Properties of Solutions

Atkins 7th: Sections 7.4-7.5; Atkins 8th & 9th: 5.4-5.5

The Properties of Solutions

Liquid Mixtures

Colligative Properties
Boiling point elevation
Freezing point depression
Solubility
Osmosis

Activities
Solvent Activity
Solute Activity

Last updated: Nov. 19, 2012, minor edits slide 1

Liquid Mixtures

Gibbs energy of mixing for two liquids is calculated the same as for gases. For two liquids A and B (**note that * signifies pure substance**):

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

Upon mixing, the chemical potentials are given by $\mu_J = \mu_J^* + RT \ln x_J$

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

Thus, the Gibbs energy of mixing is

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

and the entropy of the mixing of two liquids is

$$\Delta_{mix} S = -nR (x_A \ln x_A + x_B \ln x_B)$$

meaning that the **ideal enthalpy of mixing** is zero.

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

Same expressions as for mixing of two perfect gases. But...

Liquid Mixtures: Miscibility

Solution ideality is quite different from perfect gas behaviour:

- **Perfect gases**: no interactions between the molecules
- **Ideal solutions**: interactions between molecules, but average of interactions between A and B molecules is same as average interactions A-A and B-B in pure liquids
- **Real solutions**: Composed of molecules for which A-A, A-B, B-B interactions are all different from one another

Somtimes, molecules of one type might cluster together (additional contribution to entropy), so:

- Enthalpy change might be large and +ve
- Negative entropy change
- Positive Gibbs energy for mixing

In this case, separation is spontaneous, and liquids are **immiscible** (example, CCl_4 and H_2O, which are non-polar and polar, respectively)

Liquids can also be **partially miscible**, which means that they are miscible only in certain compositions (partially dissolve in one another)

Real Solutions & Excess Functions

(a) H^E

(b) V^E
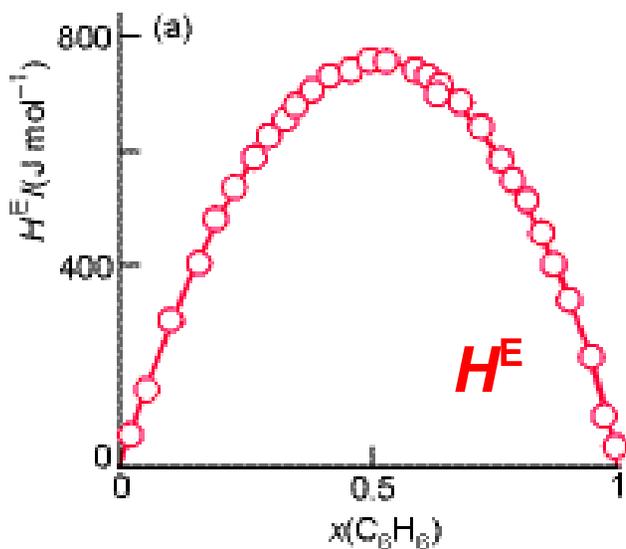
Thermodynamic properties of real solutions are described with **excess functions**, X^E

For example, the **excess entropy**, S^E, is the difference between the observed thermodynamic function and the function for an ideal solution:

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

So, the further excess energies are from zero indicates the degree to which a solution is non-ideal - a **regular solution** has $H^E \neq 0$, $S^E = 0$, with two kinds of molecules distributed randomly (like ideal solution), but having different interactions with one another
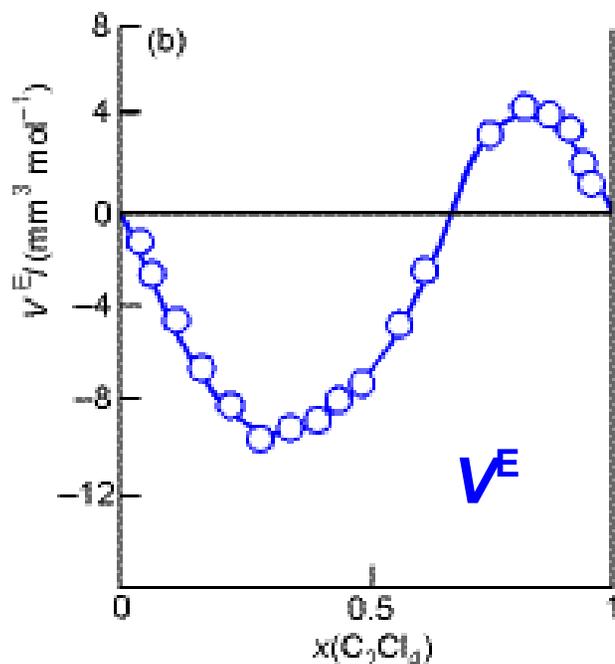
(a) The **benzene/cyclohexane mixing**, shows that mixing is endothermic

(b) **Tetrachloroethane/cyclohexane** mixing shows a volume contraction at low C_2Cl_4 fractions, and expansion at high C_2Cl_4 fractions

Colligative Properties

Colligative properties literally denotes *properties which depend on a collection of particles*

- **Boiling point elevation**
- **Freezing point depression**
- **Solubility of liquids and solids**
- **Osmotic pressure**

Each of these properties is going to depend on the composition of the mixture (i.e., the relative mole fractions of the components)

There is no reference in these properties to the identities of the solutes and/or solvents - strictly dependent upon composition

Important Assumptions:
- Solute is not volatile, does not contribute to the chemical potential of the solvent vapour
- Solute does not dissolve in solid solvent (this is not the most common case, but does cut the mathematics down a lot!) - so pure solid solvent separates when the mixture is frozen

Colligative Properties: Common Features

All colligative properties result from lowering of the chemical potential of the solvent from the presence of a solute

Solute

In x_A negative, since $x < 1$

Pure solvent

μ_A^*

Solvent + solute

$$\mu_A = \mu_A^* + RT \ln x_A$$
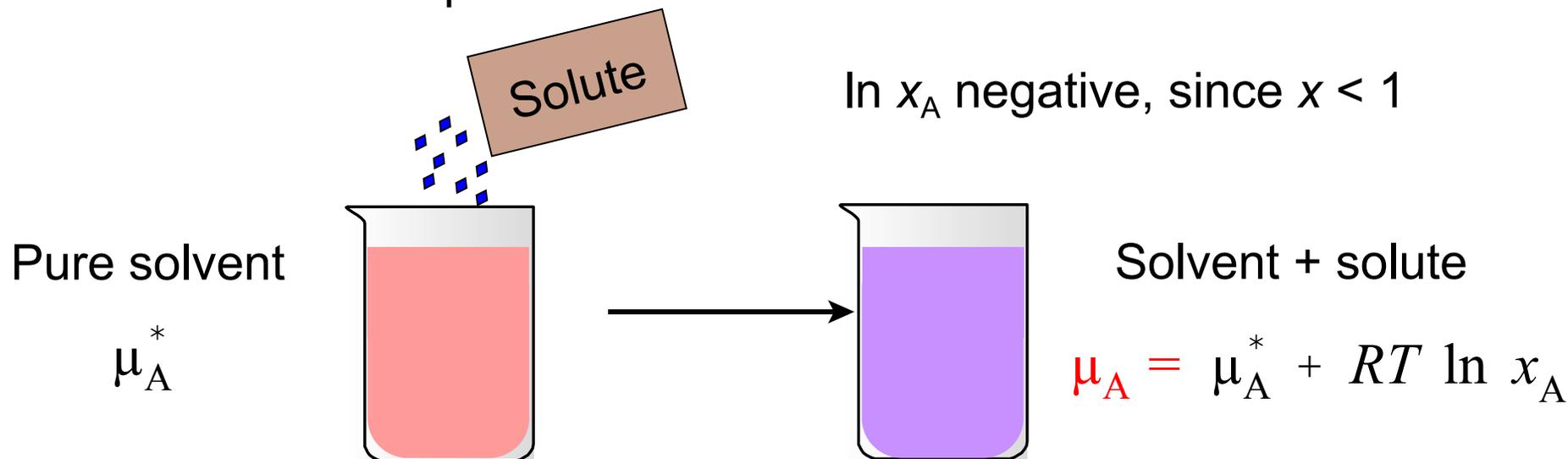
What causes the **lowering of chemical potential of a liquid**?

Not the energies of interactions between solvent and solute molecules, since lowering of energy occurs even in ideal solutions ($\Delta_{mix}H = 0$)

Entropy must be the driving force for lowering the chemical potential of a liquid once the solute has been added

Solvents, Solutes and Entropy

There is no direct effect of the solute on the chemical potential of the solvent vapour, since solute is not in the vapour phase
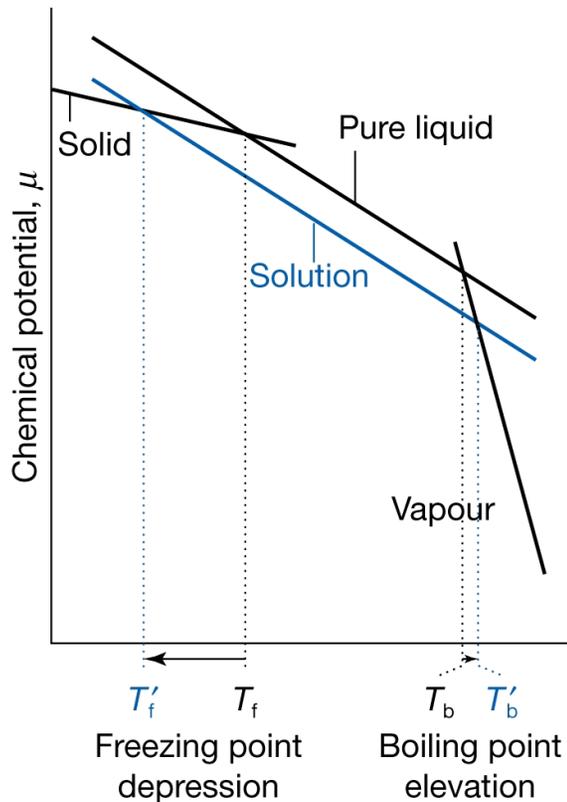
Reduction of the chemical potential of the **solution** (down from that of a **pure liquid**) implies that:
- liquid-vapour equilibrium occurs at a higher temperature (**boiling point elevation**)
- liquid-solid equilibrium occurs at a lower temperature (**freezing point depression**)

(a) Solvent with entropy S^* & p_A^*, vapour pressure reflects tendency to greater entropy
(b) Solution with $S > S^*$, therefore weaker tendency to form gas (i.e., greater entropy), so $p_A < p_A^*$ and T_{bp} is elevated
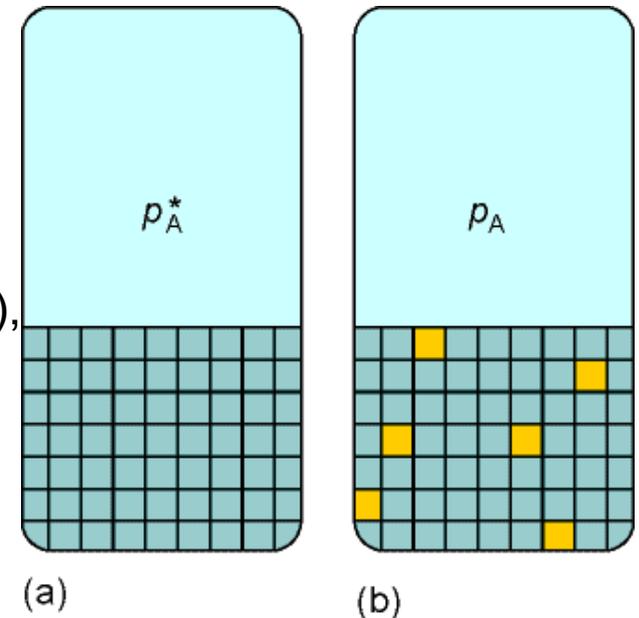
Increased disorder in the liquid also opposes tendency to freeze (go to higher order), so a lower temperature is required to hit solid-liquid eqb.

Boiling Point Elevation*

Heterogeneous equilibrium: between solvent in solution and solvent vapour at 1 atm, where solvent is A and solute is B (involatile)

A(g)

$\mu_A^*(g,p)$

Equal at equilibrium

$\mu_A(l)$

A(l) + B
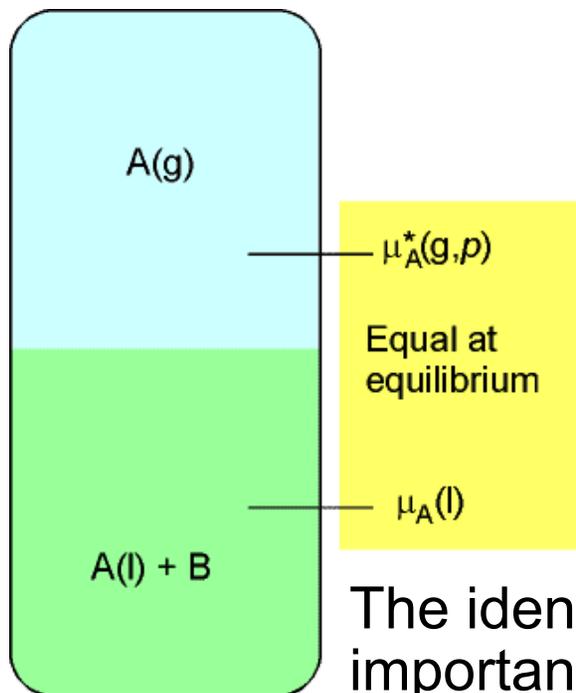
Equilibrium occurs at some temperature when:

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

The presence of some mole fraction x_B causes an increase in the normal boiling point from T^* to $T^* + \Delta T$, where

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

The identity of solute is irrelevant: just the mole fraction is important, so boiling point elevation is a colligative property

Value of ΔT depends on the solvent, biggest changes occur for solvents with high boiling points. For practical applications, mole fraction of B is proportional to its **molality**, b (mol kg^{-1}), in dilute solutions, and

$$\Delta T \;=\; K_b b$$

K_b is the empirical (& unfortunately named) **ebullioscopic constant**

Freezing Point Depression

Heterogeneous equilibrium: pure solid solvent A and solution with solvent present in mole fraction x_B. At the freezing point:

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

A(l) + B

$\mu_A(l)$

Equal at equilibrium

$\mu_A^*(s)$

A(s)

Only difference from boiling point elevation is the presence of $\mu_A^*(s)$ instead of $\mu_A^*(g)$. Thus,

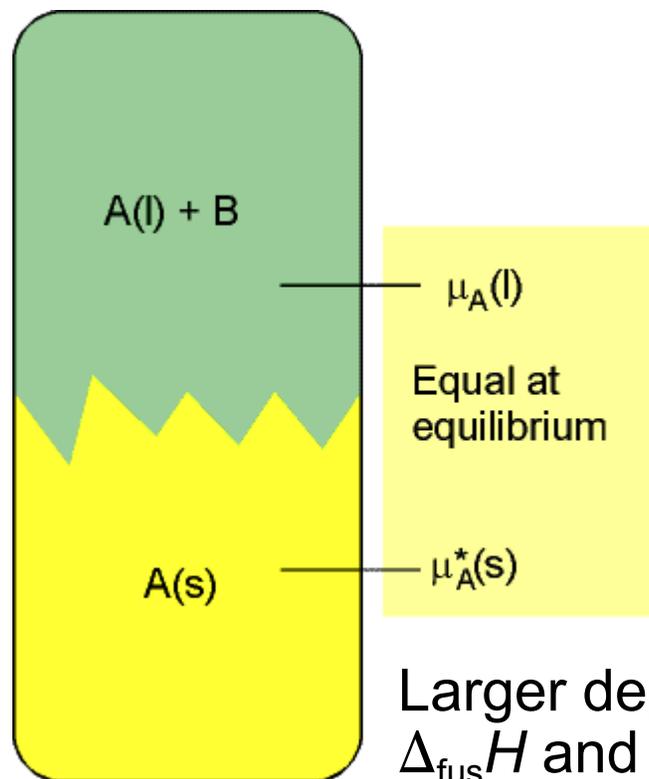$$\Delta T = K'x_B \qquad K' = \frac{RT^{*2}}{\Delta_{fus}H}$$

where ΔT is the freezing point depression, T^* - T, and $\Delta_{fus}H$ replaces $\Delta_{vap}H$

Larger depressions are observed for solvents with low $\Delta_{fus}H$ and high melting points.

If solution is dilute, mole fraction $\propto$ **molality**, b, of the solute, and

$$\Delta T = K_f b$$

where K_f is the empirical **cryoscopic constant**

Solubility

Solubility is a characteristic of the solute in a saturated solution. At a given temperature, the solubility of a substance is the concentration of a saturated solution at that temperature.

If solid and liquid are in contact, solid dissolves until the solution is **saturated** (the equilibrium state). Chemical potentials of solid solute, μ_B^*, and B in solution μ_B, are equal.

B(dissolved in A)

μ_B(solution)

Equal at equilibrium

B(s) — μ_B^*(s)
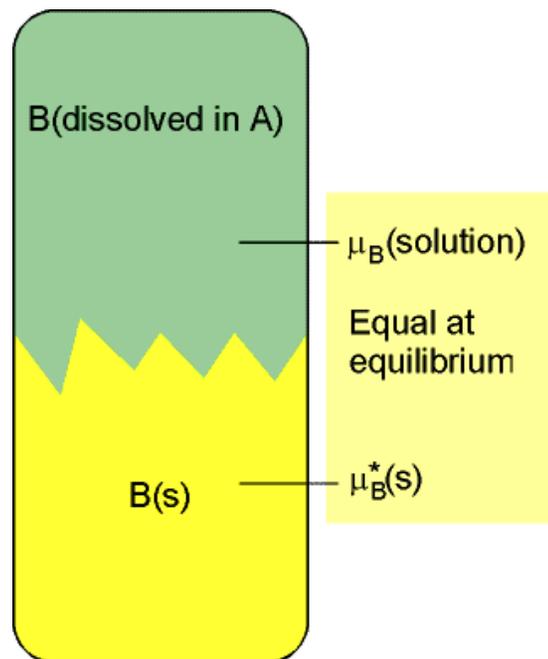
Since: solute (in solution) $\rightleftharpoons$ solute (solid)
then: μ (in solution) = μ (solid)

Solute (in solution): $\mu_B = \mu_B^*(l) + RT \ln x_B$

**Eqb. μ's are equal:** $\mu_B^*(s) = \mu_B^*(l) + RT \ln x_B$

Solubilities are expressed in a number of ways (e.g., g solute / 100 g solvent); but mole fractions are the most useful, since $\mu = \mu^* + RT \ln x_B$ for an ideal solution.

Solubility is not a perfectly colligative property, but may be estimated from the same techniques we've been discussing - *questionable approximations, but accurate in some cases*

Solubility, 2

We wish to know the mole fraction of solute B dissolved in solution at temperature T. How do we get this? Rearrange the eqb. equation on the previous slide, and substitute in the Gibbs-Helmholz equation:

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

$$\ln x_B = -\frac{\Delta_{fus}H}{RT} + \frac{\Delta_{fus}S}{R} + \frac{\Delta_{fus}H}{RT^*} - \frac{\Delta_{fus}S}{R}$$

$$= -\frac{\Delta_{fus}H}{RT} + \frac{\Delta_{fus}H}{RT^*}$$

$$= \boxed{-\frac{\Delta_{fus}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right) = \frac{\Delta_{fus}H}{R}\left(\frac{T - T^*}{T^*T}\right)}$$
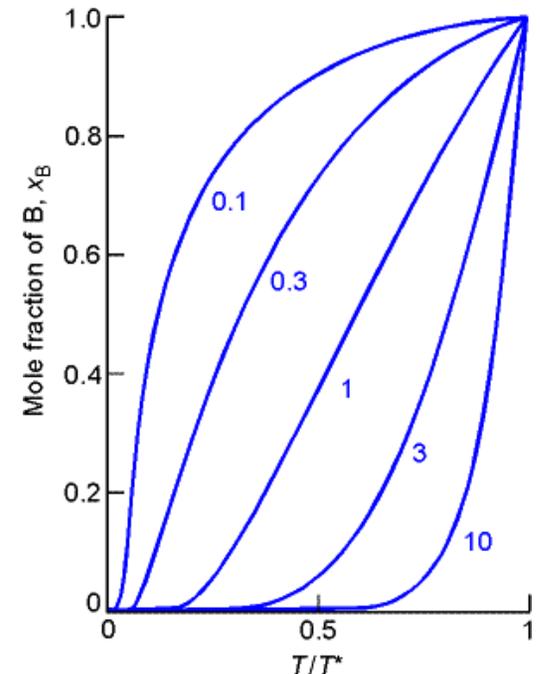
where $\Delta_{fus}H$ and T^* are for the pure solute (which must be a non-electrolyte). The expression becomes less valid as we move further away from T^*, since $\Delta_{fus}H$ is known to vary with temperature.

The plot on the RHS shows variation of solubility (mole fraction of solute in saturated solution) with temperature. Curve labels = $\Delta_{fus}H/RT^*$. Solubility of B drops exponentially as T is lowered from T^* ($T/T^* = 1$ is the m.p. of pure B).

Osmosis[†]

There are many times in nature when a solvent will pass spontaneously through a **semipermeable membrane**, which is a membrane permeable to solvent, but not solute

The **osmotic pressure**, Π, is the pressure that must be applied to stop the influx of solvent - one of the most important examples is the transport of fluids through living cell membranes - also the basis of **osmometry**, the determiniation of molecular mass by measurement of osmotic pressure

To treat osmosis thermochemically, we note that at equilibrium, chemical potential on each side of the membrane must be equal

This equality implies that for dilute solutions the osmotic pressure is given by the **van't Hoff equation**

$$\Pi \quad = \quad [B]RT$$

where [B] = n_B/V is the molar concentration of the solute. Proof follows:
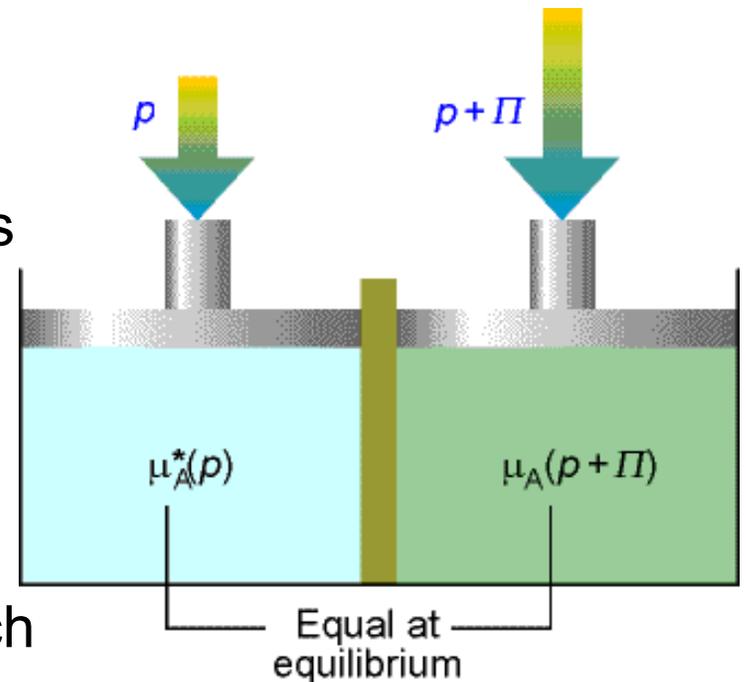
Osmosis, 2

On the right, the opposing pressure arises from the head of the solution that osmosis produces. Equilibrium is established when the hydrostatic pressure of the solution in the column is equal to the osmotic pressure

Pure solvent side: $\mu_A^*(p)$ at pressure p
Solution side: $x_A < 1$, so μ_A^* is lowered by solute to μ_A; however, μ_A is now increased by greater pressure, $p + \Pi$

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

Account for the presence of solute

$$\mu_A(x_A, \; p + \Pi) \;=\; \mu_A^*(p + \Pi) \;+\; RT \ln x_A$$
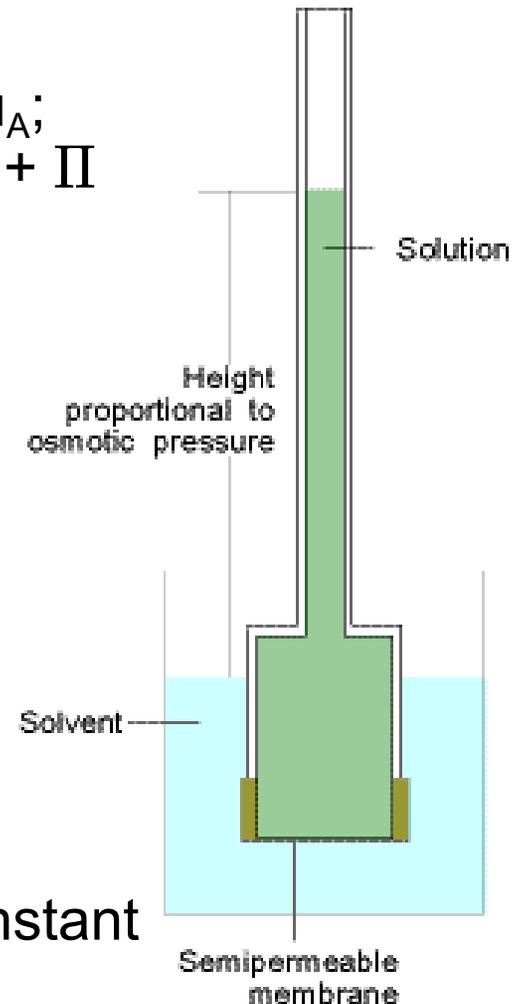
Take pressure into account:

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

Combining equations, we have

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

Dilute solutions: x_A replaced by $\ln(1 - x_B) \approx -x_B$ & V_m constant

$$RT x_B \;=\; \Pi V_m$$

Solution

Height proportional to osmotic pressure

Solvent

Semipermeable membrane
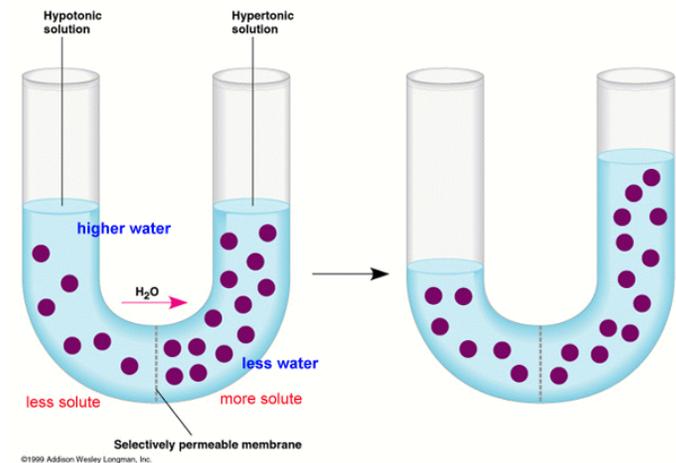
Osmosis: Some Examples

Special sample chamber with a selectively permeable membrane:

Diffusion, osmosis and **dialysis** are the basis of transports across membranes (dialysis is selective passage of solute)

Reverse osmosis involves applying a pressure to force the pure solvent (e.g., water) through a semipermeable membrane. Normally, the water would be diffusing through the membrane into the solution, diluting the solute concentration. Reverse osmosis finds many applicatons in water purification.

Osmosis: Living Cells

Living cells regulate concentrations of solutes:

Cells placed in concentrated salt solutions (hypertonic solutions) collapse, while cells that are hypertonic themselves (hypotonic solution) have the potential to burst.

Cells placed in 10% salt solution
(hypertonic solution)

NaCl   NaCl   NaCl   NaCl

H_2O

H_2O H_2O H_2O
H_2O
H_2O
H_2O

H_2O H_2O
H_2O
NaCl
NaCl
NaCl

*

H_2O
H_2O NaCl H_2O
H_2O NaCl

NaCl   NaCl
H_2O H_2O
H_2O

NaCl

H_2O
NaCl

NaCl   NaCl
H_2O H_2O

H_2O
Cells are plasmolyzed

Osmometry

Osmotic pressure is easily measured, and is quite large. Osmometry can be applied for the determination of molecular weights of large molecules (proteins, synthetic polymers), which dissolve to produce less than ideal solutions. Van't Hoff can be rewritten is virial form

$$\Pi \;=\; [\text{B}]RT \,\{1 \;+\; B[\text{B}] \;+\; ...\}$$

where B is the empirically determined **osmotic virial coefficient**

Osmotic pressure is measured at various concentrations, c, and plotting Π/c against c is used to determine the molar mass of B
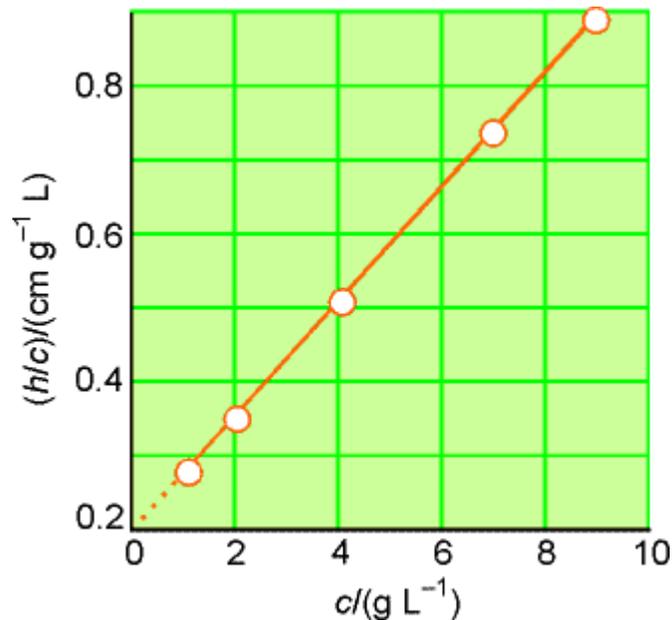
Consider the example of poly(vinyl chloride) PVC, in cyclohexanone at 298 K

Pressures are expressed in terms of heights of solution, $\rho = 0.980$ g cm^{-3} in balance with the osmotic pressure

Osmometry, 2

c(g L^{-1})	1.00	2.00	4.00	7.00	9.00
h(cm)	0.28	0.71	2.01	5.10	8.00

Use $\Pi = [B]RT\{1 + B[B] + ...\}$ with $[B] = c/M$, where c is the mass concentration and M is the molar mass. The osmotic pressure is related to the hyrdostatic pressure by $\Pi = \rho gh$, where $g = 9.81$ m s^{-2}. Then:

$$\frac{h}{c} = \frac{RT}{\rho gM}\left(1 + \frac{Bc}{M} + ...\right) = \frac{RT}{\rho gM} + \left(\frac{RTB}{\rho gM^2}\right)c + ...$$

Plot h/c vs. c to find M, expecting a straight line with intercept $RT/\rho gM$ at $c = 0$. The data give an intercept of $c = 0.21$, and

c(g L^{-1})	1.00	2.00	4.00	7.00	9.00
h/c(cm g^{-1} L)	0.28	0.36	0.53	0.729	0.889

Thus:

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

$$= \frac{(8.31451 \text{ JK}^{-1}\text{mol}^{-1}) \times 298 \text{ K}}{(980 \text{ kg m}^{-3}) \times (9.81 \text{ m s}^{-2})} \times \frac{1}{2.1 \times 10^{-3} \text{ m}^4\text{kg}^{-1}}$$

$$= 1.2 \times 10^2 \text{ kg mol}^{-1}$$

Activities

Just like real gases have **fugacities** to describe deviations from perfect gas behaviour, solvents have activities. (We will not really be focusing on this area in this course, but it is here for posterity)

Chemical potential of solvent (similar equ'ns set up for solute, see 7.6):

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

Activity a_A is a kind of **effective mole fraction** or **effective concentration**, like fugacity is an effective pressure

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

All solvents obey Raoult's law, $(p_A/p_A^* = x_A)$ as the concentration of the solute approches zero, the activity of the solvent approaches the mole fraction as $x_A \to 1$. We can define an activity coeffcient γ_A

$$a_A \to x_A \quad \text{as} \quad x_A \to 1$$
$$a_A \to \gamma_A x_A \qquad \gamma_A \to 1 \quad \text{as} \quad x_A \to 1$$
$$\mu_A = \mu_A^* + RT \ln x_A + RT \ln \gamma_A$$