{\mu_A^*(g) - \mu_A^*(l)}{RT} = \frac{\Delta_{vap}G}{RT} \qquad \frac{d\ln x_A}{dT} = \frac{1}{R}\frac{d(\Delta_{vap}G/T)}{dT} = \frac{\Delta_{vap}H}{RT^2}$$

$$\int_0^{\ln x_A} d\ln x_A = -\frac{1}{R}\int_{T^*}^{T}\frac{\Delta_{vap}H}{T^2}dT, \qquad \ln(1-x_B) = \frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

$$x_B \ll 1, \qquad x_B = \frac{\Delta_{vap}H}{R}\left(\frac{1}{T^*} - \frac{1}{T}\right)$$

$$\frac{1}{T^*} - \frac{1}{T} = \frac{T - T^*}{TT^*} \approx \frac{\Delta T}{T^{*2}}, \qquad \Delta T = K_b b,$$

where K_b is empirical boiling - point constant



Synoptic Table 5.2* Freezing-point and boiling-point constants

	$K_f/(\mathrm{K\ kg\ mol^{-1}})$	$K_b/(\mathrm{K\ kg\ mol^{-1}})$
Benzene	5.12	2.53
Camphor	40	
Phenol	7.27	3.04
Water	1.86	0.51

5.5 Colligative properties

(c) The depression of freezing point

When a pure solid (A) is in equilibrium with a solution including solute of a mole fraction x_B, (See. Fig. 5.24)

$$\mu_A{}^*(s) = \mu_A{}^*(l) + RT\ln x_A \qquad \Delta T = K' x_B \qquad K' = \frac{RT^{*2}}{(\Delta H)_{fus}}$$

In the dilute solution, $\Delta T = K_f b$

(K_f : empirical freezing-point constant)

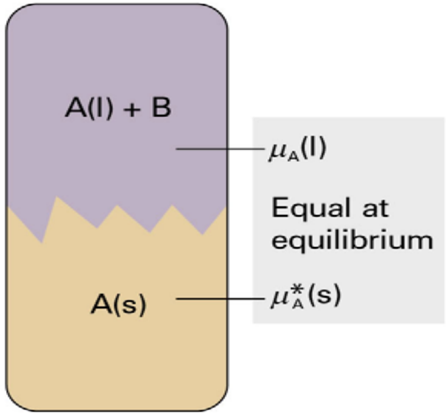


Fig. 5.24 The heterogeneous equilibrium involved in the calculation of the lowering of freezing point is between A in the pure solid and A in the mixture, A being the solvent and B a solute that is insoluble in solid A.

(d) Solubility

-When a solid solute is left in contact with a solvent, it dissolves until the solution is saturated

-saturation : a state of equilibrium between undissolved solute and dissolved solute)

In a saturated solution, the chemical potential of the pure solid solute = the chemical potential of B

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

$$\mu_B{}^*(s) = \mu_B{}^*(l) + RT\ln x_B$$ (See. Fig. 5.25)

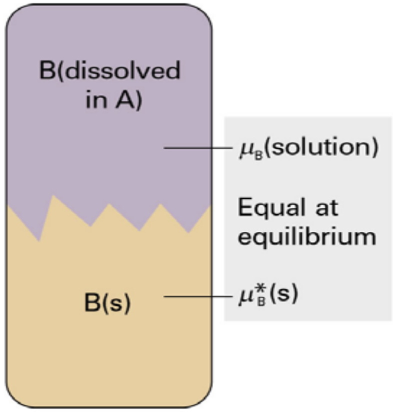


Fig. 5.25 The heterogeneous equilibrium involved in the calculation of the solubility is between pure solid B and B in the mixture.

5.5 Colligative properties

Justification 5.2 *(The solubility of an ideal solute.)*

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

$$= \frac{\Delta_{fus}H}{R}\left(\frac{1}{T_f} - \frac{1}{T}\right)$$

Relate $d\ln x_B$ to the change in temperature by differentiation and apply the Gibbs-Helmholtz equation

$$\boxed{\int_0^{\ln x_B} d\ln x_B = \frac{1}{R}\int_{T_f}^{T} \frac{\Delta_{fus}H}{T^2}dT}$$

- The solubility of B decreases exponentially as the temperature is lowered from its melting point.
- Solutes with high melting points and large enthalpies of melting have low solubilities at normal temperature.

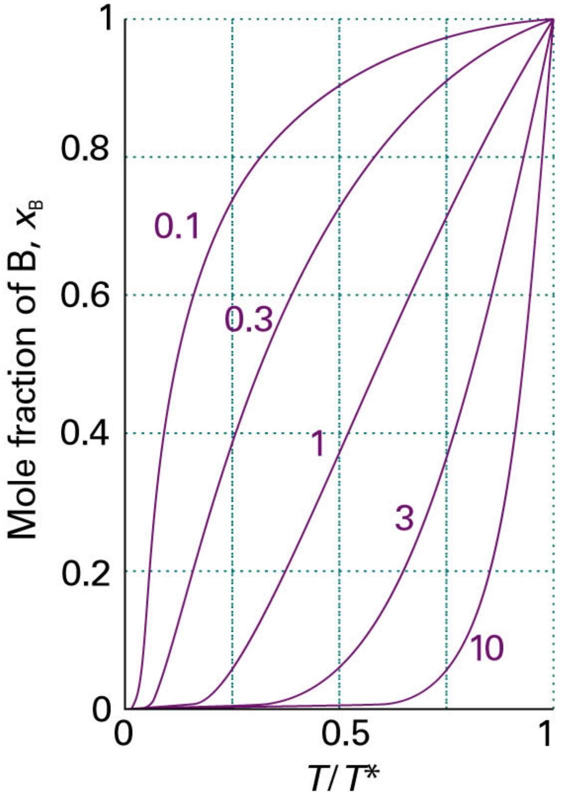


Fig. 5.26 The variation of solubility (the mole fraction of solute in a saturated solution) with temperature (T^* is the freezing temperature of the solute). Individual curves are labelled with the value of $\Delta_{fus}H/RT^*$.

5.5 Colligative properties

(e) Osmosis

- Osmosis : spontaneous passage of a pure solvent into a solution separated from it by a semipermeable membrane (not for solute) (See. Fig. 5.27)
- Osmotic pressure (Π) : the pressure that must be applied to the solution to stop the influx of solvent
- Osmometry : the determination of molar mass by the measurement of Π
- Simple arrangement (see Fig. 5.29): at equilibrium,
  hydrostatic pressure of solution = osmotic pressure Π

$$\mu_A^*(p) = \mu_A(x_A, p+\Pi)$$

$$\mu_A(x_A, p+\Pi) = \mu_A^*(p+\Pi) + RT\ln x_A$$

$$G(p_f) = G(p_i) + \int_{p_i}^{p_f} V\,dp \qquad \text{at constant } T$$

$$\mu_A^*(p+\Pi) = \mu_A^*(p) + \int_p^{p+\Pi} V_m\,dp$$

$$\boxed{-RT\ln x_A = \int_p^{p+\Pi} V_m\,dp}$$

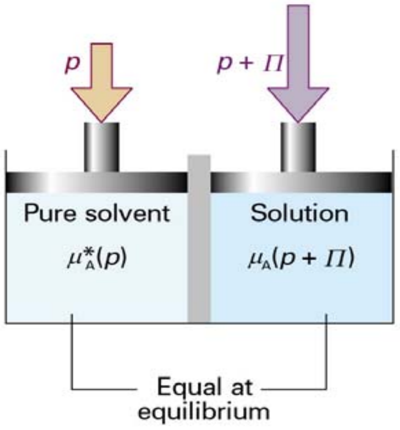


Fig. 5.27 The equilibrium involved in the calculation of osmotic pressure, Π, is between pure solvent A at a pressure p on one side of the semipermeable membrane and A as a component of the mixture on the other side of the membrane, where the pressure is $p + \Pi$.

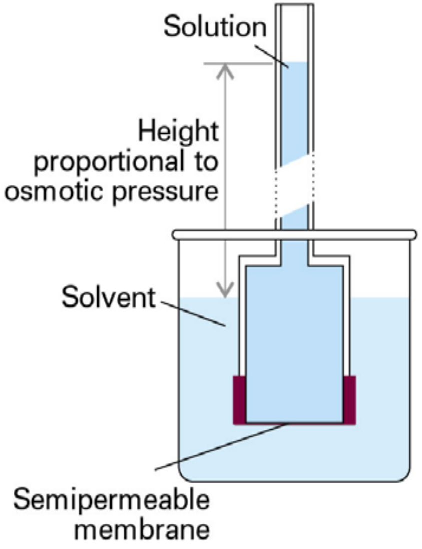


Fig. 5.29 In a simple version of the osmotic pressure experiment, A is at equilibrium on each side of the membrane when enough has passed into the solution to cause a hydrostatic pressure difference.

5.5 Colligative properties

Since $\ln x_A = \ln(1-x_B) \approx -x_B$, and assuming V_m (molar vol. of solvent) is constant,

$$RTx_B = \Pi V_m$$

When the solute is dilute, $x_B \approx n_B/n_A$ and $n_A V_m = V$,

$$\boxed{\Pi = [B]RT \text{: Van't Hoff equation}}$$

($[B] = n_B/V$ is the molar concentration of the solute)

In general,

$$\Pi = [\mathrm{J}]RT\{1 + B[\mathrm{J}] + \cdots\}$$

where B is the osmotic virial coefficient

*Fugacity - Gases

For a perfect gas $V = nRT/p$,

$$G(p_f) = G(p_i) + nRT\int_{p_i}^{p_f}\frac{dp}{p} = G(p_i) + nRT\ln\frac{p_f}{p_i}$$

If we set $p_i = p^o$,

$$G(p) = G^o + nRT\ \ln\frac{p}{p^o}$$

p dependence of *G* for a real gas
(See Fig. 5.7)

Replacing the true pressure, *p*, by an effective pressure, ***f*** :

$$G_m = G^o{}_m + RT\ \ln\frac{f}{p^o}$$

***f* : fugacity**

If we express the fugacity as $f = \phi p$, ϕ is the dimensionless fugacity coefficient ϕ is related to the compression factor, Z of the gas between p = 0 and p : $\ln\phi = \int_0^p \frac{Z-1}{p}dp$

Using $G(p_f) = G(p_i) + \int_{p_i}^{p_f} Vdp$ and $G_m = G^o{}_m + RT\ln\frac{f}{p^o}$,

(1) $\int_{p'}^{p} V_m dp = G_m - G'_m = RT\ln\frac{f}{f'}$ If the gas is perfect , (2) $\int_{p'}^{p} V_{perfect\ ,m} dp = RT\ \ln\frac{p}{p'}$

(1)-(2) $\int_{p'}^{p}(V_m - V_{perfect\ ,m})dp = RT\left(\ln\frac{f}{f'} - \ln\frac{p}{p'}\right) \rightarrow \ln\left(\frac{f}{p}\times\frac{p'}{f'}\right) = \frac{1}{RT}\int_{p'}^{p}(V_m - V_{perfect,m})dp$

When $p'\rightarrow 0$, the gas behaves perfectly and $f' \approx p'$. Therefore, $f'/p'\rightarrow 1$ as $p'\rightarrow 0$.

$\ln\frac{f}{p} = \frac{1}{RT}\int_0^p (V_m - V_{perfect,m})dp$ With $f = f/p$, $\ln\phi = \frac{1}{RT}\int_0^p (V_m - V_{perfect m})dp$

$$\ln\phi = \int_0^p \frac{Z-1}{p}dp$$

For a perfect gas : $\mathbf{V_{perfect,m} = RT/p}$, For a real gas : $\mathbf{V_m = RTZ/p}$

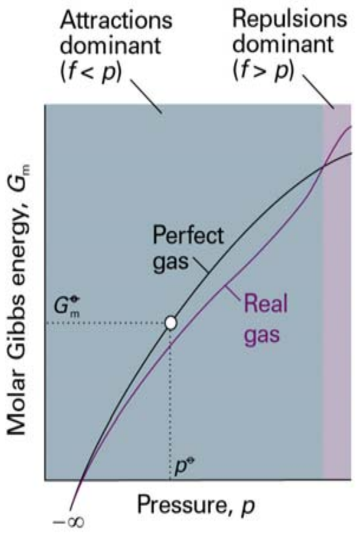


Fig. 3.24 The molar Gibbs energy of a real gas. As $p \rightarrow 0$, the molar Gibbs energy coincides with the value for a perfect gas (shown by the black line). When attractive forces are dominant (at intermediate pressures), the molar Gibbs energy is less than that of a perfect gas and the molecules have a lower 'escaping tendency'. At high pressures, when repulsive forces are dominant, the molar Gibbs energy of a real gas is greater than that of a perfect gas. Then the 'escaping tendency' is increased.

Activities

5.6 The solvent activity

The different definitions of standard states and activities (see Table 5.3)

The general form of the chemical potential of a real or ideal solvent, $\mu_A = \mu_A^* + RT \ln \frac{p_A}{p_A^*}$

For an ideal solution obeying Raoult's law, $\mu_A = \mu_A^* + RT \ln x_A$

When the solution doesn't obey Raoult's law, $\mu_A = \mu_A^* + RT \ln a_A$

$a_A = \frac{p_A}{p_A^*}$: **activity** (a kind of 'effective' mole fraction)

$a_A \rightarrow x_A$ as $x_A \rightarrow 1$

Let γ = activity coefficient, then

$a_A = \gamma_A x_A \quad \gamma_A \rightarrow 1$ as $x_A \rightarrow 1$

Consequently, at all *T and p,*

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

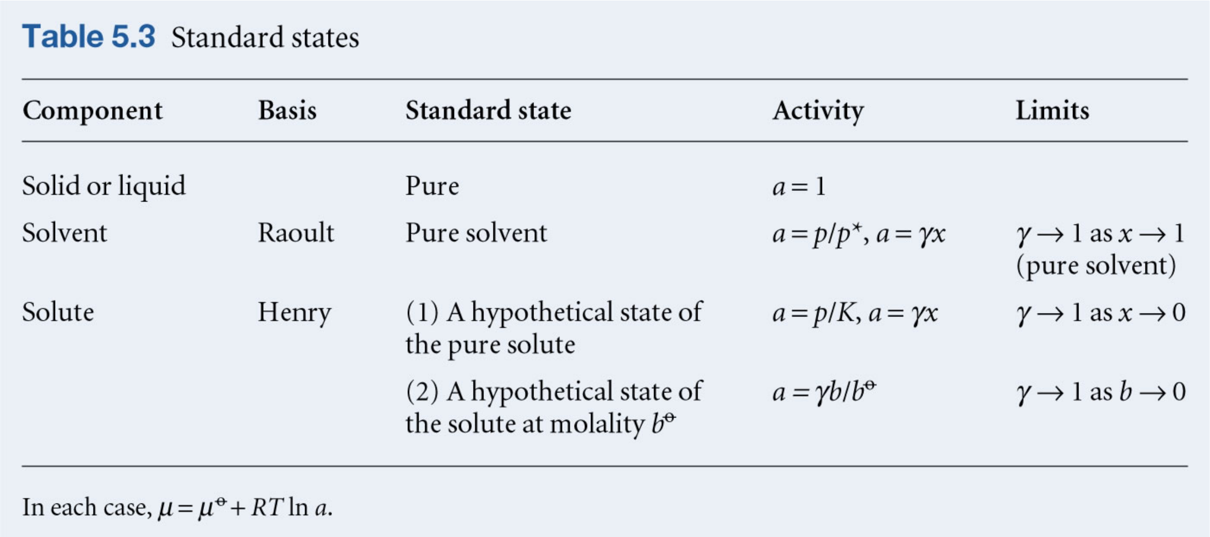


Table 5.3 Standard states

Component	Basis	Standard state	Activity	Limits
Solid or liquid		Pure	$a = 1$	
Solvent	Raoult	Pure solvent	$a = p/p^*$, $a = \gamma x$	$\gamma \rightarrow 1$ as $x \rightarrow 1$ (pure solvent)
Solute	Henry	(1) A hypothetical state of the pure solute	$a = p/K$, $a = \gamma x$	$\gamma \rightarrow 1$ as $x \rightarrow 0$
		(2) A hypothetical state of the solute at molality $b^\ominus$	$a = \gamma b/b^\ominus$	$\gamma \rightarrow 1$ as $b \rightarrow 0$

In each case, $\mu = \mu^\ominus + RT \ln a$.

5.7 The solute activity

Solutes approach ideal-dilute (Henry's law) behavior as $x_B \rightarrow 0$, not as $x_B \rightarrow 1$

(a) Ideal-dilute solutions

Vapour pressure of a solute *B* satisfying Henry's law, $\boldsymbol{p_B = K_B x_B}$

$$\mu_B = \mu_B{}^* + RT \ln \frac{p_B}{p_B{}^*} = \mu_B{}^* + RT \ln \frac{K_B}{p_B{}^*} + RT \ln x_B$$

A new standard chemical potential : $\mu_B{}^o = \mu_B{}^* + RT \ln \dfrac{K_B}{p_B{}^*}$

Consequently, $\mu_B = \mu_B{}^o + RT \ln x_B$

(b) Real solutes

To express the deviations from ideal-dilute, a_B is introduced in place of x_B :

$$\mu_B = \mu_B{}^o + RT \ln a_B \qquad a_B = \frac{p_B}{K_B} \qquad a_B = \gamma_B x_B$$

$a_B \rightarrow x_B$ and $\gamma_B \rightarrow 1$ as $x_B \rightarrow 0$ (at all *T*, *p*)

5.7 The solute activity

Measuring activity in real solutions (see Fig. 5.31)

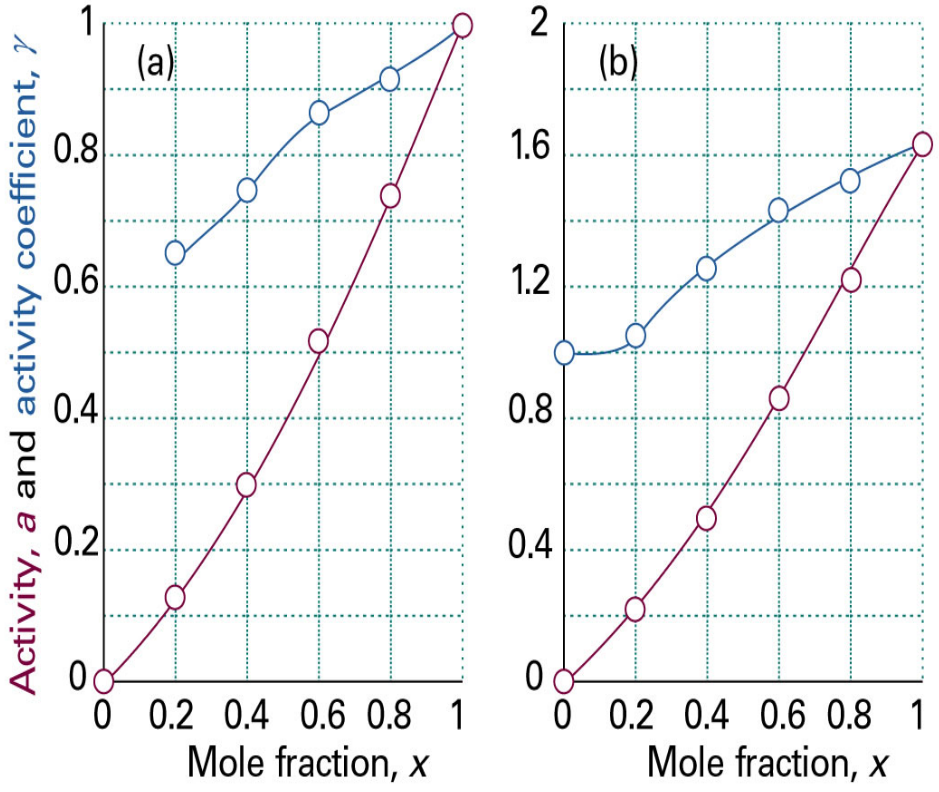


Fig. 5.31 The variation of activity and activity coefficient of chloroform (trichloromethane) and acetone (propanone) with composition according to (a) Raoult's law, (b) Henry's law.

5.7 The solute activity

(c) Activities in terms of molalities

Using molalities, *b* in place of mole fraction *x* $\mu_B = \mu_B^o + RT\ln b_B$

- $\mu_B = \mu_B^o$ when $b_B = b^o$ (1 mol kg^{-1})

-$b_B \rightarrow 0$, $\mu_B \rightarrow -\infty$: as the solution becomes diluted, the solute becomes increasingly stabilized.

$a_B = \gamma_B \dfrac{b_B}{b^o}$ where $\gamma_B \rightarrow 1$ as $b_B \rightarrow 0$ (at all *T*, *p*)

Therefore, the chemical potential of a real solute at any molality : $\mu = \mu^o + RT\ln a$

(d) The biological standard state

- In biochemistry, it is common to adopt the biological standard state ($a = 10^{-7}$, corresponding to pH = 7) rather than the conventional standard state of hydrogen ions ($a = 1$, pH = 0)
- In case of hydrogen ions,

$$\mu_{H^+} = \mu_{H^+}^{o} + RT\ln a_{H^+} = \mu_{H^+}^{o} - (RT\ln 10)\times pH \qquad (\because \ln x = (\ln 10)\log x)$$

$$\mu_{H^+}^{\oplus} = \mu_{H^+}^{o} - 7RT\ln 10$$

At 298.15 *K*, 7*RT*ln10=39.96 *kJmol*$^{-1}$, so the two standard values differ by about 40 *kJmol*$^{-1}$.

5.8 The activities of regular solutions

For a regular solution : *HE* ≠ 0 but *SE* = 0

$\ln\gamma_A = \beta x_B^{\ 2}$ $\ln\gamma_B = \beta x_A^{\ 2}$ **: Margules equations**

Justification 7.3

For mixing of a nonideal solution, $\Delta_{mix}G = nRT\{x_A \ln a_A + x_B \ln a_B\}$

By using $a = \gamma x$ $\Delta_{mix}G = nRT\{x_A \ln x_A + x_B \ln x_B + x_A \ln\gamma_A + x_B \ln\gamma_B\}$

Using $\ln\gamma_A = \beta x_B^{\ 2}$ $\ln\gamma_B = \beta x_A^{\ 2}$ and $x_A + x_B = 1$,

$$\begin{aligned}\Delta_{mix}G &= nRT\{x_A \ln x_A + x_B \ln x_B + \beta x_A x_B^{\ 2} + \beta x_B x_A^{\ 2}\}\\ &= nRT\{x_A \ln x_A + x_B \ln x_B + \beta x_A x_B (x_A + x_B)\}\\ &= nRT\{x_A \ln x_A + x_B \ln x_B + \beta x_A x_B\}\end{aligned}$$

Activity coefficients behave correctly for dilute solutions :

$\gamma_A \rightarrow 1$ as $x_B \rightarrow 0$ and $\gamma_B \rightarrow 1$ as $x_A \rightarrow 0$

5.8 The activities of regular solutions

For the activity of *A* using the Margules eqn,

$$a_A = \gamma_A x_A = x_A e^{\beta x_B{}^2} = x_A e^{\beta(1-x_A)^2}$$

Using $a_A = \dfrac{p_A}{p_A{}^*}$ $\quad p_A = \left\{ x_A e^{\beta(1-x_A)^2} \right\} p_A{}^*$ (see Fig. 5.32)

- $\beta = 0$: ideal solution (in accordance with Raoult’s law)

- $\beta > 0$: endothermic mixing, unfavourable solute-solvent interactions

  $p_{vap}{}^{real} > p_{vap}{}^{ideal}$

- $\beta < 0$: exothermic mixing, favourable solute-solvent interactions

  $p_{vap}{}^{\mathrm{real}} < p_{vap}{}^{ideal}$

- All the curves approach linearity and coincide with the Raoult’s law as $x_A \rightarrow 1$ and $e^{\beta(1-xA)^2} \rightarrow 1$

- If $x_A \ll 1$, $\quad p_A = x_A e^{\beta} p_A{}^*$

  the form of Henry’s law if $K = e^{\beta} p_A{}^*$

  K is different for each solute-solvent system

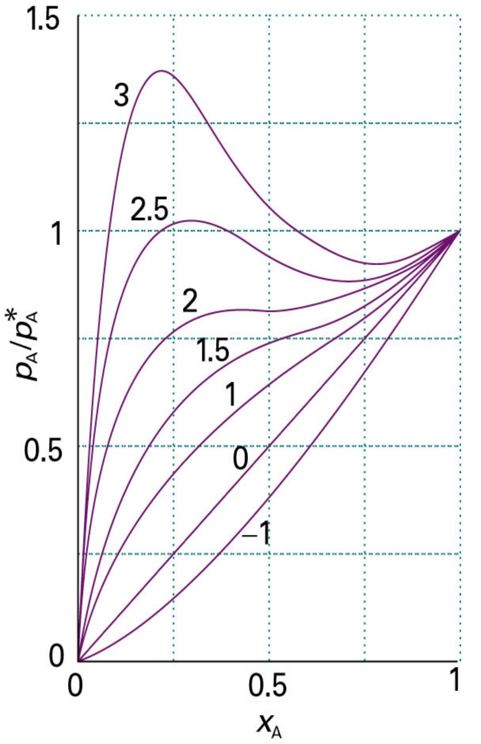


Fig. 5.32 The vapour pressure of a mixture based on a model in which the excess enthalpy is proportional to $\beta x_A x_B$. An ideal solution corresponds to $\beta = 0$ and gives a straight line, in accord with Raoult’s law. Positive values of β give vapour pressures higher than ideal. Negative values of β give a lower vapour pressure.

5.9 The activities of ions in solution

(a) Mean activity coefficients

The chemical potential of a univalent cation M^+ → μ_+ & univalent anion X^- → μ_-

The molar Gibbs energy of an ideal solution : $G_m^{ideal} = \mu_+^{ideal} + \mu_-^{ideal}$

But in a real solution,

$$G_m = \mu_+ + \mu_- = \mu_+^{ideal} + \mu_-^{ideal} + RT\ln\gamma_+ + RT\ln\gamma_- = G_m^{ideal} + RT\ln\gamma_+\gamma_-$$

Introduce the ***<u>mean activity coefficient :</u>*** $\gamma_\pm = (\gamma_+\gamma_-)^{1/2}$

Express the individual chemical potentials of ions :

$$\mu_+ = \mu_+^{ideal} + RT\ln\gamma_\pm \qquad \mu_- = \mu_-^{ideal} + RT\ln\gamma_\pm$$

The molar Gibbs energy of the ions is the sum of their partial molar Gibbs energies :

$$G_m = p\mu_+ + q\mu_- = G_m^{ideal} + pRT\ln\gamma_+ + qRT\ln\gamma_-$$

The mean activity coefficient: $\gamma_\pm = (\gamma_+^P\gamma_-^q)^{1/s}$, $s = p + q$

The chemical potential of each ion : $\mu_i = \mu_i^{ideal} + RT\ln\gamma_\pm$, $G = p\mu_+ + q\mu_-$

5.9 The activities of ions in solution

(b) The Debye-Huckel limiting law

Oppositely charged ions attract one another.

↓

Near any given ions, there is an excess of counter ions.

↓

The chemical potential of any given central ion is lowered as a result of its electrostatic interaction with its ionic atmosphere. (see Fig. 5.33)

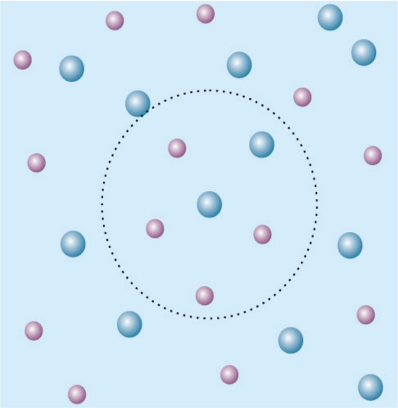


Fig. 5.33 The picture underlying the Debye–Hückel theory is of a tendency for anions to be found around cations, and of cations to be found around anions (one such local clustering region is shown by the circle). The ions are in ceaseless motion, and the diagram represents a snapshot of their motion. The solutions to which the theory applies are far less concentrated than shown here.

5.9 The activities of ions in solution

The lowered energy = The difference between G_m and G_m^{ideal}

As a result, $G_m - G_m^{ideal} = RT \ln \gamma_{\pm}$

The activity coefficient can be calculated from the **Debye-Huckel** limiting law

$$\log \gamma_{\pm} = -|z_+ z_-| A I^{1/2}$$,

A = 0.509, for a aqueous solution at 25°C

I = The dimensionless ionic strength of the solution

$$\boxed{I = \frac{1}{2}\sum_i z_i^2 (b_i / b°)}$$

Z_i is the charge number of an ion i, and b_i is its molality

The ionic strength of solutions consisting of two types of ion at molalities b_+ and b_- : $I = \frac{1}{2}(b_+ z_+^2 + b_- z_-^2)/b°$

Table 5.4 summarizes the relation of ionic strength and molality

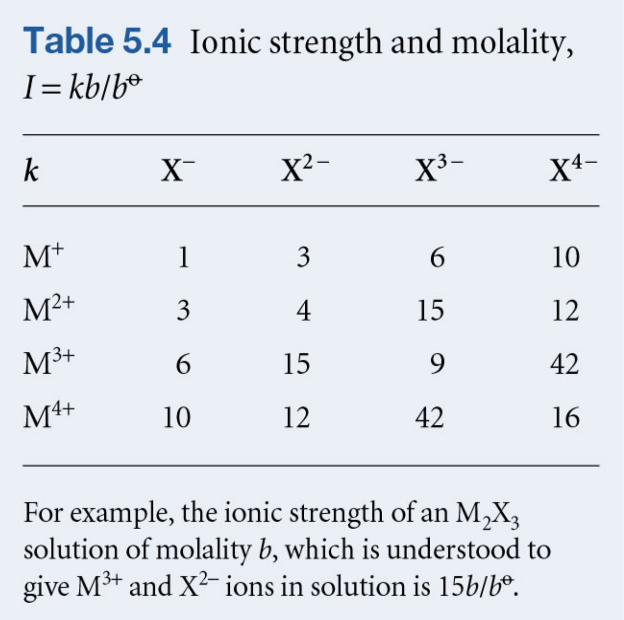


Table 5.4 Ionic strength and molality, $I = kb/b^{\ominus}$

k	X^-	X^{2-}	X^{3-}	X^{4-}
M^+	1	3	6	10
M^{2+}	3	4	15	12
M^{3+}	6	15	9	42
M^{4+}	10	12	42	16

For example, the ionic strength of an M_2X_3 solution of molality b, which is understood to give M^{3+} and X^{2-} ions in solution is $15b/b^{\ominus}$.

5.9 The activities of ions in solution

(c) The extended Debye-Huckel law

When the ionic strength of the solution is too high, the activity coefficient can be estimated from the extended **Debye-Huckel** law:

$$\boxed{\log \gamma_{\pm} = -\frac{A|z_+ z_-| I^{1/2}}{1 + BI^{1/2}} + CI}$$

where *B* and *C* are dimensionless constants.

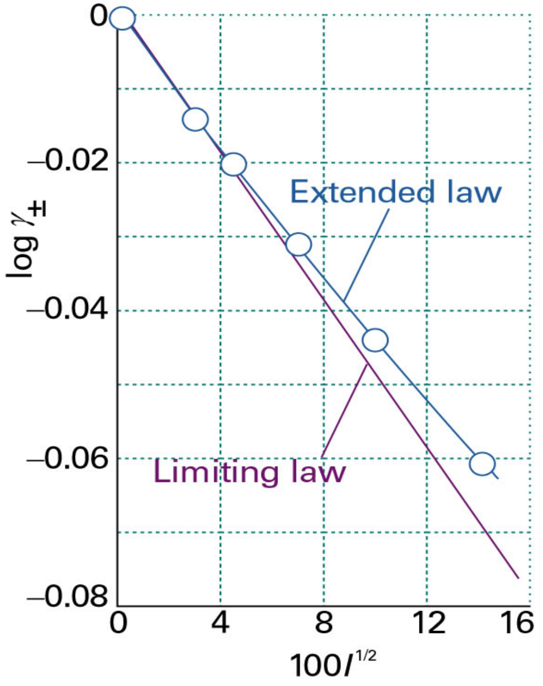


Fig. 5.35 The extended Debye–Hückel law gives agreement with experiment over a wider range of molalities (as shown here for a 1,1-electrolyte), but it fails at higher molalities.