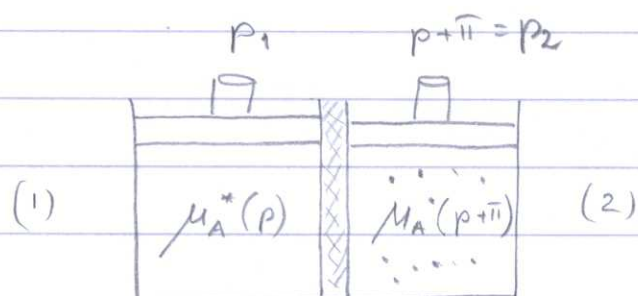


## OSMOSIS

(3)

The passage of a pure solvent into a solution separated by a semipermeable membrane

The osmotic pressure  $\Pi$  is the pressure that must be applied to stop it in flux.



pure solvent  
semipermeable m.

At equilibrium;  
the chemical potential  
of the solvent must be  
the same on each side of the membrane.

On the pure solvent side (1);  $\mu_A^*(P)$

On the solution side (2);  $\mu$  is lowered by the presence of a solute, raised by greater pressure

Our expression for  $\mu$ :

$$\mu = \mu^0 - \bar{S} \cdot T + \bar{V} \cdot P + RT \ln(\gamma/m)$$

temperature same on both sides.

Introduction of mole fraction (intermezzo)

The mole fraction of component  $i$  in a mixture is:

$$X_i \equiv \frac{m_i}{m_{\pm}}, \quad \text{where}$$

$$m_{\pm} (\text{total}) = \sum_i m_i = m_{\text{H}_2\text{O}} + \sum_i m_i \approx m_{\text{H}_2\text{O}}$$

The volume of the solution containing  $i$  substances,  $V = m_{\text{H}_2\text{O}} \cdot \bar{V}_{\text{H}_2\text{O}} + m_i \cdot \bar{V}_i \approx m_{\text{H}_2\text{O}} \cdot \bar{V}_{\text{H}_2\text{O}}$

$$\text{Then becomes: } X_i = \frac{m_i}{m_{\pm}} = \frac{m_i}{m_{\text{H}_2\text{O}}} = \frac{m_i}{V} \cdot \bar{V}_{\text{H}_2\text{O}} = c_i \cdot \bar{V}_{\text{H}_2\text{O}}$$

$$\text{Hence: } \mu_i = \mu_0^i + RT \cdot \ln c_i = \mu_0^i + RT \cdot \ln \left( \frac{X_i}{\bar{V}_{\text{H}_2\text{O}}} \right)$$

$$= \left\{ \mu_0^i - RT \ln (\bar{V}_{\text{H}_2\text{O}}) \right\} + RT \cdot \ln X_i$$

$$= \underline{\mu_0^i(x)} + RT \ln X_i$$

Back to osmosis

$$\mu_{\text{H}_2\text{O}} (\text{side 1}) = \mu_{\text{H}_2\text{O}} (\text{side 2})$$

$$\mu_0^{\text{H}_2\text{O}}(x) + \bar{V} P_1 + RT \ln X_1 = \mu_0^{\text{H}_2\text{O}} + \bar{V} \cdot P_2 + RT \ln X_2$$

$$\Rightarrow \bar{V} \cdot \pi \equiv \bar{V} (P_2 - P_1) = RT (\ln X_1 - \ln X_2)$$

For dilute solutions:

$$\text{side 2: } \ln(X_{\text{H}_2\text{O}}) = \ln(1 - X_i) \approx -X_i$$

$$\text{side 1: } \ln 1 = 0$$

$$\Rightarrow \bar{V} \cdot \pi = RT \cdot X_i$$

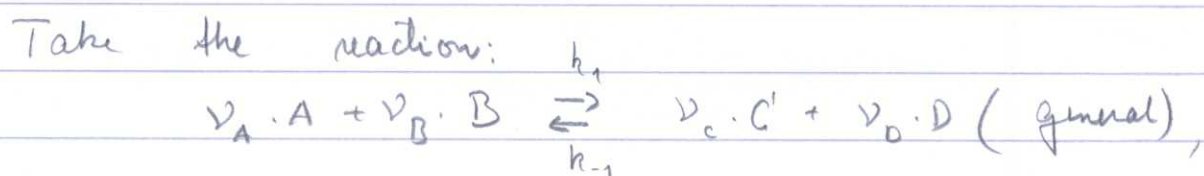
(5)

$$x = \frac{m}{M_+} \quad , \quad n_0$$

$$\underline{\pi} = RT \frac{m}{M_+ \bar{v}} = \underline{RT c}$$

Is as the gas law.

### LAW OF MASS ACTION (chemical equilibrium)



where the  $\nu$ 's are the stoichiometric numbers for the reaction. The reaction is described by a single parameter,  $\xi$ , which is:

$$dm_A = -\nu_A \cdot d\xi, \quad dm_B = -\nu_B \cdot d\xi$$

in general  $dm_i = \nu_i \cdot d\xi$ ,  $\ominus$  for reactants  
and  $\oplus$  for products (C, D).

The change in Gibbs free energy for the system:

$$dG = \sum_i \mu_i \cdot dm_i = \sum_i \mu_i \cdot \nu_i \cdot d\xi \equiv A \cdot d\xi,$$

A is the affinity of the reaction.

When the reaction has reached the equilibrium,

$$\frac{dG}{d\xi} = 0, \quad \text{or}$$

$$A = 0 = \sum \mu_i \cdot \nu_i$$

(6)

$$\Rightarrow \sum_i (\mu_0^i + RT \ln c_i) \cdot \nu_i = 0, \text{ or:}$$

$$-\Delta G_0 \equiv -\sum \mu_0^i \cdot \nu_i = RT \cdot \ln \left[ \frac{C_C^{\nu_C} \cdot C_D^{\nu_D}}{C_A^{\nu_A} \cdot C_B^{\nu_B}} \right], \text{ or}$$

$$\frac{[C]^{\nu_C} \cdot [D]^{\nu_D}}{[A]^{\nu_A} \cdot [B]^{\nu_B}} = e^{-\frac{\Delta G_0}{RT}} \equiv K$$

law of mass action.

$K$ ; the equilibrium constant, sometimes written:

$$-\Delta G_0 = RT \cdot \ln K$$

A closer look at  $\Delta G_0 = \sum \mu_0^i \cdot \nu_i$

$$\Delta G = \left( \sum_i \mu_0^i \cdot \nu_i + RT \sum \ln c_i \cdot \nu_i \right) \cdot \Delta \xi$$

assume all concentrations to be 1 molar (standard conditions), and  $\Delta \xi = 1 \text{ mole}$ ,

Hence:

$$\frac{\Delta G}{\Delta \xi} \equiv \sum \mu_0^i \cdot \nu_i \equiv \Delta G_0,$$

$\Delta G_0$ , introduced above, means  $\Delta G$  for 1 mole at standard conditions. From earlier:

$$\Delta G = \Delta U - T \cdot \Delta S$$

Equilibrium is determined both by  $\Delta U$  and  $\Delta S$ , the entropy change.