Simple Mixtures

Atkins 7th, Ch. 7: Sections 7.1-7.3; 8th & 9th, Ch. 5: Sections 5.1-5.3

Thermodynamic Description of Mixtures

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Simple Mixtures

We now go from the behavior of simple single substance systems to mixtures of substances. In general, these will still be **non-reacting substances** and we will be dealing mostly with the **energetics of the mixing process itself** and to a lesser extent with the types of nonideal interactions which can take place between different substances. We will also start to learn how to deal with liquid solutions, which will increase the arsenal of systems that we know how to deal with.

Mainly, we will deal with non-reactive **binary mixtures**, which have components A and B, making use of the relation:

$$x_A + x_B = 1$$

We have already used such **mole fractions** to describe the partial pressures of mixtures of gases which give rise to a total pressure
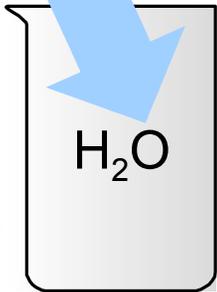
$$p_A + p_B + ... = (x_A + x_B + ...)p = p$$

Partial Molar Volume

The **partial molar volume** is the contribution that one component in a mixture makes to the total volume of a sample

Add 1.0 mol H_2O

Add 1.0 mol H_2O

Volume increases
by 18 cm^3 mol^{-1}

H_2O

Large
volumes

EtOH

Volume increases
by 14 cm^3 mol^{-1}

Molar volume of H_2O:
18 cm^3 mol^{-1}

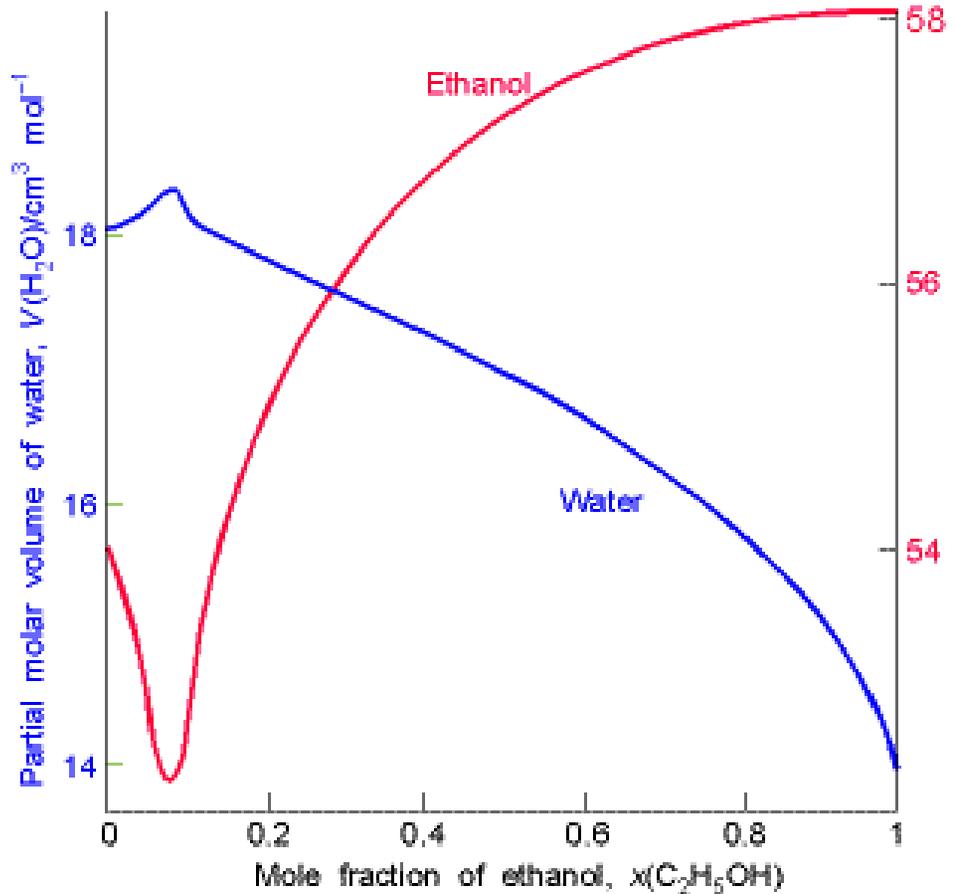Partial molar volume of
H_2O in EtOH: 14 cm^3 mol^{-1}

The different increase in total volume in the H_2O/EtOH example depends on the identity of the molecules that surround the H_2O. The EtOH molecules pack around the water molecules (i.e., **solvate**) differently than how water molecules pack around water molecules: the increase in the molar volume is only 14 cm^3 mol^{-1}!

Partial molar volume of substance A in a mixture is the change in volume per mole of A added to the large volume of the mixture

Partial Molar Volume, 2

The **partial molar volume** of components of a mixture vary as the mixture goes from pure A to pure B - that is because the molecular environments of each molecule change (i.e., packing, solvation, etc.)

Partial molar volumes of a water-ethanol binary mixture are shown at 25 °C across all possible compositions
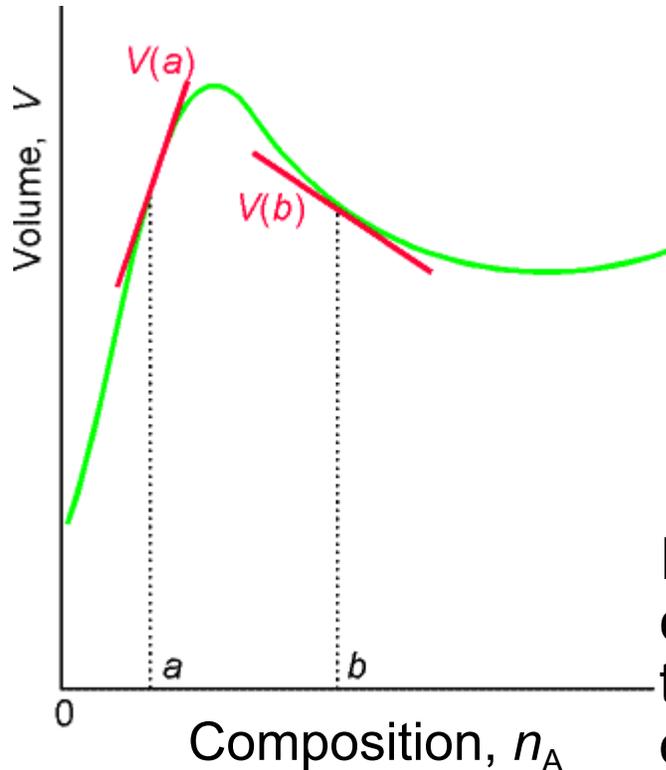
The partial molar volume, V_J, of a substance J is defined as

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

where n' signifies that all other substances present are constant

Partial Molar Volume, 3

The **partial molar volume** is the slope of a plot of total volume as the amount of J in the sample is changed (volume vs. composition)

For a binary mixture, the composition can be changed by addition of dn_A of A and dn_B of B, with the total volume changing by

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

$$= V_A dn_A + V_B dn_B$$

If partial molar volumes are known for the two components, then at some temperature T, the total volume V (state function, always positive) of the mixture is

$$V = n_A V_A + n_B V_B$$

Partial molar volumes vary with composition (different slopes at compositions a and b) - partial molar volume at b is negative (i.e., the overall sample volume decreases as A is added)

Partial Molar Volume, 4

The **partial molar volume** can be measured by fitting the observed volume (as function of composition) using a curve fitting program (find the parameters that give the best fit of a particular function to the experimental data)

If the function is found, the slope at any point (any composition) can be determined by differentiation; for example, if V has the following function

$$V = A + Bn_A + C(n_A^2 - 1)$$

with constants A, B and C (note this is not A and B), then the partial molar volume of A at any composition is

$$V_A = \left(\frac{\partial V}{\partial n_A}\right)_{p,T,n_B} = B + 2Cn_A$$

and the partial molar volume of component B is obtained by rearranging $V = n_A V_A + n_B V_B$:

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

Partial Molar Gibbs Energies

The concept of **partial molar quantity** can be applied to **any extensive state function**. For example, for a pure substance in a mixture, the chemical potential can be defined as the **partial molar Gibbs energy**

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

So chemical potential of a substance is the slope of the total Gibbs energy of a mixture wrt amount of substance of interest, J
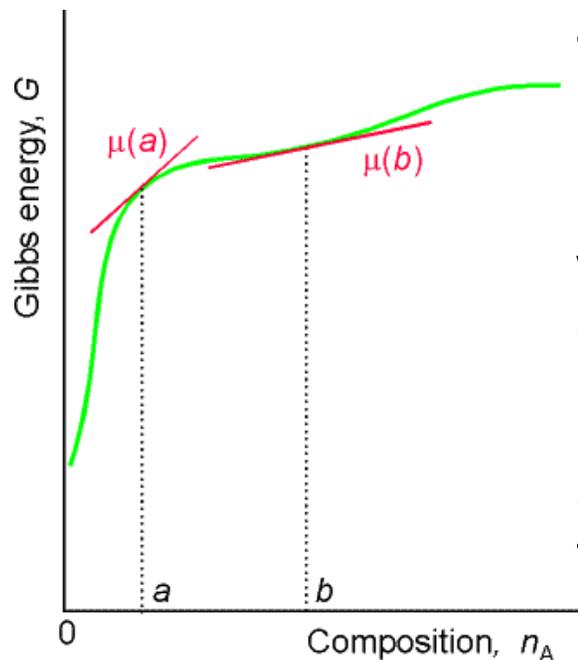
Total Gibbs energy is

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

where μ_J are chemical potentials for that particular composition of the mixture

Each individual chemical potential of the substances in a mixture make a contribution to the total Gibbs energy of the substance

Partial Molar Gibbs Energies, 2

Gibbs energy depends on composition, pressure and temperature (so, *G* may change if any of these variables change - which they may!) For a system with components A, B, ...

$$dG = V\,dp - S\,dT + \mu_A\,dn_A + \mu_B\,dn_B + ...$$

which is a **fundamental equation of classical thermodynamics**

At constant temperature and pressure,

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

In Chapter 4, we saw that under these conditions, $dG = dw_{e,max}$ (the maximum non-expansion work)

$$dw_{e,max} = \mu_A\,dn_A + \mu_B\,dn_B + ...$$

What does this mean? Non-expansion work can happen just from changing system composition at constant pressure and temperature (e.g., **battery**, chemical rxn in two sites called **electrodes**, and the work the battery produces comes from reactants going to products)

More on Chemical Potential

Chemical potential tells us even more than just about variation in *G*

$$G = U + pV - TS$$

so for an infinitesimal change in *U*, we can write

$$\begin{aligned} dU &= -p\,dV - V\,dp + S\,dT + T\,dS + dG \\ &= -p\,dV - V\,dp + S\,dT + T\,dS + (V\,dp - S\,dT + \mu_A\,dn_A + \mu_B\,dn_B + ...) \\ &= -p\,dV + T\,dS + \mu_A\,dn_A + \mu_B\,dn_B + ... \end{aligned}$$

and at constant volume and entropy

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

and if that's not enough...what about *H* and *A*??? These too also depend upon the composition of a mixture! **Chemical potential is IMPORTANT!**

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

Gibbs-Duhem Equation[†]

Since $G = n_A \mu_A + n_B \mu_B$, and μ_J depend on composition, for a binary mixture G may change by

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

But at constant temperature and pressure, since G is a state function

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

This special case holds for multiple components, and is the **Gibbs-Duhem equation**

$$\sum_J n_J d\mu_J = 0$$

So, for our binary mixture, if one partial molar quantity increases, the other must decrease

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

This holds for all partial molar quantities - in binary mixtures, the partial molar quantity of one component can be determined from measurements of the other   **Example 7.1/5.1 - in class**
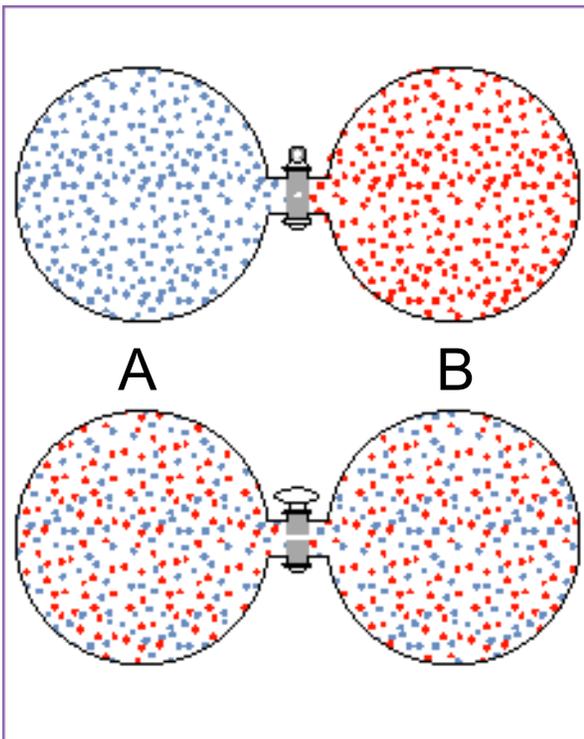
Thermodynamics of Mixing

Dependence of Gibbs energy on mixture composition is

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

and at constant T and p, systems tend towards a lower Gibbs energy

The simplest example of mixing: What is the Gibbs free energy if we take two pure ideal gases and mix them together? Consider gas A and gas B, both in separate containers at pressure p at temperature T.

A   B

The chemical potentials are at their "pure values" at this point. Gibbs energy is

$$G_i \;=\; n_A \mu_A \;+\; n_B \mu_B$$

$$\;=\; n_A\left\{\mu_A^o \;+\; RT\,\ln\left(\frac{p}{p^{\,o}}\right)\right\} \;+\; n_B\left\{\mu_B^o \;+\; RT\,\ln\left(\frac{p}{p^{\,o}}\right)\right\}$$

We can simplify things by letting p denote the pressure relative to p^o, writing

$$G_i \;=\; n_A\left\{\mu_A^o \;+\; RT\,\ln p\right\} \;+\; n_B\left\{\mu_B^o \;+\; RT\,\ln p\right\}$$
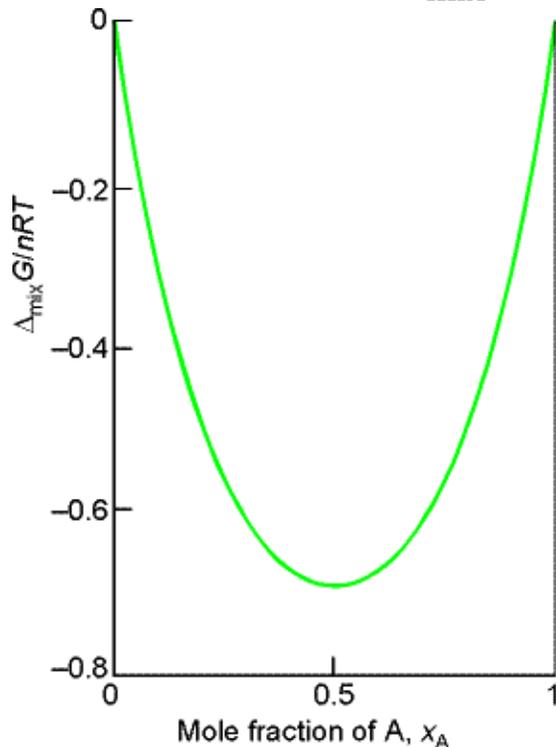
Gibbs Energy of Mixing[*]

After mixing, the partial pressures of the gases are p_A and p_B, where the total pressure is $p = p_A + p_B$. The total Gibbs energy is then

$$G_f = n_A\left\{\mu_A^o + RT \ln p_A\right\} + n_B\left\{\mu_B^o + RT \ln p_B\right\}$$

The difference in Gibbs energies, $G_f - G_i$, is the **Gibbs energy of mixing**

$$\Delta_{mix}G = n_A RT \ln\left(\frac{p_A}{p}\right) + n_B RT \ln\left(\frac{p_B}{p}\right)$$

We use mole fractions, replacing n_J with $x_J n$:

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

Since the mole fractions are never greater than 1, the ln terms are negative, and $\Delta_{mix}G < 0$

This allows is to conclude that mixing processes are spontaneous, and gases mix spontaneously in all proportions

*Mixing of gases and effusion

Calculating Gibbs Energy of Mixing

Two containers of equal volume are partitioned from one another, with one containing 3.0 mol H_2 and the other 1.0 mol N_2 at 25°C. Calculate the Gibbs energy of mixing when the partition is removed
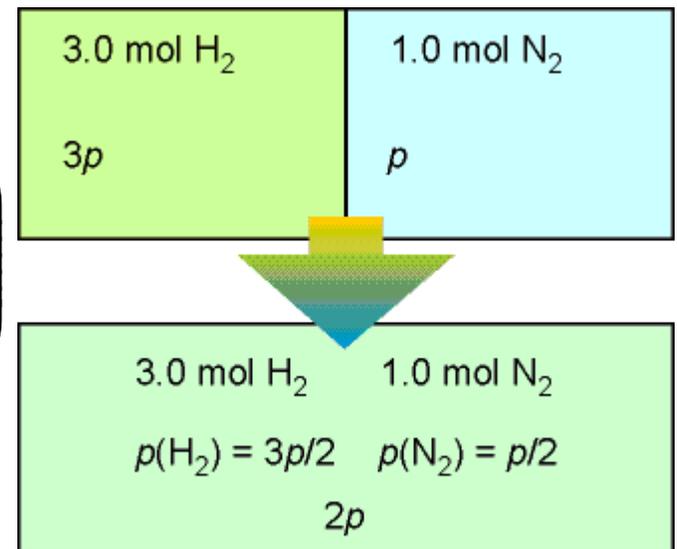
We assume ideal gas behaviour, with pressure of N_2 being p, pressure of H_2 being $3p$. Volume of each gas will double, & partial pressures fall by 2

$$G_i = (3.0 \text{ mol})\left\{\mu_{H_2}^o + RT \ln 3p\right\} + (1.0 \text{ mol})\left\{\mu_{N_2}^o + RT \ln p\right\}$$

$$G_f = (3.0 \text{ mol})\left\{\mu_{H_2}^o + RT \ln \frac{3}{2}p\right\} + (1.0 \text{ mol})\left\{\mu_{N_2}^o + RT \ln \frac{1}{2}p\right\}$$

Gibbs energy of mixing is the difference between the above quantities

$$\Delta_{mix}G = (3.0 \text{ mol}) \, RT \ln \left(\frac{\frac{3}{2}p}{3p}\right) + (1.0 \text{ mol}) \, RT \ln \left(\frac{\frac{1}{2}p}{p}\right)$$

$$= -(3.0 \text{ mol}) \, RT \ln 2 - (1.0 \text{ mol}) \, RT \ln 2$$
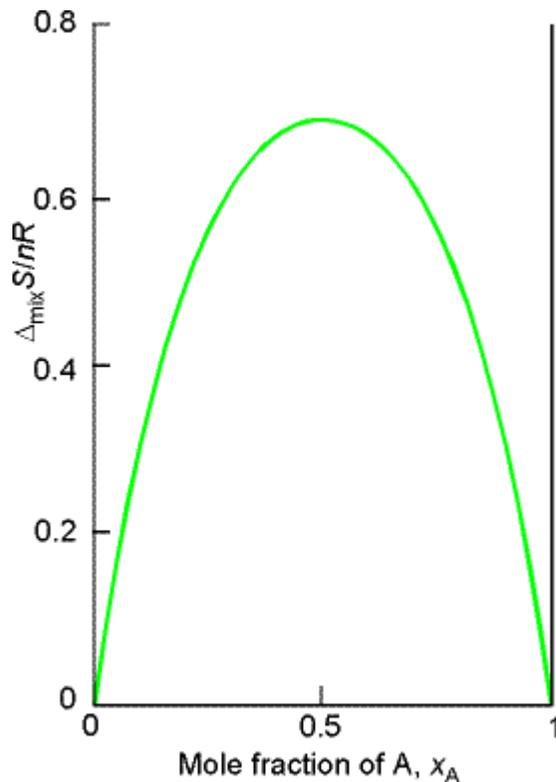
$$= -(4.0 \text{ mol}) \, RT \ln 2 = -6.9 \text{ kJ}$$

Other Thermodynamic Mixing Functions

Since $(\partial G/\partial T)_{p,n} = -S$ and $\Delta_{mix}G = nRT\,(x_A \ln x_A + x_B \ln x_B)$
it follows that for a mixture of perfect gases, the **entropy of mixing** is

$$\Delta_{mix}S = -\left(\frac{\partial \Delta_{mix}G}{\partial T}\right)_{p,n_A,n_B} = -nR\,(x_A \ln x_A + x_B \ln x_B)$$

Since $\ln x < 0$, then $\Delta_{mix}S > 0$ for mixtures of all compositions

We expect this increase in disorder, since dispersal of one gas into another implies greater disorder in the system

Example: $\Delta_{mix}G = -(4.0\ mol)RT \ln 2$, so
$\Delta_{mix}S = (4.0\ mol)R \ln 2 = +23\ J\ K^{-1}$

The isothermal isobaric **enthalpy of mixing** of two gases is found from $\Delta G = \Delta H - T\Delta S$, and we find

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

This is expected for a system in which there are no interactions between the molecules in the mixture

Chemical Potentials of Liquids

Quantities relating to pure substances will be denoted with asterisks, so the chemical potential of pure liquid A is $\mu_A^*(l)$. Since the vapour pressure of pure liquid A is p_A^*, the chemical potential of A in the vapour is $\mu_A^o + RT \ln p_A^*$ (p_A^* as relative pressure p_A^*/p^o)
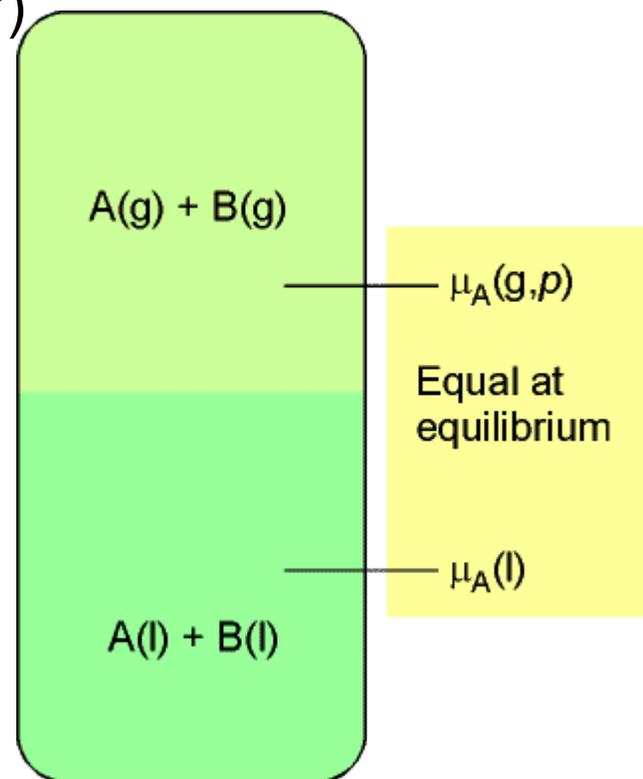
Chemical potentials are at equilibrium:

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

If another substance is present (e.g., a solute in the liquid), chemical potential of A in the liquid is μ_A and vapour pressure is p_A

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

Combine to eliminate the standard potential:

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

A(g) + B(g)

$\mu_A(g,p)$

Equal at equilibrium

$\mu_A(l)$

A(l) + B(l)

The chemical potential of A depends on its partial vapour pressure, it follows that chemical potential of liquid A is related to its partial pressure
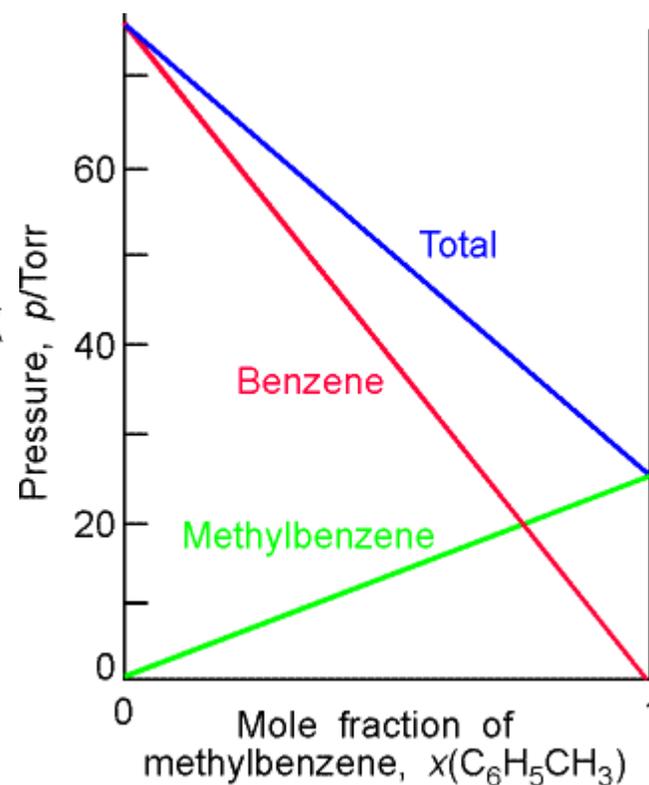
Raoult's Law

After experimenting with mixtures of similar liquids, 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

$$p_A = x_A p_A^*$$

Some mixtures obey Raoult's law very closely, especially when they are structurally similar - these are called **ideal solutions**, and they obey

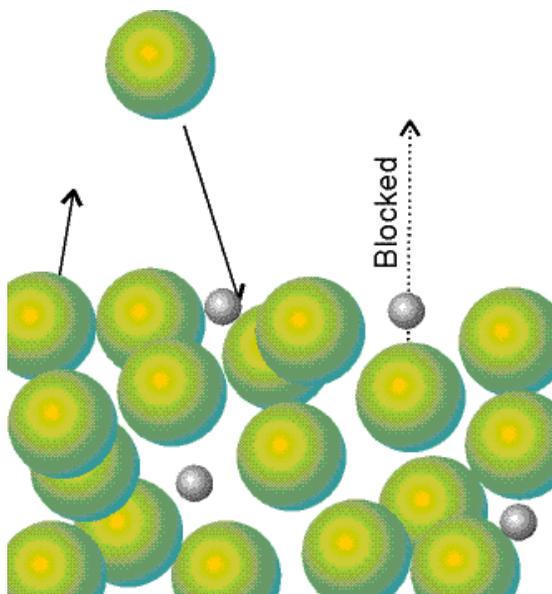$$\mu_A = \mu_A^* + RT \ln x_A$$
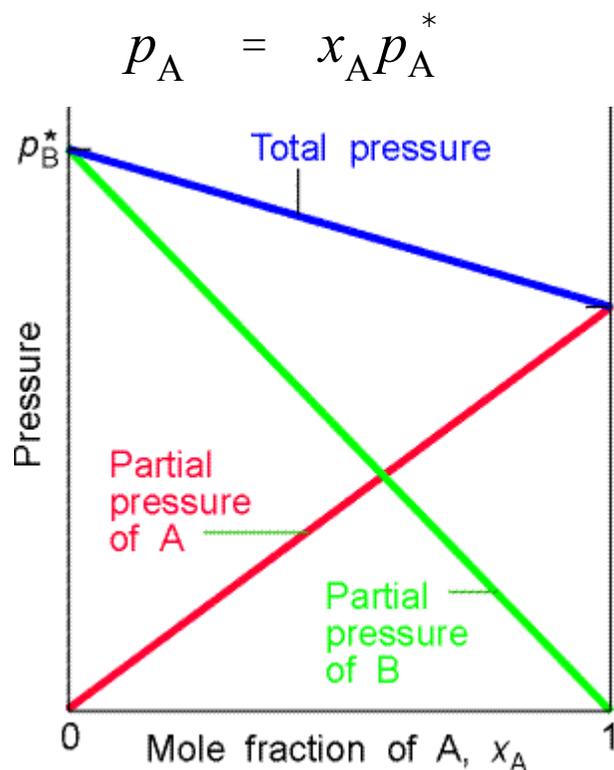
Ideal binary mixture

Mixture of benzene and toluene

Molecular Interpretation of Raoult's Law

We have to consider the rate at which molecules leave and enter solution to understand Raoult's law

The presence of a second component hinders molecules from leaving the solution, but does not inhibit the rate at which they return

The rate at which A molecule leave the surface is proportional to the number of them at the surface, which is proportional to their mole fraction

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

where k is a proportionality constant. The rate at which molecules return is proportional to their gas phase concentration, which is proportional their partial pressure

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

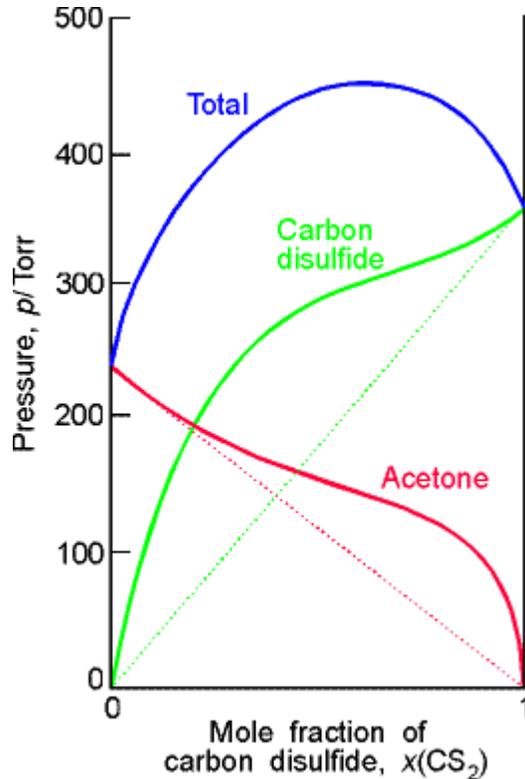At equilibrium, rates of vapourization and condensation are equal, so

$$kx_A \ = \ k'p_A \qquad p_A \ = \ \frac{k}{k'}x_A$$

For a pure liquid, $x_A = 1$, so $\quad p_A^* \ = \ \frac{k}{k'}$

Departure from Raoult's Law, Dilute Solutions

Some solution mixtures behave very differently from Raoult's law, notably with mixtures of structurally and chemically dissimilar liquids

Mixture of CS_2 and acetone:

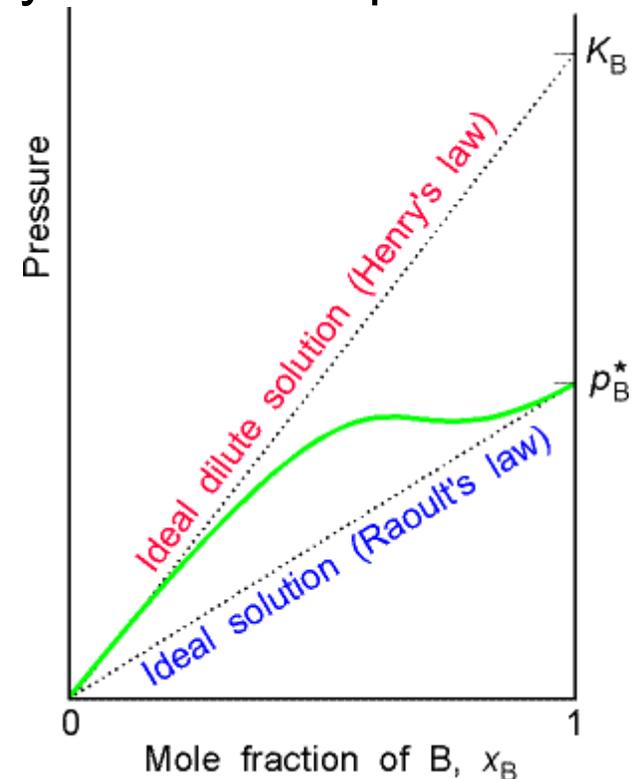Ideal dilute solution, consider the solute (B): **Henry's law**

$$p_B = x_B K_B$$

Ideal solution, consider the solvent (A): **Raoult's law**

$$p_A = x_A p_A^*$$

- When the solvent is nearly pure (i.e., A is the major component), it has a vapour pressure proportional to the mole fraction with slope p_A^*
- When B is the minor component (the solute) the vapour pressure has a different constant of proportionality

Henry's Law

The English chemist William Henry found that for real solutions at low concentrations, although the vapour pressure of the solute is proportional to the mole fraction, the constant of proportionality is not the vapour pressure of the pure substance

$$p_B = x_B K_B$$

Here x_B is the mole fraction of the solute B, and K_B is an empirically determined constant with pressure dimensions. K_B is chosen so that a plot of vapour pressure of B against mole fraction is tangent to the experimental curve at $x_B = 0$

Such solutions are called **ideal-dilute solutions**

Solvent behaves like a slightly modified pure liquid

Solute behaves entirely differently from its pure state (since its molecules are surrounded by solvent molecules), unless the molecules of the two components are very similar
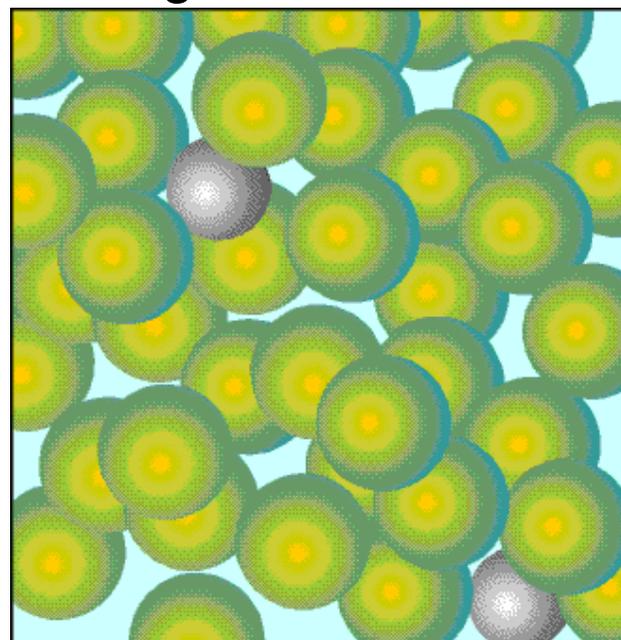
The Validity of Raoult's & Henry's Laws

Consider a acetone (A) and chloroform (C) mixture at 35°C

x_C	0	0.20	0.40	0.60	0.80	1
p_C (Torr)	0	35	82	142	200	273
p_A (Torr)	347	250	175	92	37	0

K = 175 Torr for (A) and K = 165 Torr for (C)

When mole fractions of (A) or (C) are near 1, Raoult's Law predicts the partial pressures

When mole fractions of (A) or (C) are near 0, Henry's Law predicts the partial pressures (ideal dilute solutions)

In both cases, there are some deviations from this predicted behaviour
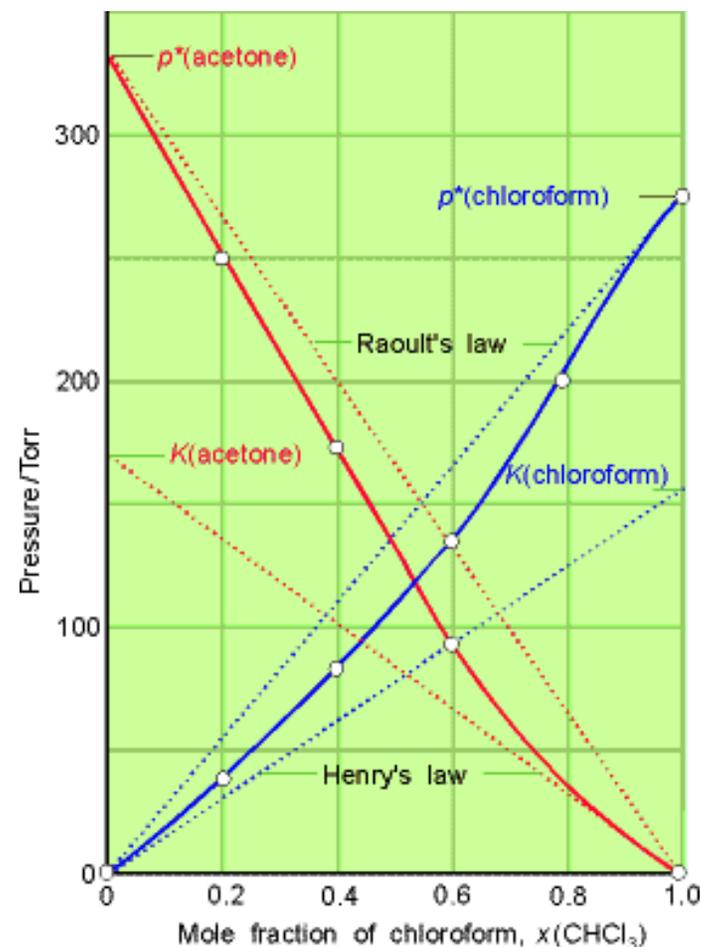
Using Henry's Law[*]

Estimate the molar solubility of oxygen in water at 25°C and partial pressure of 160 Torr, its partial pressure at sea level

The amount of O_2 dissolved is very small, and $x_J = p_J/K$, so

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

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

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

So the molar solubility of oxygen is 2.69 x 10^{-4} mol kg^{-1} corresponding to concentration of 2.7 x 10^{-4} mol L^{-1}

Henry's law constants are very well known by biochemists for treatment of gas behaviour in fats and lipids. Henry's law is also very important in understanding respiration processes: especially when partial pressure of O_2 is abnormal, such as in mountaineering, scuba diving, and in the use of gaseous anaesthetics