

Simple mixtures

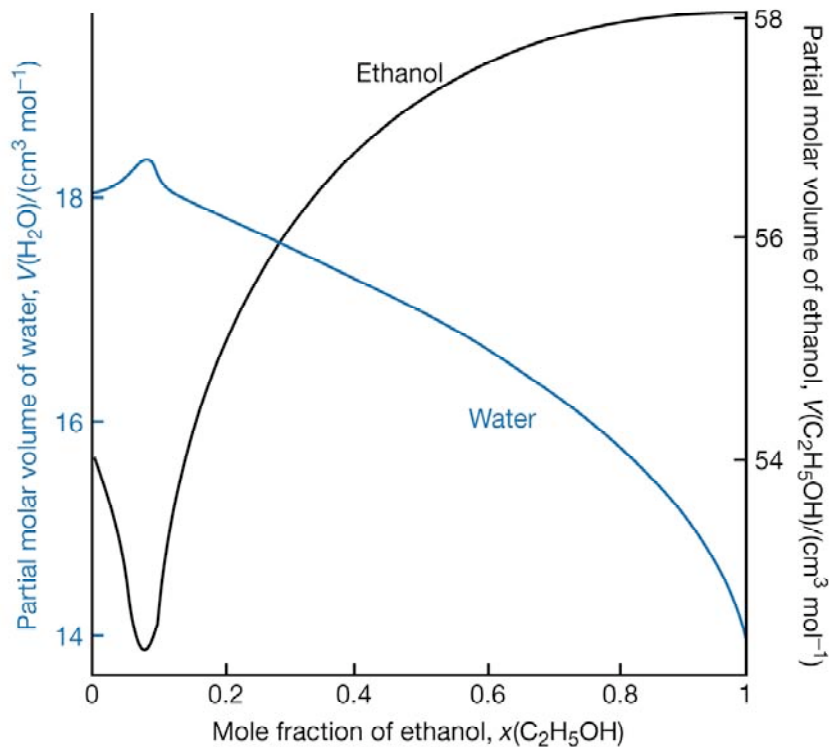
Before dealing with chemical reactions, here we consider mixtures of substances that do not react together. At this stage we deal mainly with binary mixtures (mixtures of two components, A and B). We therefore often be able to simplify equations using the relation $x_A + x_B = 1$. A restriction in this chapter – we consider mainly non-electrolyte solutions – the solute is not present as ions.

The thermodynamic description of mixtures

We already considered the partial pressure – the contribution of one component to the total pressure, when we were dealing with the properties of gas mixtures. Here we introduce other analogous partial properties.

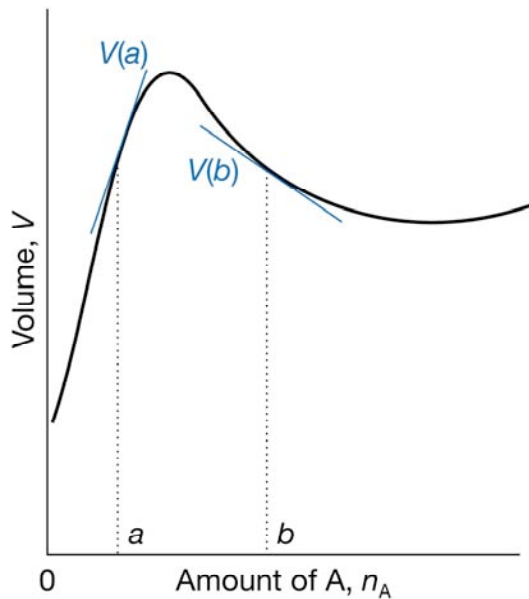
Partial molar quantities: describe the contribution (per mole) that a substance makes to an overall property of mixture.

The **partial molar volume**, V_J – the contribution J makes to the total volume of a mixture. Although 1 mol of a substance has a characteristic volume when it is pure, 1 mol of a substance can make different contributions to the total volume of a mixture because molecules pack together in different ways in the pure substances and in mixtures.



Imagine a huge volume of pure water. When a further 1 mol H_2O is added, the volume increases by 18 cm^3 . When we add 1 mol H_2O to a huge volume of pure ethanol, the volume increases by only 14 cm^3 . 18 cm^3 – the volume occupied per mole of water molecules in pure water. 14 cm^3 – the volume occupied per mole of water molecules in virtually pure ethanol. The partial molar volume of water in pure water is 18 cm^3 and the partial molar volume of water in pure ethanol is 14 cm^3 – there is so much ethanol present that each H_2O molecule is surrounded by ethanol molecules and the packing of the molecules results in the water molecules occupying only 14 cm^3 .

The partial molar volumes of the components of a mixture vary with composition because the environment of each type of molecules changes as the composition changes from pure A to pure B. This changing molecular environment and the modification of the forces acting between molecules results in the variation of the thermodynamic properties of a mixture as its composition is changed.



The formal definition of the partial molar volume: $V_J = \left(\frac{\partial V}{\partial n_J} \right)_{p,T,n'}$

n' subscript means that the amount of all other substances present is constant.

The partial molar volume is the slope of the plot of the total volume as the amount of J is changed, the pressure, temperature, and amount of the other components being constant. When the composition of the mixture is changed by the addition of dn_A of A and dn_B of B, then the total volume of the mixture changes by

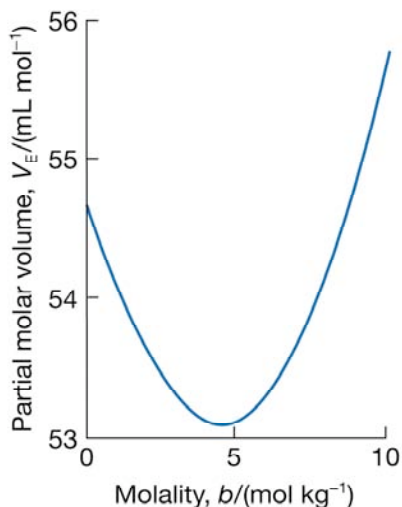
$$dV = \left(\frac{\partial V}{\partial n_A} \right)_{p,T,n_B} dn_A + \left(\frac{\partial V}{\partial n_B} \right)_{p,T,n_A} dn_B = V_A dn_A + V_B dn_B$$

Once we know the partial molar volumes V_A and V_B , we can state the total volume of the mixture:

$$V = n_A V_A + n_B V_B$$

Consider a very large sample of the mixture. When an amount n_A of A is added, the composition remains virtually unchanged but the volume increases by $n_A V_A$. Similarly, when amount n_B of B is added, the volume increases by $n_B V_B$. The total increase in volume is $n_A V_A + n_B V_B$. The mixture now occupies a larger volume but the proportions of components are still the same. Next, scoop out of this enlarged volume a sample containing n_A of A and n_B of B. Its volume is $n_A V_A + n_B V_B$. Because the volume is a state function, we could prepare the same sample simply by mixing the appropriate amount of A and B.

One method of measuring partial molar volumes is to measure the dependence of the volume on the composition and to fit the observed volume to a function of the substance. Once the function has been found, its slope can be determined at any composition by differentiation.



The total volume of an ethanol solution at 25°C containing 1.000 kg of water is found to be given by the expression

$$V/\text{mL} = 1002.93 + 54.6664b - 0.36394b^2 + 0.028256b^3$$

b – the numerical value of the molality.

Because the amount of ethanol in moles here is equal to the numerical value of the molality in moles per kg, we can write the partial molar volume of ethanol as

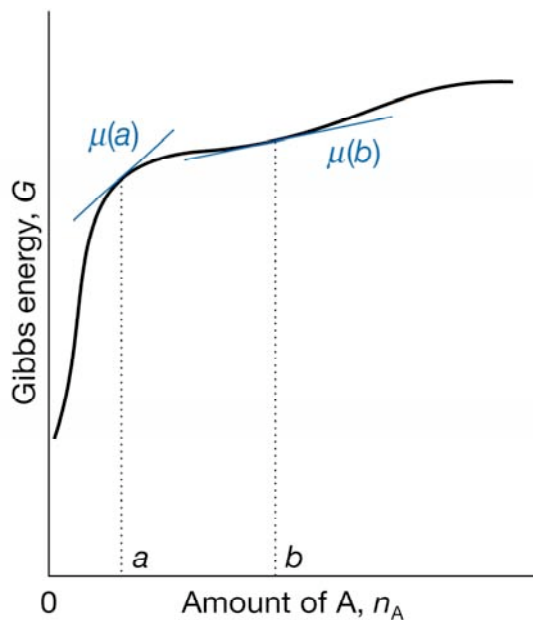
$$V_E/(\text{mL mol}^{-1}) = \left(\partial(V/\text{mL}) / \partial b \right)_{p,T,n_W} = 54.6664 - 2(0.36394)b + 3(0.028256)b^2$$

Molar volumes are always positive, but partial molar quantities need not be. Example: the limiting partial molar volume of MgSO_4 in water (its partial molar volume in the limit of zero concentration) is $-1.4 \text{ cm}^3 \text{ mol}^{-1}$, meaning that the addition of 1 mol MgSO_4 to a large volume of water results in a decrease in volume of 1.4 cm^3 : the salt breaks the open structure of water as the ions become hydrated, and it collapses slightly.

Partial molar Gibbs energies

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

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



The chemical potential is the slope of a plot of Gibbs energy against the amount of the component J, with the pressure and temperature (and the amounts of other substances) held constant. Using the same argument as for partial molar volumes, the total Gibbs energy of a binary mixture can be expressed as

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

The Gibbs energy depends on the composition, pressure, and temperature:

$$dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \dots$$

The **fundamental equation of chemical thermodynamics**

At constant pressure and temperature:

$$dG = \mu_A dn_A + \mu_B dn_B + \dots$$

Since

$$dG = dW_{\text{add,max}} \quad dW_{\text{add,max}} = \mu_A dn_A + \mu_B dn_B + \dots$$

Additional (non-expansion) work can arise from the changing composition of a system.

The wider significance of the chemical potential

$$G = U + pV - TS \qquad U = G - pV + TS$$

$$dU = -pdV - Vdp + SdT + TdS + dG$$

$$= -pdV - Vdp + SdT + TdS + (Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \dots)$$

$$= -pdV + TdS + \mu_A dn_A + \mu_B dn_B + \dots$$

At constant volume and entropy,

$$dU = \mu_A dn_A + \mu_B dn_B + \dots \quad \Rightarrow \quad \mu_J = \left(\frac{\partial U}{\partial n_J} \right)_{S,V,n'}$$

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

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

The μ_J shows how all the extensive thermodynamic properties U , H , A , G depend on the composition. This is why the chemical potential is so central to chemistry.

The Gibbs-Duhem equation

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

$$\text{Therefore,} \quad dG = \mu_A dn_A + \mu_B dn_B + n_A d\mu_A + n_B d\mu_B$$

On the other hand, at constant temperature and pressure

$$dG = \mu_A dn_A + \mu_B dn_B$$

$$\text{Thus,} \quad n_A d\mu_A + n_B d\mu_B = 0$$

This equation is a special case of the **Gibbs-Duhem equation**:
$$\sum_J n_J d\mu_J = 0$$

The significance of the Gibbs-Duhem equation – the chemical potential of one component of a mixture cannot change independently of the other components. In a binary mixture, if one partial molar quantity increases, then the other must decrease:

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

The same line of reasoning applies to all partial molar quantities. For example, where the partial molar volume of water increases, that of ethanol decreases. Moreover, a small change in the partial molar volume of A corresponds to a large change in the partial molar volume of B if n_A/n_B is large. In practice, the Gibbs-Duhem equation is used to determine the partial molar volume of one component of a binary mixture from measurements of the partial molar volume of the second component.

Example 1. Using the Gibbs-Duhem equation.

The experimental values of the partial molar volume of $K_2SO_4(aq)$ at 298 K are given by

$$V_{K_2SO_4}/(\text{cm}^3 \text{ mol}^{-1}) = 32.280 + 18.216b^{1/2}$$

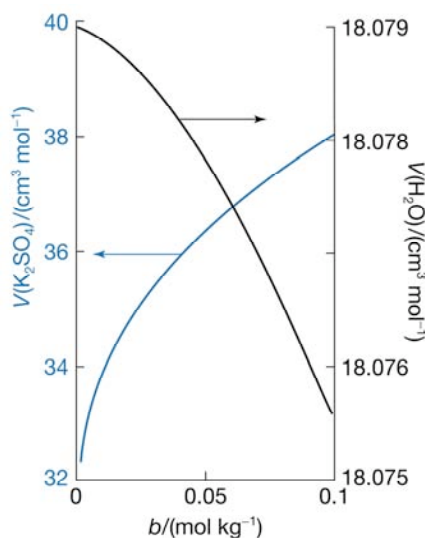
b – the numerical value of molality of K_2SO_4 . Use the Gibbs-Duhem equation to derive an expression for the partial molar volume of water in solution. The molar volume of pure water is $18.079 \text{ cm}^3 \text{ mol}^{-1}$.

A: K_2SO_4 B: H_2O $n_A dV_A + n_B dV_B = 0$

$$dV_B = -(n_A/n_B)dV_A \qquad V_B = V_B^* - \int \frac{n_A}{n_B} dV_A \qquad \frac{dV_A}{db} = 9.108b^{-1/2}$$

$$V_B = V_B^* - 9.108 \int_0^b \frac{n_A}{n_B} b^{-1/2} db \qquad \text{Molality: } b = n_A/(n_B M_B) \qquad n_A/n_B = M_B b$$

$$V_B = V_B^* - 9.108 M_b \int_0^b b^{1/2} db = V_B^* - (2/3)(9.108 M_B b^{3/2}) \qquad V_B = 18.079 - 0.1094b^{3/2}$$



The thermodynamics of mixing

The dependence of the Gibbs energy of a mixture is given by $G = n_A \mu_A + n_B \mu_B$.

At constant T and p systems tend towards lower Gibbs energy. Example: all gases mix spontaneously because the molecules of one gas can mingle with the molecules of another gas - $\Delta G < 0$. Let the amounts of two perfect gases in the two containers be n_A and n_B ; both are at temperature T and pressure p .

$$G_i = n_A \mu_A + n_B \mu_B = n_A [\mu_A^\ominus + RT \ln (p/p^\ominus)] + n_B [\mu_B^\ominus + RT \ln (p/p^\ominus)]$$

μ^\ominus - the **standard chemical potential**, the chemical potential of the pure gas at 1 bar.

If pressure is measured in bar, $p^\ominus = 1$ bar and $G_i = n_A [\mu_A^\ominus + RT \ln p] + n_B [\mu_B^\ominus + RT \ln p]$

When the partition is removed, the total pressure remains the same, but, according to Dalton's law, the partial pressures fall to $x_A p$ and $x_B p$, $x_A = n_A/n$ and $x_B = n_B/n$.

$$G_f = n_A [\mu_A^\ominus + RT \ln x_A p] + n_B [\mu_B^\ominus + RT \ln x_B p]$$

$$\Delta_{\text{mix}} G = G_f - G_i$$

$$\ln xp - \ln p = \ln(xp/p) = \ln x$$

$$\Delta_{\text{mix}} G = RT[n_A \ln x_A + n_B \ln x_B] = nRT[x_A \ln x_A + x_B \ln x_B]$$

Because both x_A and x_B are less than 1, the two logarithms are negative - $\Delta_{\text{mix}} G < 0$.

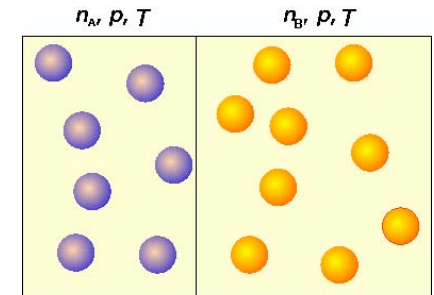
Perfect gases mix spontaneously in all proportions.

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

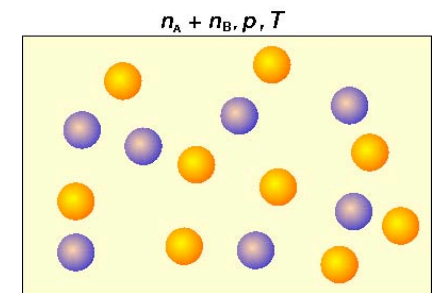
$$\Delta_{\text{mix}} H = 0 \quad \Delta_{\text{mix}} S = -nR[x_A \ln x_A + x_B \ln x_B] > 0$$

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

There is no change in enthalpy when two perfect gases mix because there are no interactions between the molecules. There is an increase in entropy because the mixed gas is more disordered than the unmixed gases - the increase in entropy is the 'driving force' of the mixing.

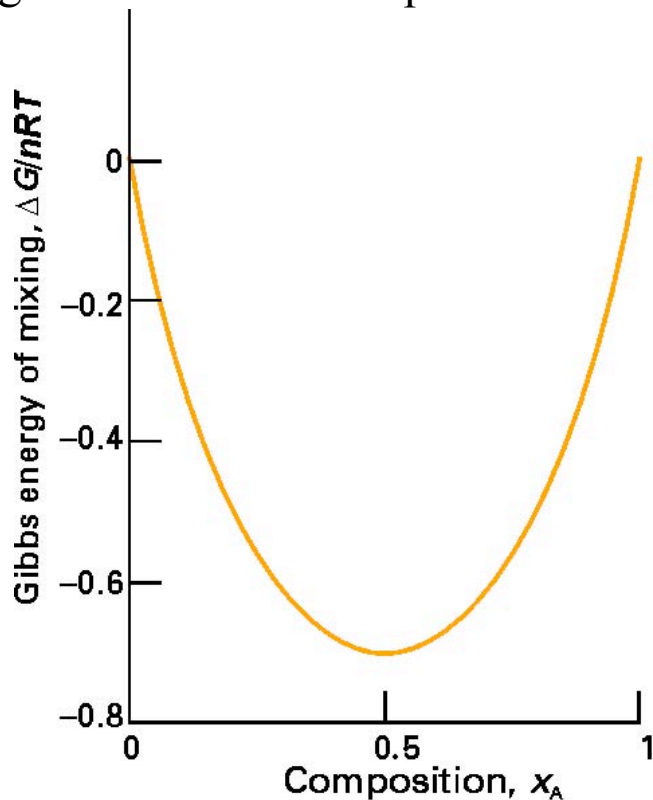


(a)

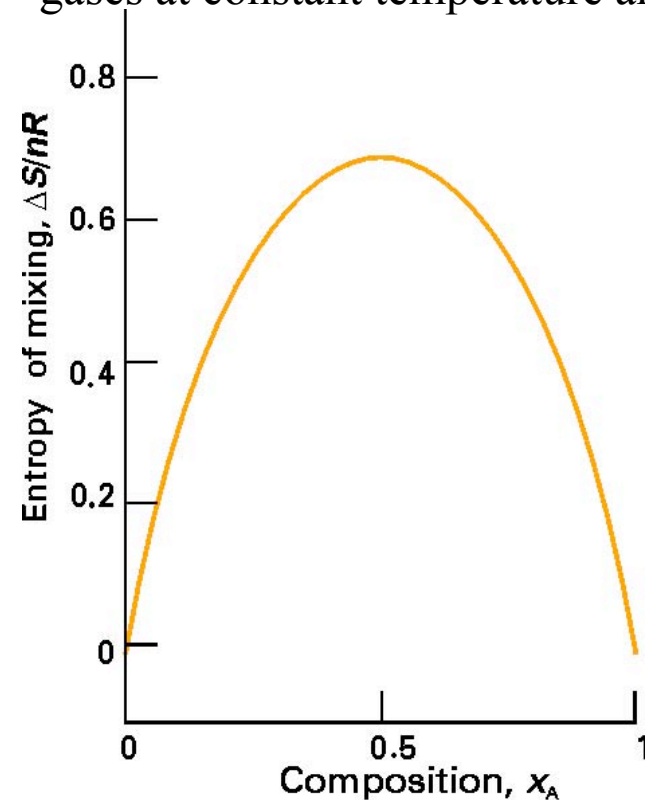


(b)

The variation of the Gibbs energy of mixing with composition for two perfect gases at constant temperature and pressure



The variation of the entropy of mixing with composition for two perfect gases at constant temperature and pressure



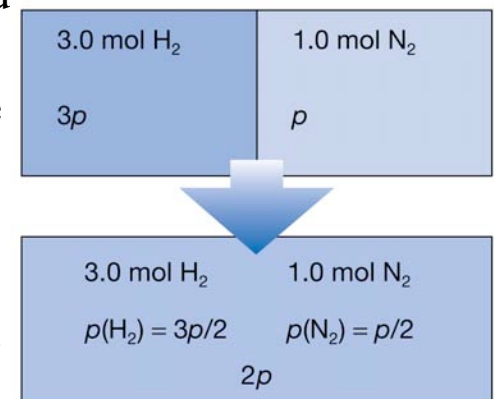
Example 2. Calculating a Gibbs energy of mixing. A container is divided into two equal compartments, one containing 3.0 mol H_2 and the other 1.0 mol N_2 both at 25°C. Calculate the Gibbs energy of mixing when the partition is removed. Assume perfect behavior.

$$G_i = (3.0 \text{ mol})[\mu^\ominus(H_2) + RT \ln 3p] + (1.0 \text{ mol})[\mu^\ominus(N_2) + RT \ln p]$$

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

$$\Delta_{\text{mix}} G = (3.0 \text{ mol})RT \ln(1/2) + (1.0 \text{ mol})RT \ln(1/2) = -(4.0 \text{ mol}) RT \ln 2$$

$$\Delta_{\text{mix}} G = -6.9 \text{ kJ}$$



The chemical potentials of liquids

Ideal solutions

We need an expression for the chemical potential of a substance in a liquid solution. We can anticipate that the chemical potential of a species should increase with concentration.

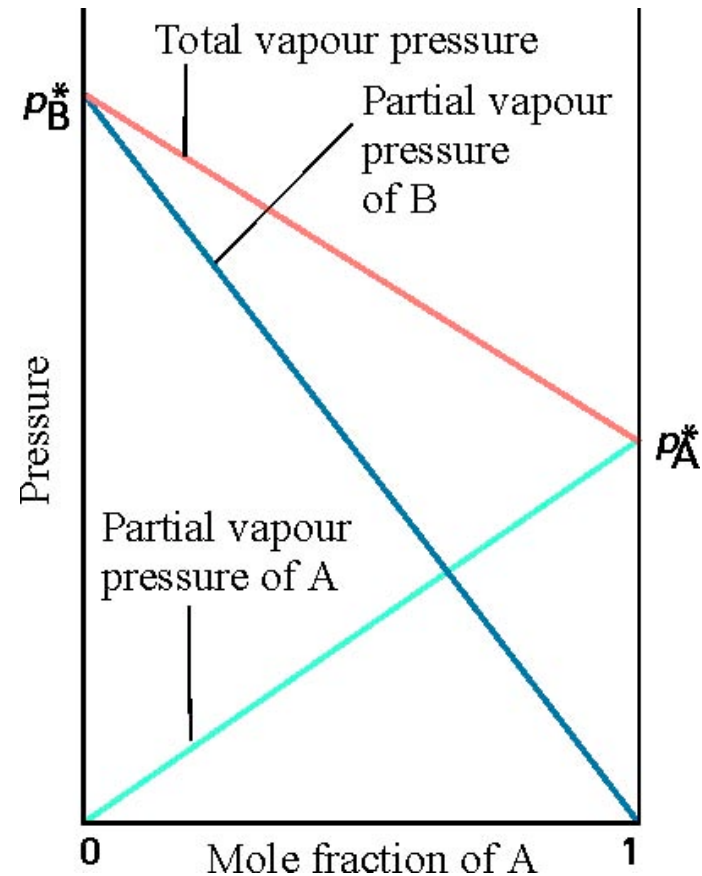
French chemist Raoult measured the **partial vapor pressure**, p_J , of each component in dynamic equilibrium with the solution and established **Raoult's law**:

The partial vapor pressure of a substance in a mixture is proportional to its mole fraction in the solution and its vapor pressure when pure.

$$p_J = x_J p_J^*$$

p_J^* - the vapor pressure of the pure substance.

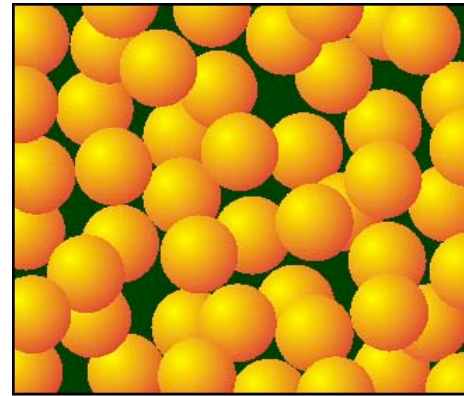
The partial vapor pressures of the two components of an ideal binary mixture are proportional to the mole fractions of the components in the liquid. The total pressure of the vapor is the sum of the two partial vapor pressures.



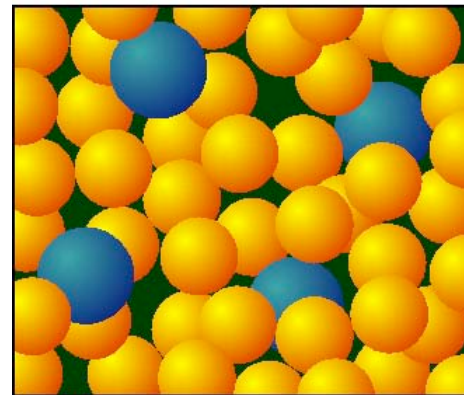
The molecular origin of Raoult's law:

The effect of the solute on the entropy of solution.

In the pure solvent, the molecules have a certain disorder and a corresponding entropy; the vapor pressure then represents the tendency of the system and its surroundings to reach a higher entropy (through vaporizing). When a solute is present, the solution has a greater disorder than the pure solvent because we cannot be sure that a molecule chosen in 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 – the vapor pressure of the solvent in the solution is lower than that of the pure solvent.



(a)



(b)

The theoretical importance of Raoult's law – relates vapor pressure to composition.

The chemical potential of a solvent

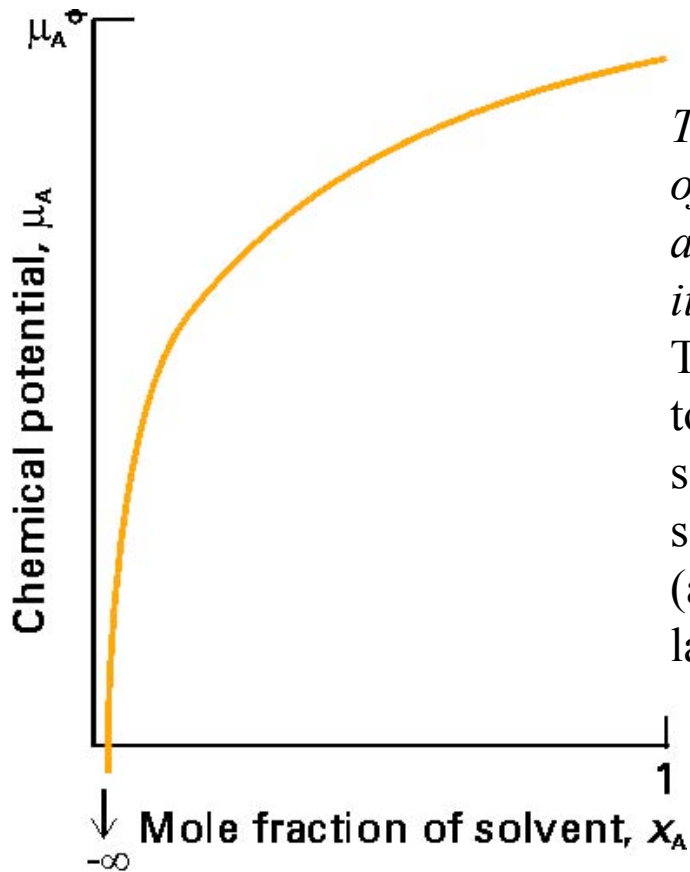
When a liquid A in a mixture is in equilibrium with its vapor at a partial pressure p_A , the chemical potential of the two phases are equal:

$$\mu_A(l) = \mu_A(g) \quad \mu_A(l) = \mu_A^\ominus(g) + RT \ln p_A \quad p_A = x_A p_A^* - \text{Raoult's law}$$

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

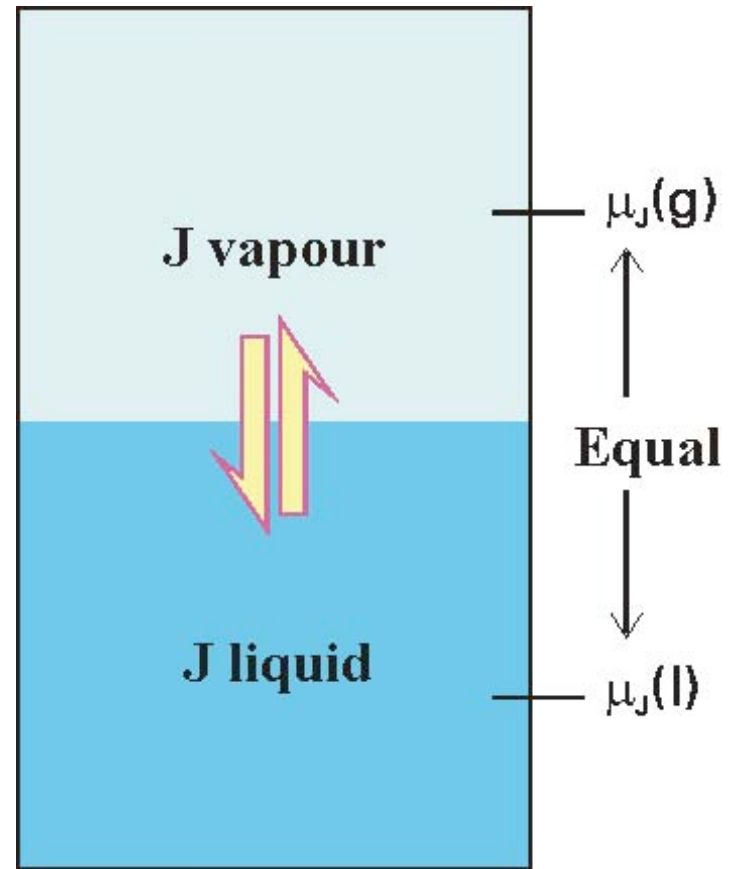
$\mu_A^\ominus(g)$ and $RT \ln p_A^*$ – independent of the composition of the mixture and we can write them as the constant μ_A^\ominus – the standard chemical potential of the liquid.

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



The chemical potential of a solvent is lower in a solution than when it is pure.

This behavior is likely to be shown by a dilute solution in which the solvent is almost pure (and obeys Raoult's law).



Molecular interpretation of Raoult's law (2)

The origin of Raoult's law can be also understood in molecular terms by considering the rates at which molecules leave and return to the liquid. The presence of a second component reduces the rate at which A molecules leave the surface but does not inhibit the rate at which they return.

The rate at which A molecules leave the surface is proportional to their number at the surface, which in turn is proportional to the mole fraction of A:

$$\text{rate of vaporization} = kx_A$$

The rate at which molecules condense is proportional to their concentration in the gas phase, which in turn is proportional to their partial pressure:

$$\text{rate of condensation} = k'p_A$$

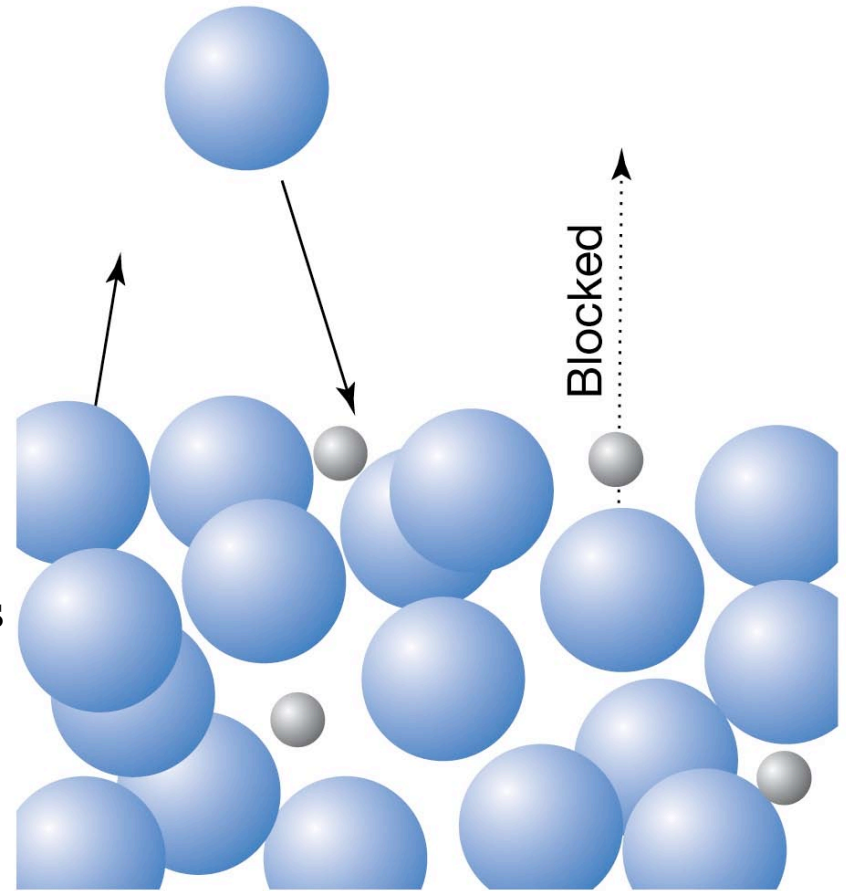
At equilibrium the two rates are equal:

$$kx_A = k'p_A \quad p_A = (k/k')x_A$$

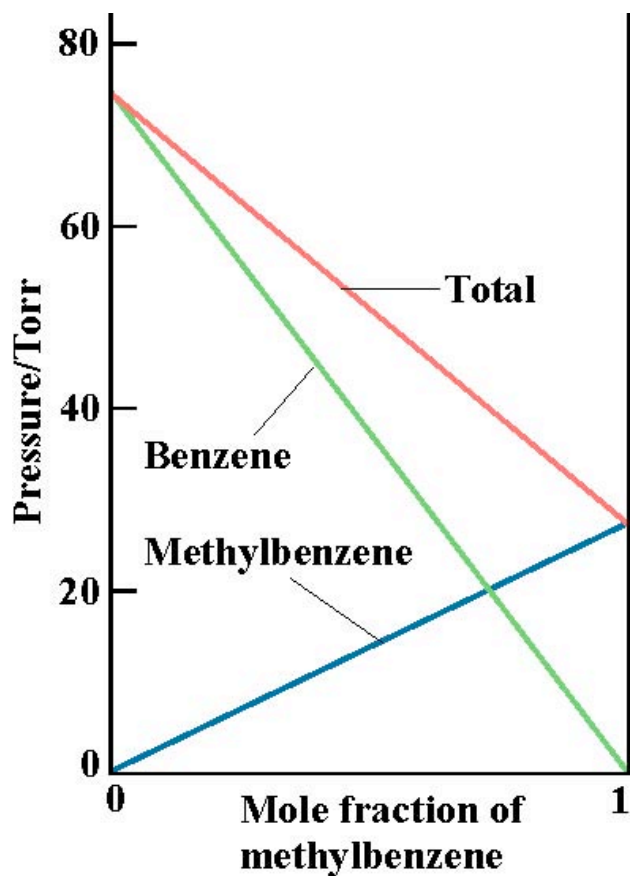
For pure liquid, $x_A = 1$, so $p_A^* = k/k'$

Therefore,

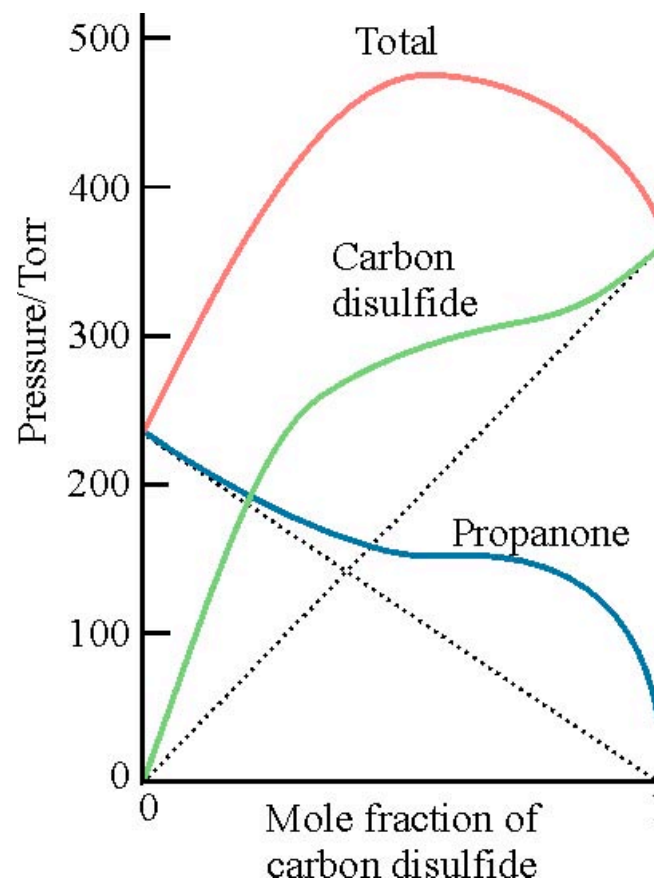
$$p_A = p_A^* x_A$$



A hypothetical solution that obeys Raoult's law throughout the composition range from pure A to pure B – **ideal solution**. The law is most reliable when the components have similar molecular shape and are held together in the liquid by similar types and strengths of intermolecular forces: a mixture of two structurally similar hydrocarbons – benzene and methylbenzene (toluene).



No mixture is perfectly ideal and all real mixtures show deviations from Raoult's law. The deviations are small for the component of the mixture that is in large excess (the solvent) and become smaller as the concentration of solute decreases. Raoult's law is reliable for the solvent when the solution is very dilute – a *limiting law*, strictly valid only in the limit of zero concentration.



Ideal-dilute solutions

Raoult's law provides a good description of the vapor pressure of the *solvent* in a very dilute solution. We cannot expect it to be a good description of the vapor pressure of the solute – a solute in dilute solution is very far from being pure.

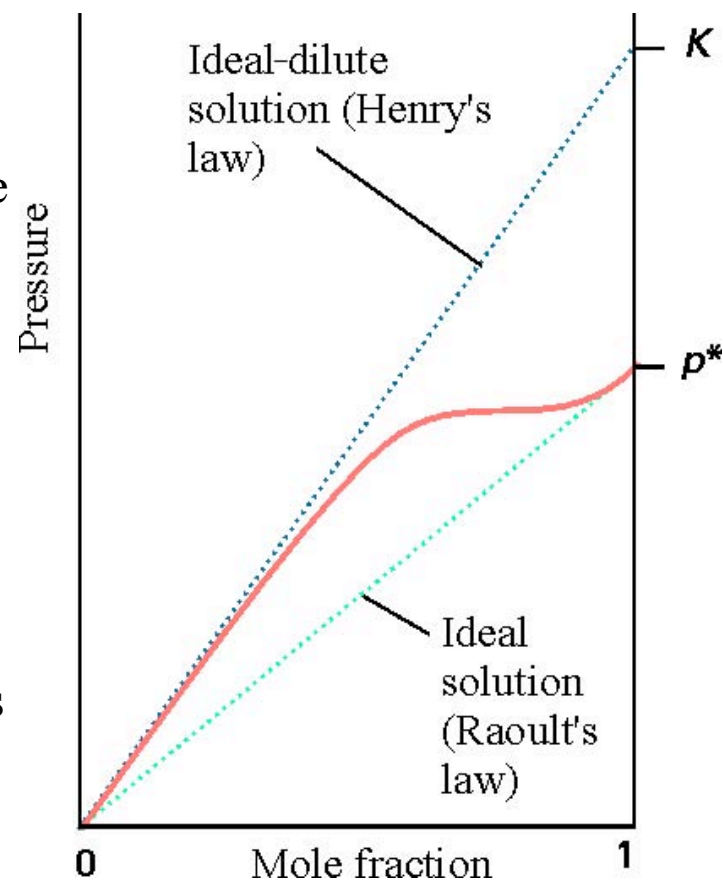
In a dilute solution, each solute molecule is surrounded by nearly pure solvent, so its environment is quite unlike that in pure solute and it is very unlikely its vapor pressure will be related to that of pure solute. It is found experimentally that in dilute solutions the vapor pressure of the solute is proportional to its mole fraction, just as for the solvent. Unlike the solvent, the constant of proportionality is not the vapor pressure of the pure solute.

Henry's law: *The vapor pressure of a volatile solute B is proportional to its mole fraction in a solution:*

$$p_B = x_B K_B$$

K_B – **Henry's law constant** – characteristic of the solute and chosen so that the straight line is tangent to the experimental curve at $x_B = 0$.

When a component (the solvent) is almost pure, it behaves in accord with Raoult's law and has a vapor pressure that is proportional to the mole fraction in the liquid mixture, and a slope p^* , the vapor pressure of the pure substance. When the same substance is the minor component (the solute), its vapor pressure is still proportional to its molar fraction, but the constant of proportionality is now K .



Example 3. Verifying Raoult's and Henry's laws

The partial vapor pressures of each component in a mixture of propanone (acetone, A) and trichloromethane (chloroform, C) were measured at 35°C with the following results:

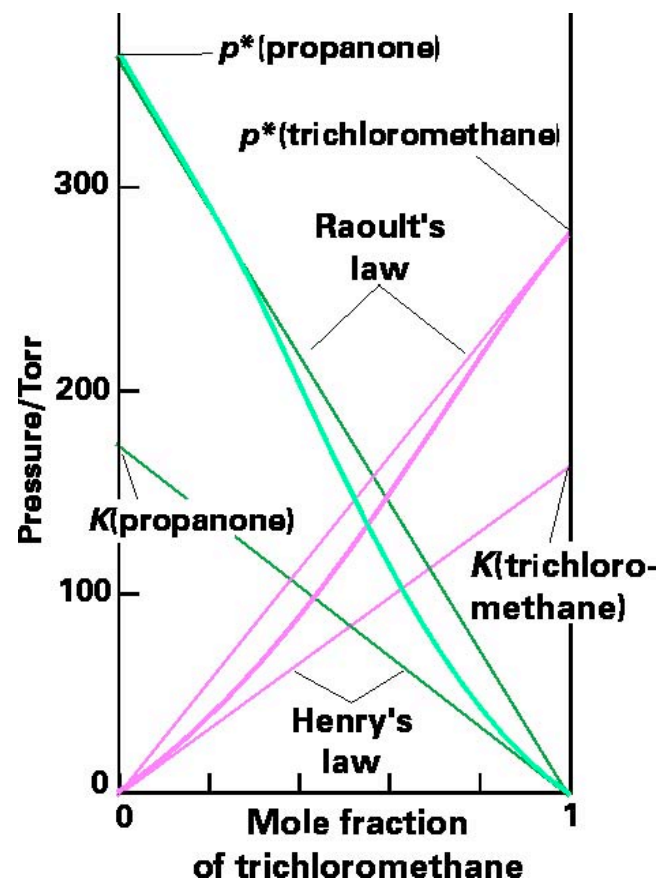
x_C	0	0.20	0.40	0.60	0.80	1
p_C/Torr	0	35	82	142	219	293
p_A/Torr	347	270	185	102	37	0

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.

We need to plot the partial vapor pressures against mole fraction. To verify Raoult's law, we compare the data to the straight line $p_J = x_J p_J^*$ for each component in the region in which it is in excess and therefore acting as the solvent. We verify Henry's law by finding a straight line $p_J = x_J K_J$ that is tangent to each partial vapor pressure at low x_J where the component can be treated as the solute.

In this case, the plot shows that Henry's law requires $K_A = 175 \text{ Torr}$ and $K_C = 165 \text{ Torr}$.

The data deviate from both Raoult's and Henry's laws for even quite small departures from $x = 1$ and $x = 0$, respectively.



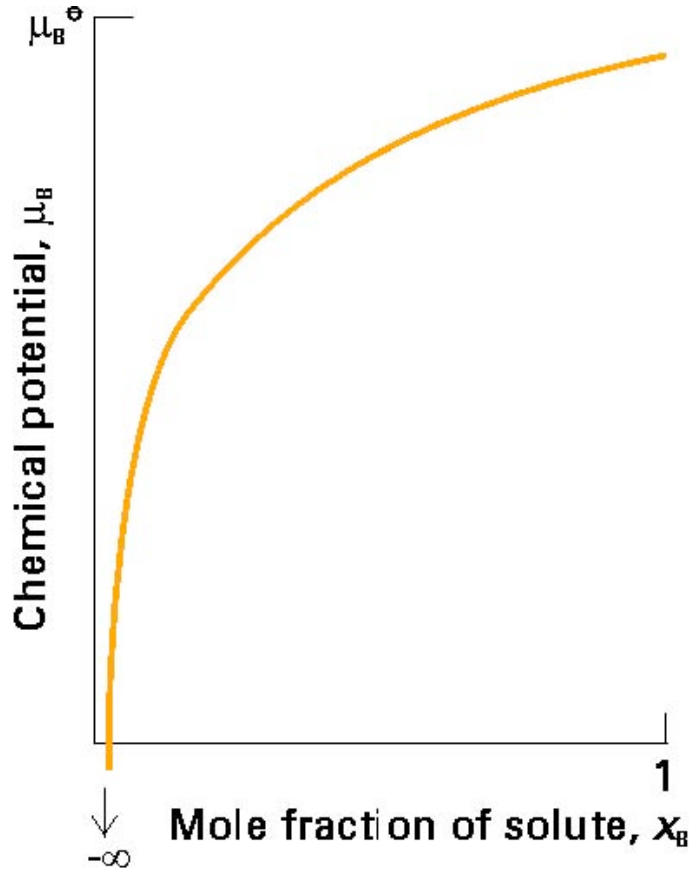
Henry's law lets us write an expression for the chemical potential of a solute in a solution:

$$\mu_B = \mu_B^\ominus + RT \ln x_B$$

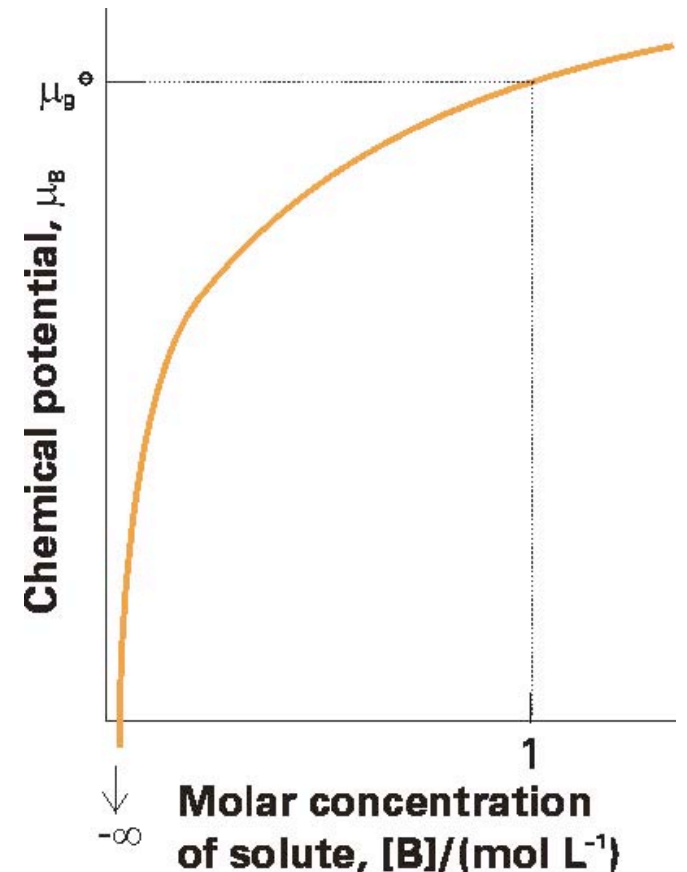
This expression applies when Henry's law is valid, in very dilute solutions. The chemical potential of the solute has its standard value when it is pure ($x_B = 1$) and a smaller value when dissolved ($x_B < 1$).

We often express the composition of a solution in terms of molar concentration of the solute, $[B]$, rather than as a mole fraction. The molar fraction and the molar concentration are proportional to each other in dilute solutions: $x_B = \text{constant} \times [B]$.

$$\mu_B = \mu_B^\ominus + RT \ln(\text{constant}) + RT \ln [B] \quad \mu_B = \mu_B^{\ominus'} + RT \ln [B]$$



The chemical potential of the solute has its standard value when the molar concentration of the solute is 1 mol L^{-1} .



The Henry's law constants for many gases have been measured and are available in tables. They are often used in calculations relating to gas solubilities, as the estimation of the concentration of O₂ in natural waters or the concentration of carbon dioxide in blood plasma. To apply Henry's law, we treat gas as the solute and use its partial pressure above the solvent to calculate the mole fraction in the solution:

$$x_B = p_B/K_B$$

Example 4. Using Henry's law.

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

The mole fraction of solute is given by Henry's law. We need to calculate the mole fraction that corresponds to the stated pressure and then convert that mole fraction to a molar concentration. To do that we calculate the amount of O₂ dissolved in 1.00 kg of water (about 1.0 L of water). The solution is dilute, so the expression for the mole fraction can be simplified.

$$x_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_{H_2O}} \approx \frac{n_{O_2}}{n_{H_2O}} \quad n_{O_2} \approx x_{O_2} n_{H_2O} = \frac{p_{O_2} n_{H_2O}}{K}$$

$$n_{O_2} = (160 \text{ Torr}) \times (55.5 \text{ mol}) / (3.3 \times 10^7 \text{ Torr}) = 2.69 \times 10^{-4} \text{ mol}$$

The molality of the saturated solution is therefore $2.69 \times 10^{-4} \text{ mol kg}^{-1}$, corresponding to a molar concentration $2.7 \times 10^{-4} \text{ mol L}^{-1}$.

Henry's law constants for gases in blood and fats are important for respiration, especially when the partial pressure of oxygen is abnormal (mountaineering and diving). Decreasing atmospheric pressure – lower molar solubility of O₂ in blood – respiration is impaired at high altitudes. Higher pressure – higher O₂ solubility – a diver cannot return to the surface too rapidly to avoid the formation of O₂ bubbles in the bloodstream.

The properties of solutions. Liquid mixtures

Ideal solutions

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

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

After the mixing:

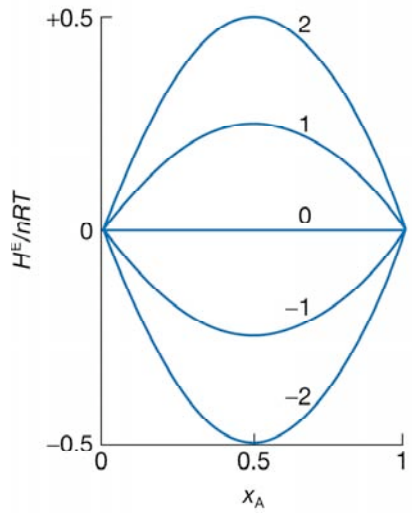
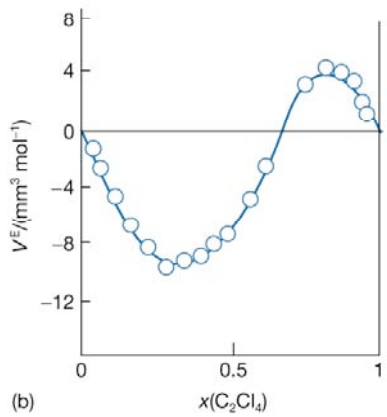
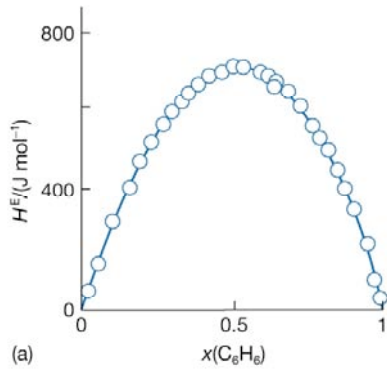
$$G_f = n_A \{ \mu_A^* + RT \ln x_A \} + n_B \{ \mu_B^* + RT \ln x_B \}$$

$$\Delta_{\text{mix}} G = nRT \{ x_A \ln x_A + x_B \ln x_B \} \quad \text{with } n = n_A + n_B$$

$$\Delta_{\text{mix}} S = -nR \{ x_A \ln x_A + x_B \ln x_B \} \quad \Delta_{\text{mix}} H = 0$$

The driving force for mixing is the increasing entropy of the system as the molecules mingle and the enthalpy of mixing is zero. However, 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 pure liquids.

Real solutions – A-A, A-B, and B-B interactions are all different. Enthalpy changes when liquids mix in real solutions and there is also an additional contribution to entropy arising from the way in which the molecules of one type might cluster together instead of mingling freely with the others. If the enthalpy change is large and positive or if the entropy change is negative (due to a reorganization of the molecules resulting in an ordered mixture), then the Gibbs energy might be positive for mixing. Then, separation is spontaneous and the liquids may be immiscible. Or, the liquids may be partially miscible (i.e., miscible over a certain range of compositions).



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 and the function for an ideal solution.

The **excess entropy**: $S^E = \Delta_{\text{mix}}S - \Delta_{\text{mix}}S^{\text{ideal}}$

The excess enthalpy and volume are both equal to the observed enthalpy and volume of mixing, because the ideal values are zero.

Deviations of the excess energies from zero indicate the extent to which the solutions are nonideal. A useful model – the **regular solution**: $H^E \neq 0$, $S^E = 0$. Two kinds of molecules are distributed randomly (as in ideal solution) but have different energies of interaction with each other:

(a) H^E for benzene/cyclohexane: the mixing is endothermic;

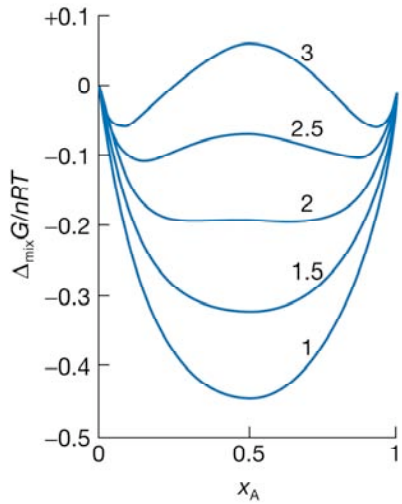
(b) V^E for tetrachloroethane/cyclopentane: there is a contraction at low tetrachloroethane mole fractions, but an expansion at high mole fractions.

Suppose that the excess enthalpy depends on composition as

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

β - a parameter: $\beta = w/RT$, w – the energy of AB interactions relative to AA and BB interactions. The plot of the function given by this equation resembles the experimental curve for H^E . If $\beta < 0$, mixing is exothermic and the solute-solvent

interactions are more favorable than the solvent-solvent and solute-solute interactions. $\beta > 0$ – endothermic mixing.



Because the entropy of mixing has its ideal value for a regular solution, the excess Gibbs energy is equal to the excess enthalpy.

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

$\Delta_{\text{mix}}G$ varies with composition differently for different values of β . For $\beta > 2$ the graph shows two minima separated by a maximum – the system will separate spontaneously into two phases with compositions corresponding to the two minima.

Colligative properties

An ideal solute has no effect on the enthalpy of solution but does affect the entropy by introducing a degree of disorder that is not present in the pure solvent – we can expect a solute to modify the physical properties of the solution.

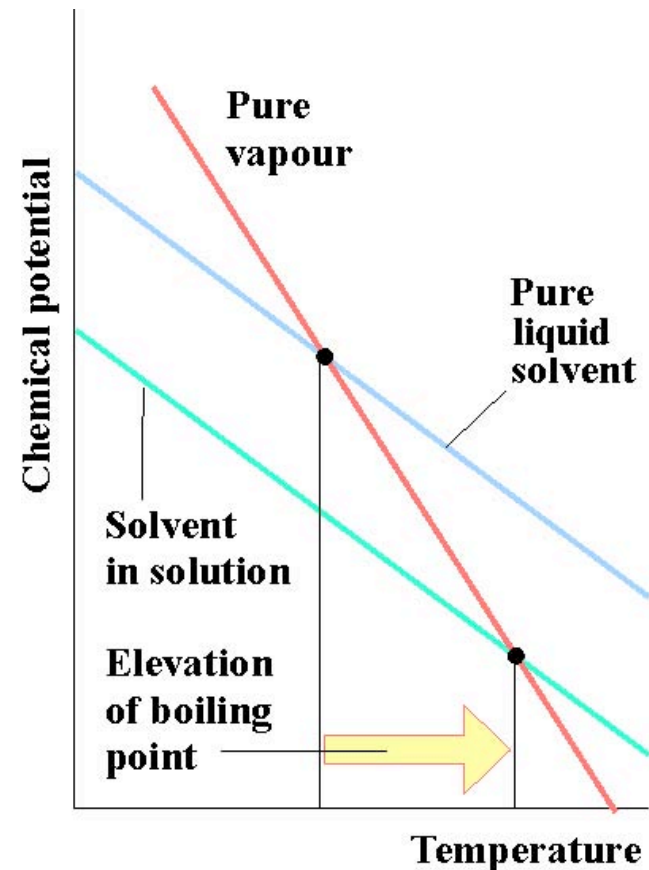
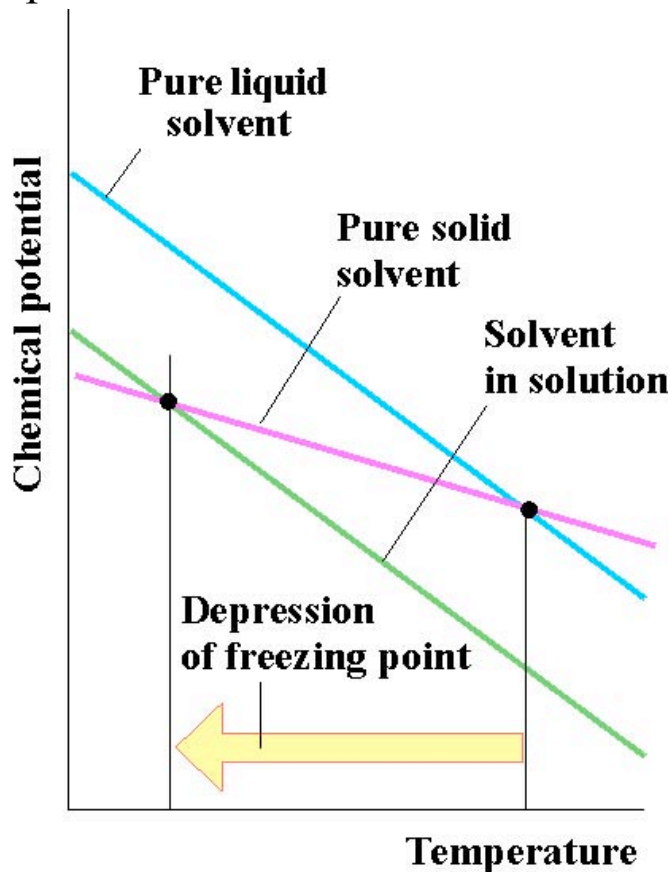
In addition to lowering the vapor pressure of the solvent, a nonvolatile solute has three main effects: (1) it raises the boiling point of the solution; (2) it lowers the freezing point; and (3) it gives rise to an osmotic pressure.

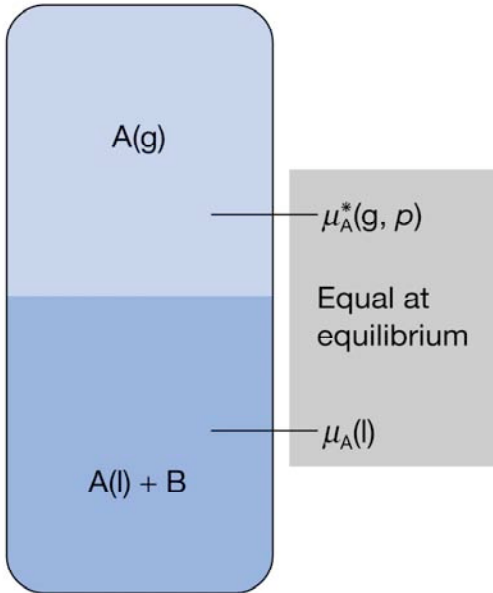
All these properties originate from changes in the disorder of the solvent and the increase in disorder is independent of the species involved – they depend only on the number of solute molecules present, not their chemical identity.

Colligative properties (‘depending on collection’)

In our consideration, we assume throughout that the solute is not volatile, so it does not contribute to the vapor. We also assume that the solute does not dissolve in the solid solvent: the pure solid solvent separates when the solution is frozen.

The origin of colligative properties is the lowering of chemical potential of the solvent by the presence of solute: $\mu_A^* + RT \ln x_A < \mu_A^*$ because $x_A < 1$ and $\ln x_A$ is negative. The freezing and boiling points correspond to the temperatures at which the graph of the molar Gibbs energy of the liquid intersect the graphs of the molar Gibbs energy of the solid and gas phases, respectively. We are dealing with mixtures – we have to think of the *partial* molar Gibbs energy (the chemical potential) of the solvent. The presence of a solute lowers the chemical potential of the liquid but, because the vapor and solid remain pure, their chemical potentials remain unchanged. As a result, the freezing point moves to lower values and the boiling point moves to higher values. The freezing point is depressed, the boiling point is elevated, and the liquid exists over a wider range of temperatures.





The elevation of boiling point

The heterogeneous equilibrium – boiling between the solvent vapor and the solvent in solution at 1 atm. A – solvent, B – solute.

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

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

$$\Delta T = Kx_B \quad K = \frac{RT^{*2}}{\Delta_{vap}H} \quad \ln(1 - x_B) = \ln x_A = \frac{\mu_A^*(g) - \mu_A^*(l)}{RT} = \frac{\Delta_{vap}G}{RT}$$

$\Delta_{vap}G$ – the Gibbs energy of vaporization of the pure solvent (A).

$$\Delta_{vap}G = \Delta_{vap}H - T\Delta_{vap}S \quad \ln(1 - x_B) = \frac{\Delta_{vap}H}{RT} - \frac{\Delta_{vap}S}{R}$$

When $x_B = 0$, the boiling point is that of the pure liquid is T^* :

$$\ln 1 = \frac{\Delta_{vap}H}{RT^*} - \frac{\Delta_{vap}S}{R} = 0$$

The difference between the two equations gives

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

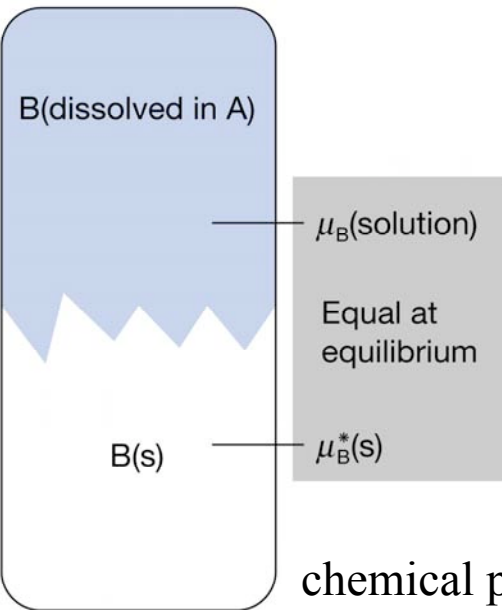
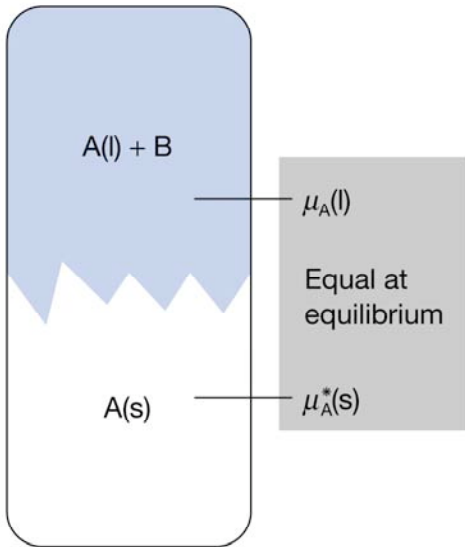
Suppose that $x_B \ll 1$, then $\ln(1 - x_B) \approx -x_B$

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

Because $T \approx T^*$

$$\frac{1}{T^*} - \frac{1}{T} = \frac{T - T^*}{TT^*} \approx \frac{\Delta T}{T^{*2}}$$

$$x_B = \frac{\Delta_{vap}H\Delta T}{RT^{*2}} \quad \Delta T = \frac{RT^{*2}}{\Delta_{vap}H} x_B$$



The equation makes no reference to the solute identity, only to its mole fraction – the elevation of boiling point is a colligative property. For practical applications: the mole fraction of B is proportional to its molality, b , so

$$\Delta T = K_b b$$

K_b – the empirical **ebullioscopic constant** of the solvent.

The depression of freezing point

The heterogeneous equilibrium – 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:

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

Similar to the case of boiling, we can derive that $\Delta T = K' x_B$ $K' = \frac{RT^{*2}}{\Delta_{fus}H}$

where $\Delta T = T^* - T$, the freezing point depression, $\Delta_{fus}H$ – the enthalpy of fusion.
 $\Delta T = K_f b$ K_f – the **cryoscopic constant**.

Solubility

When a solid solute is in a contact with a solvent, it dissolves until the solution is saturated. Saturation is a state of equilibrium between the undissolved solute with the dissolved solute. In a saturated solution the

chemical potential of the pure solid solute, $\mu_B^*(s)$, and the chemical potential of B in solution, μ_B , are equal:

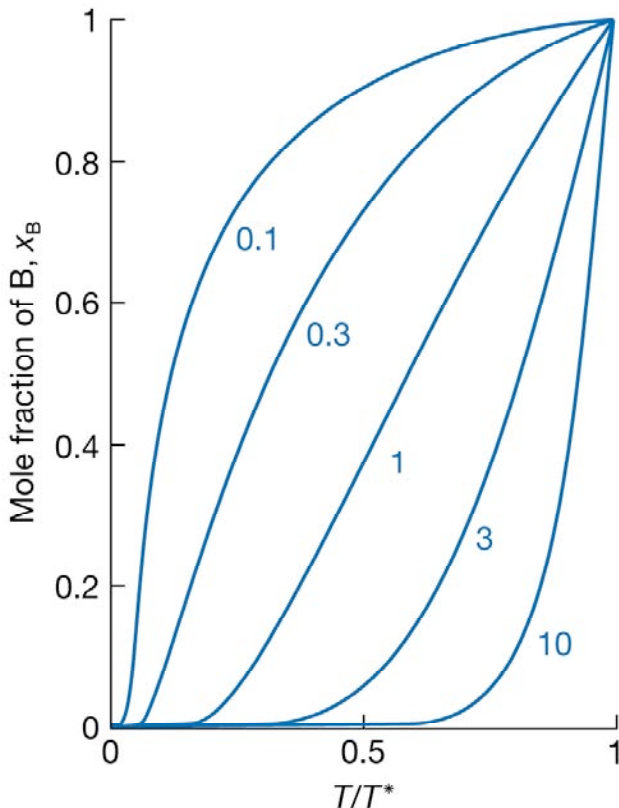
$$\mu_B = \mu_B^*(l) + RT \ln x_B \quad \mu_B^*(s) = \mu_B^*(l) + RT \ln x_B$$

In this case, we want to find the mole fraction of B in solution at equilibrium when the temperature is T .

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

At the melting point of the solute, T^* , we know that $\Delta_{fus}G = 0$ and so $\Delta_{fus}G/RT^* = 0$ and this term can be added to the right hand side of the equation:

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



The variation of solubility with temperature: individual curves are labeled with the value of $\Delta_{fus}H/RT^*$.

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 temperatures.

However, the detailed content of the equation should not be treated too seriously because it is based on highly questionable approximation – ideality of the solution. So, this approximation fails to predict that solutes will have different solubilities in different solvents, as no solvent properties appear in the expression.

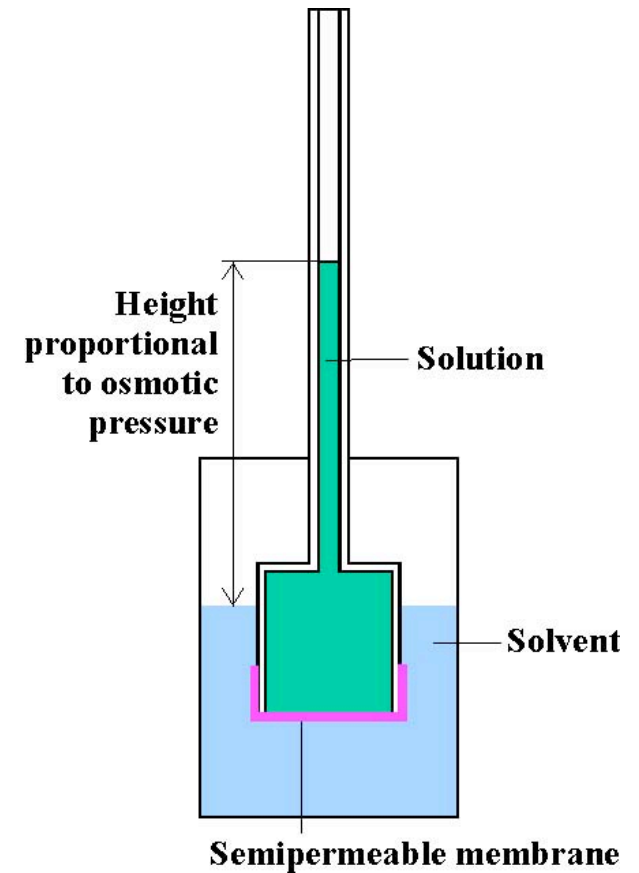
Osmosis

The passage of a pure solvent into a solution separated from it by a **semipermeable membrane** – a membrane that is permeable to the solvent but not to the solute. The membrane might have microscopic holes that are large enough to allow water molecules to pass through but not ions or carbohydrate molecules with their bulky coating of hydrating water molecules.

The **osmotic pressure**, Π - the pressure that must be applied to the solution to stop the inward flow of solvent.

Examples: transport of fluids through cell membranes, **osmometry** – the determination of molar mass by measurement of osmotic pressure, study of the binding of small molecules to proteins.

The pressure opposing the passage of solvent into the solution arises from the hydrostatic pressure of the column of solution that the osmosis itself produces. This column is formed when the pure solvent flows through the membrane into the solution and pushes the column of solution higher up to the tube. Equilibrium is reached when the downward pressure exerted by the column is equal to the upward osmotic pressure.



The van't Hoff equation

The thermodynamic treatment of osmosis – equilibrium conditions:

$$\mu_A(\text{solvent in the solution at pressure } p+\Pi) = \mu_A(\text{pure solvent at pressure } p)$$

$\mu_A^*(p)$ – the chemical potential of the pure solvent at the atmospheric pressure p .

$\mu_A(x_A, p+\Pi)$ – the chemical potential of the solvent in the solution (lowered by the solute but raised on account of the greater pressure acting on the solution).

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

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

The effect of pressure on incompressible liquid:

$$\Delta G_m = V_m \Delta p$$

$$\mu_A^*(p+\Pi) = \mu_A^*(p) + V_A \Delta p$$

$$-RT \ln x_A = \Pi V_A$$

$$x_A = 1 - x_B \quad \ln(1-x) \cong -x$$

$$RT x_B \cong \Pi V_A$$

When the solution is dilute, $x_B = n_B/n \cong n_B/n_A$

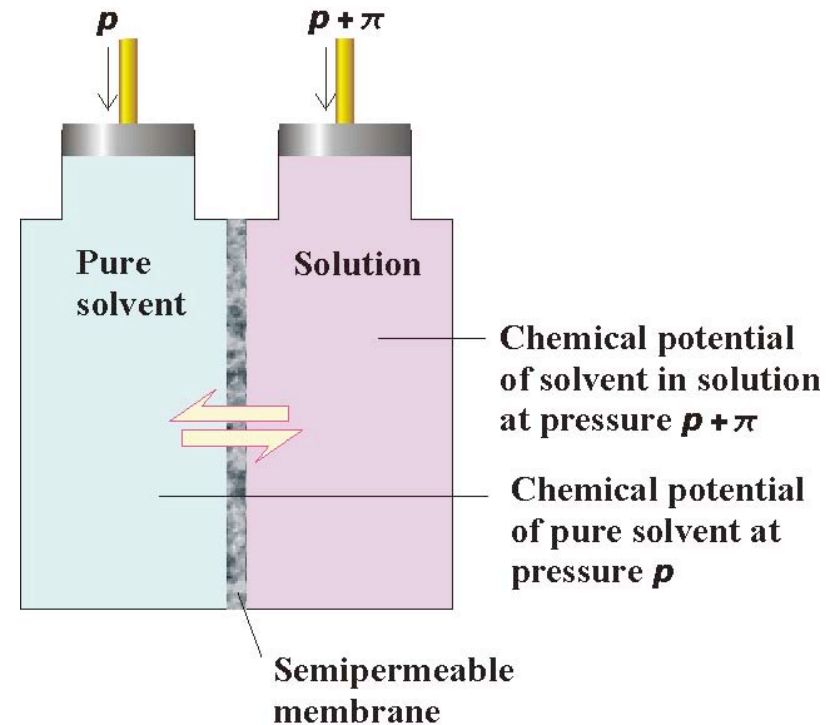
$$n_A V_A \cong V$$

$$n_B RT \cong \Pi V$$

The van't Hoff equation for the osmotic pressure

$$n_B/V = [B]$$

$$\Pi \cong [B]RT$$



Osmometry

The measurement of molar mass of proteins and synthetic polymers from the osmotic pressure of their solutions.

The solutions are far from ideal – we assume that the van't Hoff equation is only the first term of an expansion:

$$\Pi = [B]RT\{1 + B[B] + \dots\}$$

Analogical to the virial equation of state for a real gas.

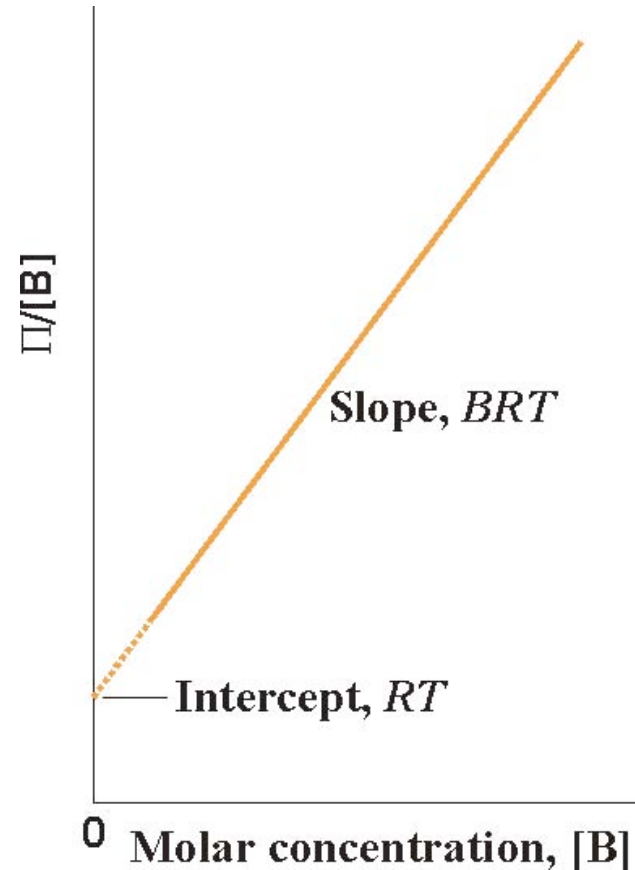
B – the osmotic virial coefficient.

$$\Pi/[B] = RT + BRT[B] + \dots$$

RT – intercept

BRT – slope

We can find the molar mass of the solute B by measuring the osmotic pressure at a series of mass concentrations and making a plot of $\Pi/[B]$ against $[B]$.



Using osmometry to determine molar mass

The osmotic pressures of solutions of an enzyme in water at 298 K. The pressures are expressed in terms of the heights of solution (of density $\rho = 0.9998 \text{ g cm}^{-3}$).

$c/(\text{g dm}^{-3})$	1.00	2.00	4.00	7.00	9.00
h/cm	0.28	0.71	2.01	5.17	8.00

We need to express the equation for $\Pi/[B]$ in terms of the mass concentration, c , and the height of the solution h :

$$\Pi = \rho gh$$

$$c = (\text{mass/volume}) = (\text{mass/amount}) \times (\text{amount/volume})$$

$$c = M \times [B]$$

$$\rho gh / (c/M) = RT + BRTc/M + \dots$$

$$h/c = RT/\rho gM + (RTB/\rho gM^2)c + \dots$$

By plotting h/c against c , the results should fall on a straight line with intercept $RT/\rho gM$ on the vertical axis at $c = 0$.

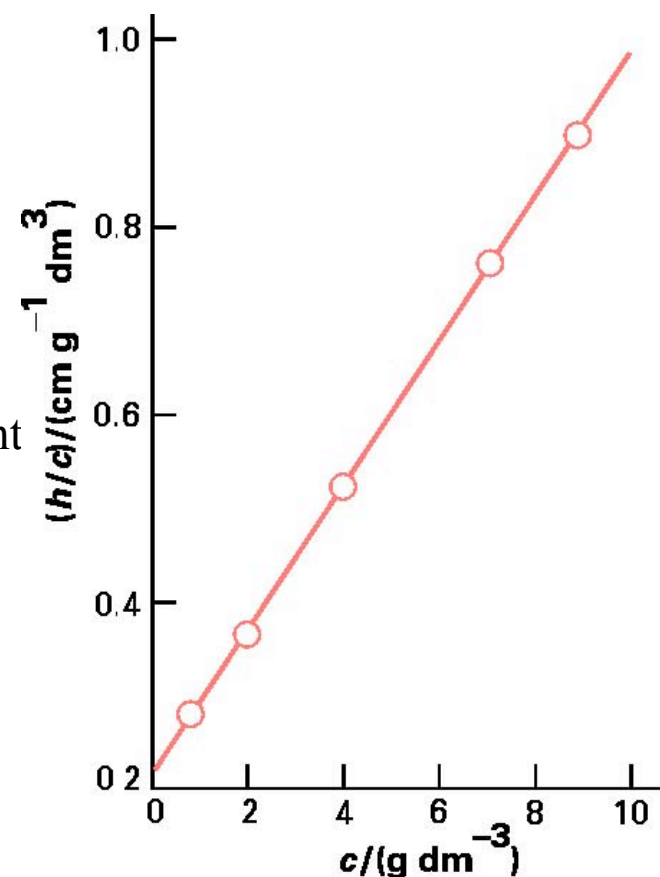
$c/(\text{g dm}^{-3})$	1.00	2.00	4.00	7.00	9.00
$h/\text{cm} / c/\text{g dm}^{-3}$	0.28	0.36	0.503	0.739	0.889

The intercept is found at

$$h/c = 0.21 \text{ cm g}^{-1} \text{ dm}^3 = 2.1 \times 10^{-3} \text{ m}^4 \text{ kg}^{-1}$$

$$M = (RT/\rho g) / 2.1 \times 10^{-3} \text{ m}^4 \text{ kg}^{-1} = (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) / \{ (999.8 \text{ kg m}^{-3}) \times (9.81 \text{ m s}^{-2}) \times (2.1 \times 10^{-3} \text{ m}^4 \text{ kg}^{-1}) \} = 120 \text{ kg mol}^{-1}$$

The molar mass of the enzyme is about 120 kDa.



Activities

No actual solutions are ideal. However, we can adjust the expressions developed above to take into account deviations from ideal behavior.

The solvent activity

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

p_A^* – the vapor pressure of pure A, p_A – the vapor pressure of A when it is a component of a solution. For an ideal solution, the solvent obeys Raoult's law at all concentrations:

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

The standard state of the solvent is pure liquid (at 1 bar) and is obtained when $x_A = 1$. The form of the equation can be preserved when the solution does not obey Raoult' law:

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

a_A – the **activity** of A, an 'effective' mole fraction, just as the fugacity is an effective pressure. We can conclude that $a_A = p_A/p_A^*$

Thus, the activity of a solvent can be determined experimentally simply by measuring the vapor pressure.

For example, the vapor pressure of 0.500 M $\text{KNO}_3(\text{aq})$ is 749.7 Torr, so the activity of water in the solution at this temperature is

$$a_A = 749.7 \text{ Torr} / 760.0 \text{ Torr} = 0.9864$$

All solvents obey Raoult's law ($p_A/p_A^* = x_A$) increasingly closely as the concentration of solute approaches zero, therefore, the activity of the solvent approaches the mole fraction as $x_A \rightarrow 1$:

$$a_A \rightarrow x_A \quad \text{as} \quad x_A \rightarrow 1$$

The **activity coefficient**, γ : $a_A = \gamma_A x_A$ $\gamma_A \rightarrow 1$ as $x_A \rightarrow 1$ $\mu_A = \mu_A^* + RT \ln x_A + RT \ln \gamma_A$

The solute activity

Ideal-dilute solutions

A solute B that satisfies Henry's law has a vapor pressure given by $p_B = K_B x_B$. Then

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

Both K_B and p_B^* are characteristics of the solute, so the second term may be combined with

the first to give a new standard chemical potential: $\mu_B^\ominus = \mu_B^* + RT \ln \frac{K_B}{p_B^*}$ $\mu_B = \mu_B^\ominus + RT \ln x_B$

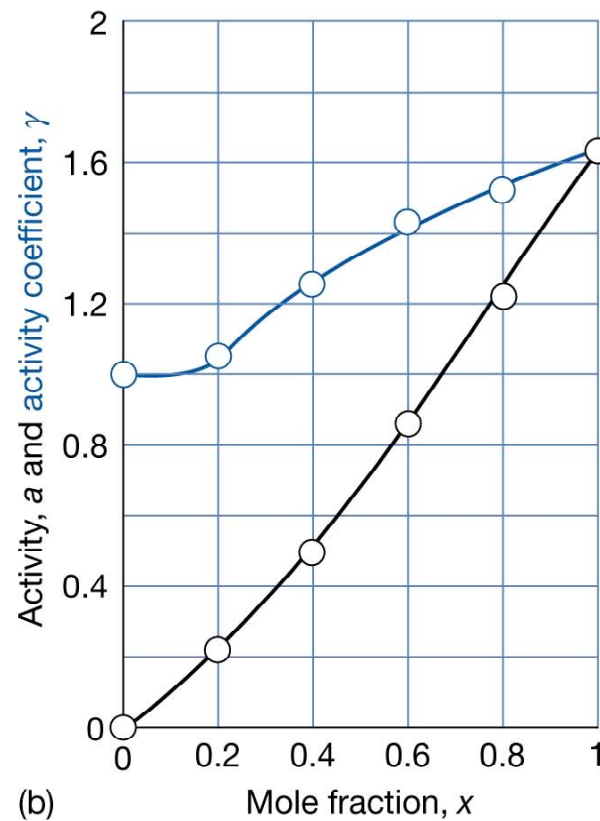
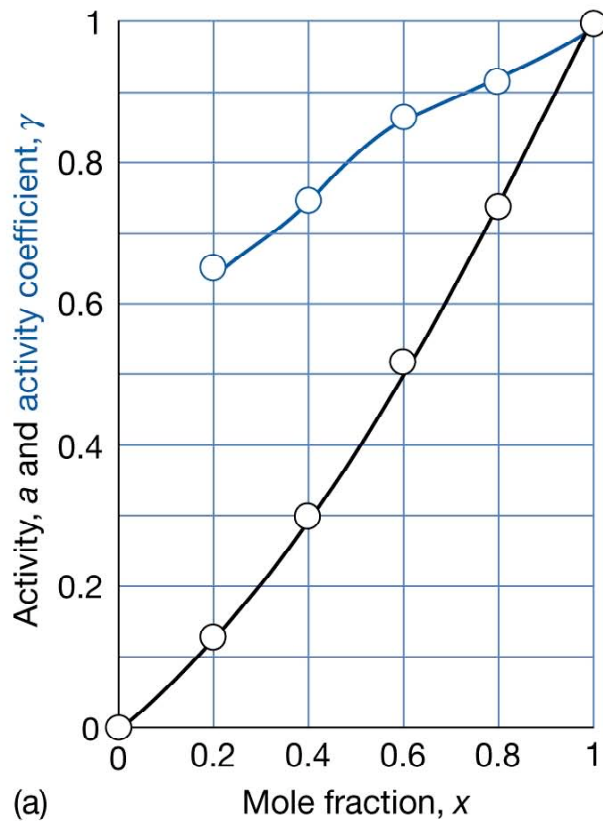
Real solutes

We now permit deviations from ideal-solute, Henry's law behavior and introduce a_B in place of x_B

$$\mu_B = \mu_B^\ominus + RT \ln a_B$$

All the deviations from ideality are captured in the activity a_B . $a_B = p_B/K_B$ $a_B = \gamma_B x_B$

Because the solute obeys Henry's law as its concentration goes to zero, $\gamma_B \rightarrow 1$ as $x_B \rightarrow 0$: deviations of the solute from ideality disappear as zero concentration is approached.



- (a) Raoult's law
 (b) Henry's law

Example 6. Measuring activity.
 Use the partial pressures measured for acetone and chloroform to calculate the activity and activity coefficient of chloroform in acetone at 25°C treating it first as a solvent and then as a solute. For the activity of chloroform as a solvent (the Raoult's law activity), calculate $a = p/p^*$ and $\gamma = a/x$. For its activity as a solute (the Henry's law activity), $a = p/K$ and $\gamma = a/x$.

x_C	0	0.20	0.40	0.60	0.80	1
p_C/Torr	0	35	82	142	200	273

Because $p^* = 273$ Torr and $K = 165$ Torr, we construct the following table:

x_C	0	0.20	0.40	0.60	0.80	1
From Raoult's law (chloroform regarded as the solvent):						
a	0	0.13	0.30	0.52	0.73	1.00
γ		0.65	0.75	0.87	0.91	1.00

From Henry's law (chloroform regarded as the solute):

a	0	0.21	0.50	0.86	1.21	1.65
γ	1	1.05	1.25	1.43	1.51	1.65

$\gamma \rightarrow 1$ as $x \rightarrow 1$ in the Raoult's law case, but $\gamma \rightarrow 1$ as $x \rightarrow 0$ in the Henry's law case.

Activities in terms of molalities

The selection of a standard state is entirely arbitrary. In chemistry, compositions are often expressed as molalities, b , in place of mole fractions and it is convenient to write

$$\mu_B = \mu_B^\ominus + RT \ln b_B$$

Here μ^\ominus has a different value from the standard values introduced earlier: the chemical potential of the solute has its standard value μ^\ominus when the molality of B is equal to b^\ominus (1 mol kg⁻¹). As $b_B \rightarrow 0$, $\mu_B \rightarrow -\infty$: as the solution becomes diluted, so the solute becomes increasingly stabilized. The practical consequence – it is very difficult to remove the last traces of a solute from a solution.

We can incorporate deviations from ideality by introducing a dimensionless activity a_B and a dimensionless activity coefficient γ_B : $a_B = \gamma_B(b_B/b^\ominus)$ $\gamma_B \rightarrow 1$ as $b_B \rightarrow 0$ $\mu = \mu^\ominus + RT \ln a$

The biological standard state

The conventional standard state of hydrogen ions (unit activity corresponding to pH = 0) is not appropriate to normal biological conditions. In biochemistry it is common to adopt the **biological standard state** with pH = 7 (an activity of 10^{-7} , neutral solution) and to label the corresponding standard thermodynamic functions as G^\oplus , H^\oplus , μ^\oplus , and S^\oplus .

$$\mu_{H^+} = \mu_{H^+}^\ominus + RT \ln a_{H^+} = \mu_{H^+}^\ominus - (RT \ln 10) \times pH \qquad \mu_{H^+}^\oplus = \mu_{H^+}^\ominus - 7RT \ln 10$$

At 298.15 K, $7RT \ln 10 = 39.96 \text{ kJ mol}^{-1}$, so the two standard values differ by about 40 kJ mol⁻¹.

The activities of regular solutions

In regular solutions the activity coefficients are given by

$$\ln \gamma_A = \beta x_B^2 \quad \ln \gamma_B = \beta x_A^2 \quad \text{Margules equations}$$

The Gibbs energy of mixing to form a nonideal solution is

$$\Delta_{\text{mix}} G = nRT \{x_A \ln a_A + x_B \ln a_B\}$$

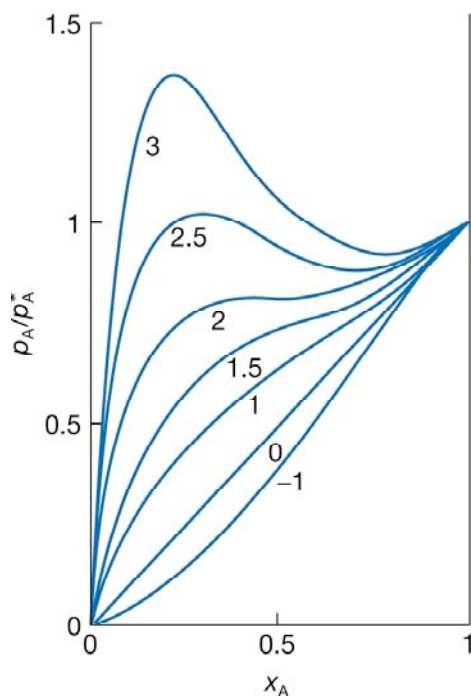
$$\Delta_{\text{mix}} G = nRT \{x_A \ln x_A + x_B \ln x_B + x_A \ln \gamma_A + x_B \ln \gamma_B\}$$

$$\Delta_{\text{mix}} G = nRT \{x_A \ln x_A + x_B \ln x_B + \beta x_A x_B^2 + \beta x_B x_A^2\} = nRT \{x_A \ln x_A + x_B \ln x_B + \beta x_A x_B (x_A + x_B)\}$$

$$= nRT \{x_A \ln x_A + x_B \ln x_B + \beta x_A x_B\},$$

which gives us the correct equation for $\Delta_{\text{mix}} G$ in regular solutions.

We can use the Margules equations to write the activity of A as $a_A = \gamma_A x_A = x_A e^{\beta x_B^2} = x_A e^{\beta(1-x_A)^2}$



The activity of A is the ratio of the vapor pressure of A in solution to the vapor pressure of pure A:

$$p_A = \left\{ x_A e^{\beta(1-x_A)^2} \right\} p_A^*$$

$\beta = 0$, corresponding to an ideal solution, gives a straight line, in accord with Raoult's law. Positive values of β (endothermic mixing, unfavorable solute-solvent interactions) give vapor pressures higher than ideal. Negative values of β (exothermic mixing, favorable solute-solvent interactions) give a lower vapor pressure. All curves approach linearity and coincide with the Raoult's law line as $x_A \rightarrow 1$ and the exponential function approaches 1.

When $x_A \ll 1$,

$$p_A = x_A e^{\beta} p_A^*$$

This expression has the form of Henry's law with $K = e^{\beta} p_A^*$, which differs for each solute-solvent system. So, β can be determined from the ratio K/p_A^* .

Ion activities

$$\mu = \mu^\ominus + RT \ln a$$

The standard state – a hypothetical solution with molality $b^\ominus = 1 \text{ mol kg}^{-1}$ in which the ions behave ideally.

$$a = \gamma b / b^\ominus$$

As the solution approaches ideality (in the sense of obeying Henry's law) at low molalities, the activity coefficient tends to 1: $\gamma \rightarrow 1$ and $a \rightarrow b / b^\ominus$ as $b \rightarrow 0$

$$\mu = \mu^\ominus + RT \ln b + RT \ln \gamma = \mu^{\text{ideal}} + RT \ln \gamma$$

μ^{ideal} – the chemical potential of the ideal-dilute solution of the same molality.

Mean activity coefficients

μ_+ – the chemical potential of a univalent cation M^+

μ_- – the chemical potential of a univalent anion X^-

For an ideal solution: $G_m^{\text{ideal}} = \mu_+^{\text{ideal}} + \mu_-^{\text{ideal}}$

For a real solution: $G_m = \mu_+ + \mu_- = \mu_+^{\text{ideal}} + \mu_-^{\text{ideal}} + RT \ln \gamma_+ + RT \ln \gamma_- = G_m^{\text{ideal}} + RT \ln \gamma_+ \gamma_-$

All the deviations from ideality are contained in the last term.

There is no experimental way to separate the product $\gamma_+ \gamma_-$ into contributions from the cations and anions – the best way we can do is to assign responsibility for the nonideality equally to both kinds of ions. We introduce (for a 1,1-electrolyte) the **mean activity coefficient** as the geometric mean of the individual coefficients:

$$\gamma_\pm = (\gamma_+ \gamma_-)^{1/2}$$

The individual chemical potentials of the ions are then expressed:

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

The sum of these two chemical potentials is the same as before, but now the nonideality is shared equally.

We can generalize this approach to M_pX_q , which gives a solution of p cations and q anions:

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

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

The chemical potential of each ion: $\mu_i = \mu_i^{\text{ideal}} + RT \ln \gamma_{\pm}$

Then we get the same equation for G_m by writing $G_m = p\mu_+ + q\mu_-$.

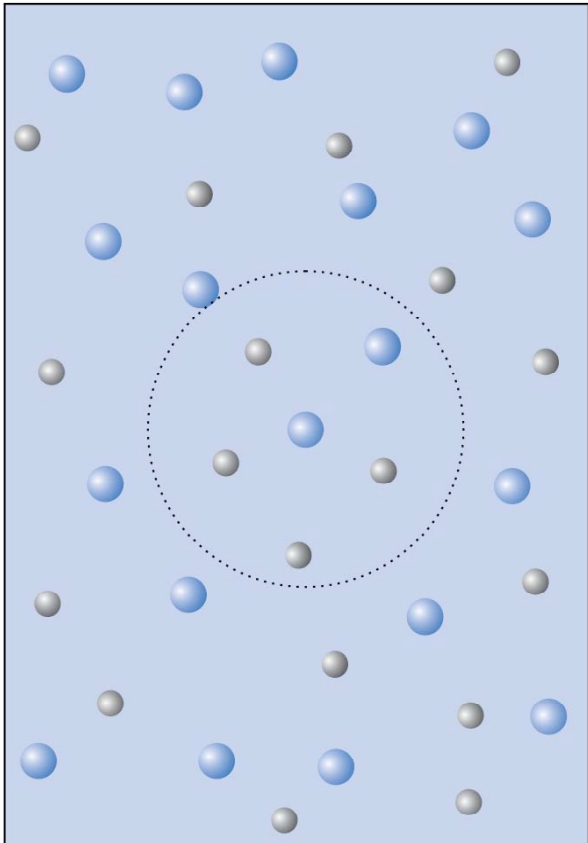
Both types of ions now share equal responsibility for the nonideality.

The Debye-Hückel limiting law

The long range and the strength of the Coulombic interaction between ions means that it is primarily responsible for the departures from ideality in ionic solutions. This is the basis of the **Debye-Hückel theory** (1923).

Oppositely charged ions attract each other – anions are more likely to be found near cations in solution and vice versa. Overall, the solution is neutral, but near any given ion there is an excess of counter ions.

Average over time, counter ions are more likely to be found near any given ion. This time-averaged spherical haze around the central ion is called **ionic atmosphere** of the central ion. The energy, and therefore the chemical potential, of any given central ion is lowered as a result of its electrostatic interaction with its atomic atmosphere. This lowering is $G_m^{\text{real}} - G_m^{\text{ideal}} = RT \ln \gamma_{\pm}$. In dilute solutions the stabilization is less important.



This model leads to the result that at very low concentrations the activity coefficient can be calculated from the **Debye-Hückel limiting law** $\log \gamma_{\pm} = -|z_+z_-|AI^{1/2}$

$A = 0.509$ for an aqueous solution at 25°C, I – the dimensionless **ionic strength** of the solution:

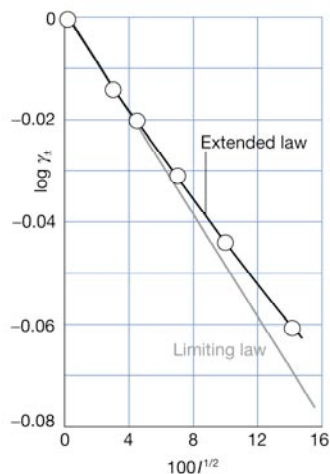
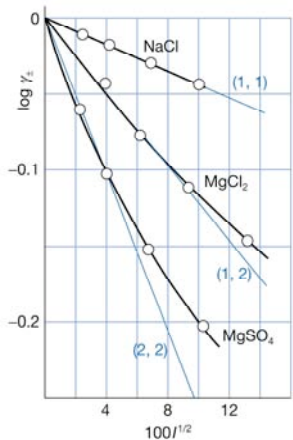
$$I = \frac{1}{2} \sum_i z_i^2 \left(\frac{b_i}{b^{\ominus}} \right) \quad z_i - \text{the charge number of an ion } i, b_i - \text{molality}$$

The sum extends over all the ions present in the solution. For solutions consisting of two types of ions at molalities b_+ and b_- : $I = \frac{1}{2} (b_+z_+^2 + b_-z_-^2) / b^{\ominus}$

The ionic strength strongly depends on the charges of the ions because the charge numbers occur as their squares.

The mean activity coefficient of $5.0 \times 10^{-3} \text{ mol kg}^{-1} \text{ KCl(aq)}$ at 25°C is calculated as

$$I = \frac{1}{2} (b_+ + b_-) / b^{\ominus} = b / b^{\ominus} \quad \log \gamma_{\pm} = -0.509 \times (5.0 \times 10^{-3})^{1/2} = -0.036 \quad \gamma_{\pm} = 0.92 \text{ (0.927 - exp.)}$$



The name ‘limiting law’ is applied to the equation

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

because ionic solutions of moderate molalities may have activity coefficients that differ from the values given by the expression, yet

all solutions are expected to conform as $b \rightarrow 0$. The more accurate equation – the **extended Debye-Hückel law**:

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

B – an adjustable empirical dimensionless constant.