

## Lecture 10

### Dilute Solutions

Solution – liquid mixture

Solvent – primary component

Solute(s) – secondary component.

In chemistry the content of the solution is often expressed with

$$\text{Molality} = m = \frac{\text{moles of solute}}{\text{Kilograms of solvent}}$$

Dilute solution – the solute molecules are much less abundant than solvent molecules.

### Chemical potentials of solvent and solute

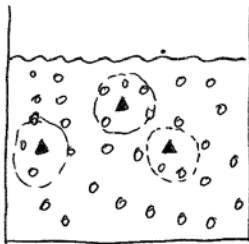
A – Solvent      B – Solute

$$\mu_A = \left( \frac{\partial G}{\partial N_A} \right)_{P,T,N_B}, \quad \mu_B = \left( \frac{\partial G}{\partial N_B} \right)_{P,T,N_B} \quad - \text{definition of chemical potentials in mixture}$$

$$G = N_A \cdot \mu_0(T, P) - \text{pure solvent } (N_B = 0)$$

$\mu_0(T, P)$  some function of temperature and pressure. For liquids and concentrated gas it can not be easily computed,  $\mu_0$  so is typically determined from experiment.

(1)  $dG = dU + PdV - TdS$  is the change in free energy.



We fix number of molecule of solvent and start adding molecules of solute. Terms  $dU$  and  $PdV$  do not depend on  $N_A$ . Both quantities depend on how a B molecule interacts with its immediate neighbors. For  $TdS$  term however, can be splitted into two terms, one independent on  $N_A$  and another comes from freedom of positioning B molecules any where in solution. This part reflects the entropy of mixing of A and B. Let us compute this mixing entropy. We again will use binomial distribution. The only difference is that to comply with chemistry convention we will keep  $N_A$  constant and add  $N_B$  in different amounts.

$$g = \frac{N!}{N_A! N_B!}, \quad N = N_A + N_B, \quad S_{mix} = k \ln g$$

$N_B$  and  $N_A$  are both large numbers so we can use the Stirling approximation.

$$\begin{aligned}
\frac{1}{k} S &= N \ln N - N - N_A \ln N_A + N_A - N_B \ln N_B + N_B = \\
&= N \ln N + N_A \ln N_A + N_B \ln N_A - N_B \ln N_A - N_B \ln N_B = \\
(2) \quad &= N \ln N - (N_B + N_A) \ln N_A + N_B \ln N_A - N_B \ln N_B = \\
&= -N \ln \left( 1 - \frac{N_B}{N} \right) + N_B \ln N_A - N_B \ln N_B = +N \left( \frac{N_B}{N} \right) + N_B \ln N_A - N_B \ln N_B
\end{aligned}$$

In the above derivation we use the fact that we have a dilute solution and therefore

$$N_B \ll N_A \approx N \text{ and } \ln \left( \frac{N_A}{N} \right) = \ln \left( \frac{N - N_B}{N} \right) = -\frac{N_B}{N}.$$

So now Gibbs free energy can be written as,

$$(3) \quad G = N_A \mu_0(T, P) + N_B f(T, P) - N_B kT - N_B kT \ln N_A + N_B kT \ln N_B$$

Where the term  $N_B f(T, P)$  comes from contributions to entropy not related to mixing.

$$(4a) \quad \mu_A = \left( \frac{\partial G}{\partial N_A} \right)_{TPN_B} = \mu_0(T, P) - \frac{N_B kT}{N_A}$$

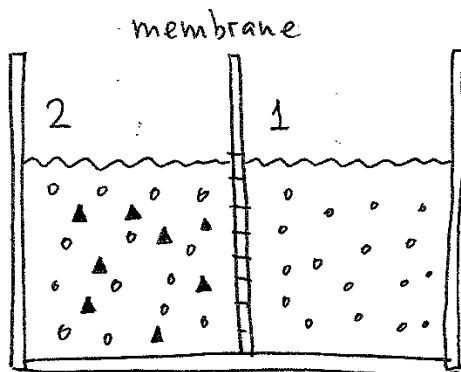
$$(4b) \quad \mu_B = \left( \frac{\partial G}{\partial N_B} \right)_{T,P,N_A} = f(T, P) + kT \ln \left( \frac{N_B}{N_A} \right)$$

$$(5) \quad \mu_B = \mu^0(T, P) + kT \ln m_B$$

We can re-write equation 4(b) in terms of molality. Molality is a constant times  $\frac{N_B}{N_A}$ .

The constant can be absorbed to the  $\mu^0(T, P)$  term to give the equation (5).

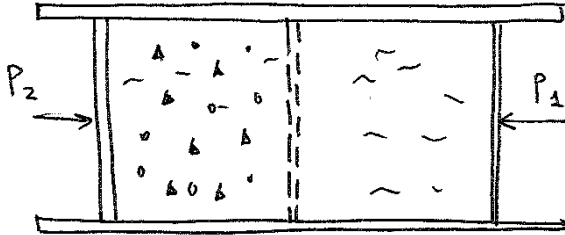
### Osmotic Pressure



Example: Cell membrane is transparent for water molecules but can block large molecules and charged ions. According to equation (4(a)) chemical potential of solvent molecule is higher in pure solvent than in solution. The species, in our case molecule of solvent “try” to flow from regions of high chemical potential (1<sup>st</sup> compartment in the

figure) to regions of low chemical potential (2<sup>nd</sup> compartment in the figure). This flow of molecules is called Osmosis.

To prevent osmosis we can apply some extra pressure to (I) part of container to counter balance the molecule flow created due to the gradient of chemical potential.



Condition for equilibrium

$$\mu_0(T, P_1) = \mu_0(T, P_2) - \frac{N_B}{N_A} kT \quad P_2 > P_1$$

$$\mu_0(T, P_2) = \mu_0(T, P_1) + \left( \frac{\partial \mu}{\partial P} \right)_T (P_2 - P_1) \quad \text{We use Taylor expansion.}$$

$$\mu_0(T, P) = \frac{1}{N} G(T, P) \Rightarrow \left( \frac{\partial \mu}{\partial P} \right)_{NT} = \frac{V}{N}$$

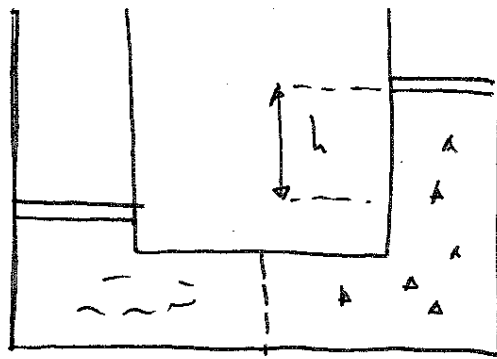
$$(P_2 - P_1) \frac{V}{N} = \frac{N_B}{N_A} kT$$

$$(P_2 - P_1) = n_B kT$$

$n_B$  - concentration, number of molecules of solute per unit volume.

**Reverse Osmosis:** The extra pressure  $[P_2 - P_1 > n_B kT]$  pushes molecules of solvent from solution compartment to pure solvent compartment. It is used, for example for desalination of seawater.

Experiment arrangement to measure osmosis pressure.



## Change in the boiling and freezing points of solutions.

We may consider two limited cases

1) Temperature is fixed. Question is how pressure of saturated vapor changes upon addition of solute.

$$\mu_0(T, P_0) = \mu_{gas}(T, P_0) - \text{pure solvent}$$

$$\mu_0(T, P_0) + \frac{\partial \mu}{\partial P}(P - P_0) - \frac{N_B}{N_A} kT = \mu_{gas}(P_0, T) + (P - P_0) \frac{\partial \mu_{gas}}{\partial P}$$

$$(P - P_0) \left( \frac{V}{N} \right)_L - \frac{N_B}{N_A} kT = (P - P_0) \left( \frac{V}{N} \right)_{gas} \quad \left( \frac{V}{N} \right)_{gas} \gg \left( \frac{V}{N} \right)_L$$

$$P = P_0 - P_0 \frac{N_B}{N_A} (\text{Raoult's law})$$

2) Pressure is fixed, how the temperature at which solution and gas are at equilibrium changes.

$$\mu_0(T_0, P_0) + (T - T_0) \left( \frac{\partial \mu_0}{\partial T} \right)_P - \frac{N_B kT}{N_A} = \mu_{gas}(T_0, P_0) + (T - T_0) \frac{\partial \mu_{gas}}{\partial T}$$

$$\mu = \frac{1}{N} G \quad \left( \frac{\partial G}{\partial T} \right)_P = -S$$

$$-(T - T_0) \left( \frac{S}{N} \right)_{liq} - \frac{N_B}{N_A} kT = -(T - T_0) \left( \frac{S}{N} \right)_{gas}$$

$$T \left[ \left( \frac{S}{N} \right)_{gas} - \left( \frac{S}{N} \right)_{liq} \right] = L - \text{latent heat of vaporization per molecule}$$

$$(T - T_0) = \frac{N_B}{N_A} \cdot \frac{kT^2}{L}$$

The difference  $(T - T_0)$  is usually small. So, equation above is usually re-written assuming  $T = T_0$  in right-hand side.

$$T - T_0 = \frac{N_B}{N_A} \cdot \frac{kT_0^2}{L}$$

Compute (or look it in text book) a difference in boiling temperature of seawater and pure water. (Do we have to compute the contributions for both Na and Cl?)

$$T_0 = 373\text{K}$$

$$L = 2260 \text{ kJ}$$

$$\mu_{Na} = 23\text{g}$$

$$\mu_{Cl} = 35\text{g}$$

1kg of seawater contains 35g of salt.