Lecture 16

Thursday, November 7, 2024 10:02

Skip Topic 5D, 5E

Topic 5F: Activities

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

$$\mu_A = \mu_A^* + RT\ln x_A$$ ideal solution obeys Raoult's Law

$$\mu_A = \mu_A^* + RT\ln \underbrace{a_A}$$ activity; "effective" mole fraction

$$a_A = \frac{p_A}{p_A^*}$$ ← empirically measured

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

$$a_A = \underbrace{\gamma_A} x_A, \quad \gamma_A \to 1 \text{ as } x_A \to 1$$

activity coefficient

$$\boxed{\mu_A = \mu_A^* + RT\ln x_A + RT\ln \gamma_A}$$

solvent activity

For solutes, approach ideal-dilute behaviour as $x_B \to 0$, not as $x_B \to 1$.

Henry's Law: $p_B = K_B x_B$, where K_B is an empirical constant

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

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

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

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

ideal-dilute solution

Real solutes :

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

$$\mu_B^* = \mu_B^\ominus - RT \ln \frac{K_B}{p_B^*}$$

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

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

$a_B = \frac{p_B}{K_B}$ activity of solute, empirically measured

$a_B = \gamma_B x_B$, $a_B \to x_B$ and $\gamma_B \to 1$ as $x_B \to 0$

Topic 6A : The Equilibrium Constant

Consider the reaction $A \rightleftharpoons B$

ξ (xi) : extent of the reaction

has dimensions of amount of substance

$$dn_A = -d\xi \,, \quad dn_B = +d\xi$$

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T}$$

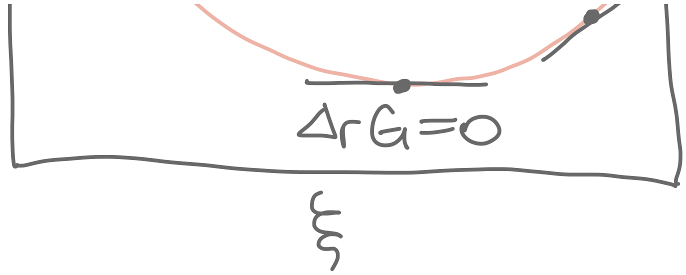
$$dG = \mu_A dn_A + \mu_B dn_B$$

$$= -\mu_A d\xi + \mu_B d\xi$$

$$= (\mu_B - \mu_A) d\xi$$

$$\left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \mu_B - \mu_A$$

$$\Delta_r G = \mu_B - \mu_A$$



endergonic

Description of Equilibrium

For A and B being perfect gases,

$$\Delta_r G = \mu_B - \mu_A$$

$$= \left(\mu_B^\ominus + RT\ln\frac{p_B}{p^\ominus}\right) - \left(\mu_A^\ominus + RT\ln\frac{p_A}{p^\ominus}\right)$$

$$\Delta_r G = \Delta_r G^\ominus + RT\ln\frac{p_B}{p_A}$$

$$\Delta_r G = \Delta_r G^\ominus + RT\ln Q, \quad \underline{Q = \frac{p_B}{p_A}}$$

reaction quotient

$$\Delta_r G^\ominus = G_m^\ominus(B) - G_m^\ominus(A) = \mu_B^\ominus - \mu_A^\ominus$$

$$\Delta_r G^\ominus = \Delta_f G^\ominus(B) - \Delta_f G^\ominus(A)$$

$0 = \Delta_r G^\ominus + RT \ln K$ at equilibrium

$$\boxed{RT \ln K = -\Delta_r G^\ominus} \qquad K = \left(\frac{p_B}{p_A}\right)_{\text{equilib}}$$

The General Case of a Reaction

$$dG = \sum_J \mu_J dn_J = \sum_J \mu_J \nu_J d\xi$$

$$= \left(\sum_J \mu_J \nu_J\right) d\xi$$

$$\left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \Delta_r G = \sum_J \mu_J \nu_J$$

$$\Delta_r G = \underbrace{\sum_J \nu_J \mu_J^\ominus}_{\Delta_r G^\ominus} + RT \sum_J \boxed{\nu_J} \ln a_J$$

$$\Delta_r G = \Delta_r G^\ominus + RT \sum_J \ln a_J^{\nu_J}$$

$$\ln x + \ln y + \ln z + \cdots = \ln xyz$$

$$\boxed{\Delta_r G = \Delta_r G^\ominus + RT \ln\left(\prod_J a_J^{\nu_J}\right)}$$

$$Q = \prod_J a_J^{\nu_J}, \quad Q = \frac{\text{activities of produc}}{\text{activities of reacto}}$$

$$\boxed{\Delta_r G = \Delta_r G^\ominus + RT \ln Q}$$

reaction Gibbs ener at an arbitrary sta

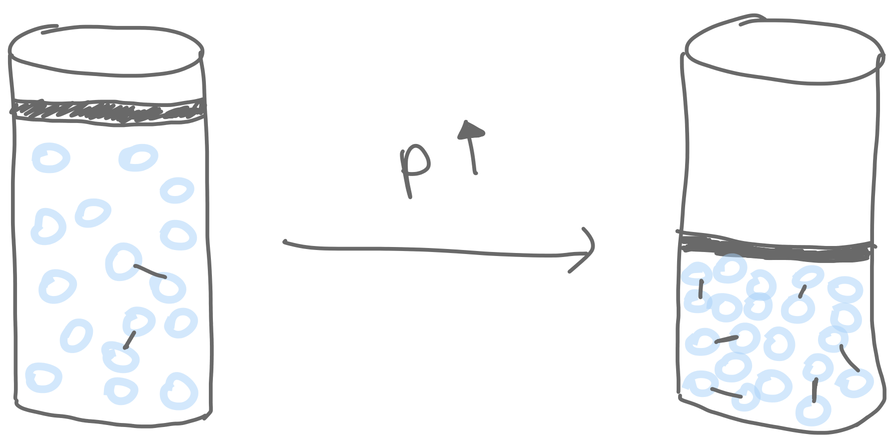
$$K = \left(\prod_J a_J^{\nu_J}\right)_{\text{equilibrium}}$$

Topic 6B: The Response of Equilibria to the Conditions

$A(g) \rightleftharpoons 2B(g)$

$$K = \frac{(p_B^2/p^{\ominus \cancel{2}})}{p_A/\cancel{p^{\ominus}}} = \frac{p_B^2}{p_A p^{\ominus}}$$

Le Chatelier's Principle: A system at equilibrium, when subjected to a disturbance, tends to respond in a way that minimizes the effect of the disturbance.



$A(g) \leftarrow\!\rightleftharpoons 2B(g)$

Suppose that there is an amount n of A present initially (and no B).

Define α: degree of dissociation of A into 2B.

At equilibrium:

	A	B
amount	$(1-\alpha)n$	$2\alpha n$
mole fraction	$\dfrac{(1-\alpha)\cancel{n}}{(1-\alpha)\cancel{n}+2\alpha\cancel{n}} = \dfrac{1-\alpha}{1+\alpha}$	$\dfrac{2\alpha\cancel{n}}{(1-\alpha)\cancel{n}+2\alpha\cancel{n}} = \dfrac{2\alpha}{1+\alpha}$

$p_J = x_J p$

$$K = \frac{p_B^2}{p_A p^\circ} = \frac{x_B^2 p^2}{x_A p\, p^\circ}$$

$$= \frac{[2\alpha/(1+\alpha)]^2 p^2}{(1-\alpha)/(1+\alpha)\, p\, p^\circ}$$

$$= \frac{4\alpha^2/(1+\alpha)^{\cancel{2}}\,p^2}{(1-\alpha)/\cancel{(1+\alpha)}\,p\,p^\ominus}$$

$$= \frac{4\alpha^2 p^{\cancel{2}}}{(1-\alpha)(1+\alpha)\,\cancel{p}\,p^\ominus}$$

$$K = \frac{4\alpha^2 p}{1-\alpha^2 p^\ominus}$$

$$(1-\alpha^2)K = 4\alpha^2 p/p^\ominus$$

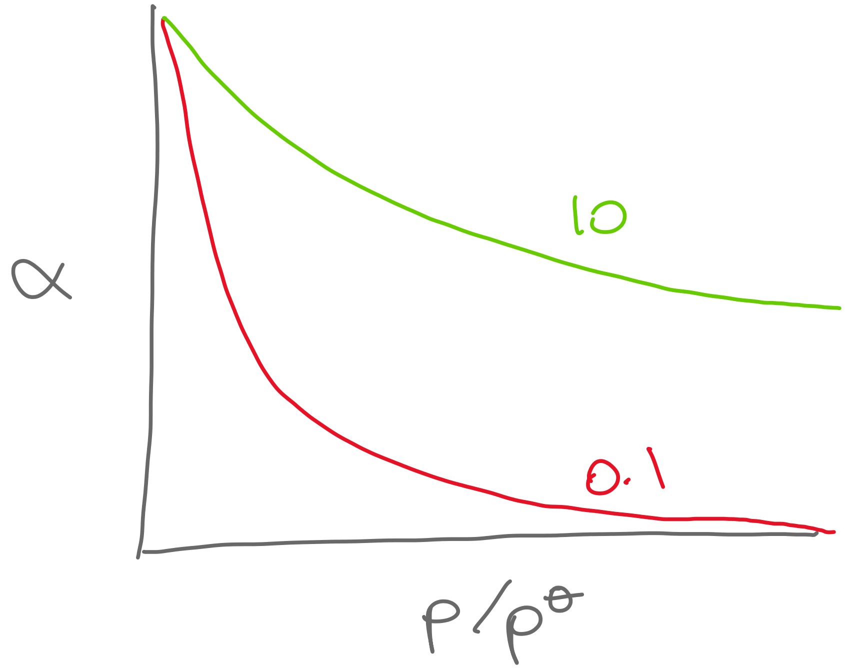
$$K - K\alpha^2 = 4\alpha^2 p/p^\ominus$$

$$K = 4\alpha^2 p/p^\ominus + K\alpha^2$$

$$K = \alpha^2(4p/p^\ominus + K)$$

$$\alpha^2 = \frac{K}{4p/p^\ominus + K} \Big/ \frac{K}{K}$$

$$\alpha = \left(\frac{1}{4p/Kp^\ominus + 1}\right)^{\frac{1}{2}}$$



van't Hoff Equation

$$\boxed{\frac{d \ln K}{dT} = \frac{\Delta_r H^{\ominus}}{RT^2}}$$