

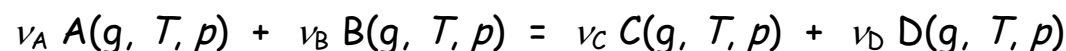
## Equilibrium in Solution

The chemical potential for molecules in solution is given by a formula that is very similar to that for ideal gases:

$$\mu_A(T, p, c_A) = \mu_A^\circ(T, p) + RT \ln c_A = \mu_A^\circ(T, p) + RT \ln[A]$$

The precise definition of the standard chemical potential  $\mu_A^\circ(T, p)$  is now more complicated; it is defined at a given pH, salt concentration, etc..., all solution properties that need to be defined in advance. We will not go through those and take it as a given that the standard state is appropriately defined.

Given a standard chemical potential  $\mu_A^\circ(T, p)$ , then the analysis that we did for the ideal gas follows straight through and we find for a solution process



that following the ideal gas analysis in our previous lecture

$$\Delta G(\varepsilon) = \varepsilon [\nu_C \mu_C^\circ(T) + \nu_D \mu_D^\circ(T)] - [\nu_A \mu_A^\circ(T) + \nu_B \mu_B^\circ(T)] + RT \ln \left( \frac{[C]^{\nu_C} [D]^{\nu_D}}{[A]^{\nu_A} [B]^{\nu_B}} \right)$$

and the equilibrium constant K comes out through

$$\Delta G_{rxn}^\circ = -RT \ln K, \quad K = e^{-\Delta G^\circ / RT}$$

Where  $K = Q_{eq} = \frac{[C]^{\nu_C} [D]^{\nu_D}}{[A]^{\nu_A} [B]^{\nu_B}}$  at equilibrium as before, and where the concentrations Q are equilibrium concentrations.

## Temperature dependence of $K$ (or $K_p$ )

$$\ln K(T) = -\frac{\Delta G^\circ}{RT} \Rightarrow \frac{d \ln K}{dT} = \frac{d}{dT} \left( -\frac{\Delta G^\circ}{RT} \right) = \frac{\Delta G^\circ}{RT^2} - \frac{1}{RT} \frac{d \Delta G^\circ}{dT}$$

But at fixed pressure and/or solutions properties ( $p = 1$  bar, pH constant, etc..)

$$\frac{d \Delta G^\circ}{dT} = \left( \frac{\partial \Delta G^\circ}{\partial T} \right)_{1 \text{ bar, pH constant, etc...}}$$

and from fundamental equation

$$dG = -SdT + Vdp \Rightarrow \left( \frac{\partial G}{\partial T} \right)_p = -S \Rightarrow \left( \frac{\partial \Delta G^\circ}{\partial T} \right)_p = -\Delta S^\circ(T)$$

$$\therefore \frac{d \ln K}{dT} = \frac{\Delta H^\circ(T) - T \Delta S^\circ(T)}{RT^2} + \frac{1}{RT} \Delta S^\circ(T)$$

$$\boxed{\frac{d \ln K(T)}{dT} = \frac{\Delta H^\circ(T)}{RT^2}}$$

Integrating:  $\ln K(T_2) = \ln K(T_1) + \int_{T_1}^{T_2} \frac{\Delta H^\circ(T)}{RT^2} dT$

At constant  $p$ :  $\Delta H^\circ(T) = \Delta H^\circ(T_1) + \Delta C_p(T - T_1)$

$$\ln K(T_2) = \ln K(T_1) + \int_{T_1}^{T_2} \frac{\Delta H^\circ(T_1) + \Delta C_p(T - T_1)}{RT^2} dT$$

Over small  $T$  ranges,  $\Delta C_p(T - T_1)$  can be assumed small and  $\Delta H^\circ$  independent of  $T$ .

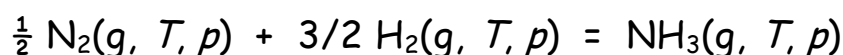
$$\Rightarrow \boxed{\ln K(T_2) \approx \ln K(T_1) + \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \ln K(T_1) + \frac{\Delta H^\circ}{R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)}$$

If  $\Delta H^\circ(T) < 0$  (Exothermic)  $T_2 > T_1$  means  $K_p(T_2) < K_p(T_1)$   
The equilibrium shifts toward reactants

If  $\Delta H^\circ(T) > 0$  (Endothermic)  $T_2 > T_1$  means  $K_p(T_2) > K_p(T_1)$   
The equilibrium shifts toward products

This is Le Chatelier's principle for Temperature

- Example: The Haber process



$$\Delta H_{rxn}^\circ(298 \text{ K}) = -46.21 \text{ kJ/mol}$$

$$\Delta G_{rxn}^\circ(298 \text{ K}) = -16.74 \text{ kJ/mol}$$

$$K_p = \frac{P_{\text{NH}_3}}{P_{\text{H}_2}^{3/2} P_{\text{N}_2}^{1/2}} = p^{-1} \frac{X_{\text{NH}_3}}{X_{\text{H}_2}^{3/2} X_{\text{N}_2}^{1/2}} = e^{\frac{16,740 \text{ J/mol}}{(8.314 \text{ J/K-mol})(298 \text{ K})}} = 860$$

For  $p = 1$  bar this is pretty good, lots of product. However, the reaction at room  $T$  is slow (this is kinetics, not thermodynamics). Raising  $T$  to 800 K can speed it up. But since  $\Delta H^\circ(T) < 0$  (exothermic), Le Chatelier tells us that the equilibrium will shift toward the reactants.

Indeed:  $K_p(800 \text{ K}) = 0.007$

What to do?  $\Rightarrow$  Note above  $K_x = \boxed{p} K_p$

Again use Le Chatelier, but with pressure! If we increase  $p$ , Eq. shifts toward products.

⇒ Run reaction at high  $T$  and high  $p$

For  $p = 1$  bar,  $T = 800$  K,  $K_p = 0.007$

$$K_X = \frac{X_{\text{NH}_3}}{X_{\text{H}_2}^{3/2} X_{\text{N}_2}^{1/2}} = (1)K_p = 0.007$$

But at  $p = 100$  bar,  $K_X = (100)K_p = 0.7$  much better!

- Heterogeneous Equilibria

If a product or reactant is a solid or liquid, it will not appear in the ratio of partial  $p$ 's for  $K_p$  or in the concentrations if the equilibrium is in solution. However, it must be used in  $\Delta G$ .

Why? Take  $\nu_A A(s) + \nu_B B(g) = \nu_C C(l) + \nu_D D(g)$

The solid and liquid are not mixed - they are pure states.

$$\Delta G = [\nu_C \mu_C(s, \text{pure}, p) + \nu_D \mu_D(g, \text{mix}, p)] - [\nu_A \mu_A(l, \text{pure}, p) + \nu_B \mu_B(g, \text{mix}, p)]$$

And for (l) or (s)  $\mu_C(\text{pure}, p) \approx \mu^\circ(\text{pure})$  (no  $p$ -dependence)

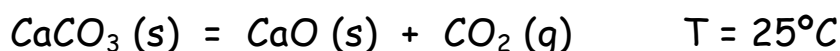
$$\Rightarrow \Delta G = \nu_C \mu_C^\circ + \nu_D \mu_D^\circ - \nu_A \mu_A^\circ - \nu_B \mu_B^\circ + RT \ln \frac{p_D^{\nu_D}}{p_B^{\nu_B}} = \Delta G^\circ + RT \ln Q$$

$$\therefore K_p = \left[ \frac{p_D^{v_D}}{p_B^{v_B}} \right]_{Eq.} \quad \underline{\text{No A or C involved.}}$$

But we still have  $\Delta G_{\text{rxn}}^{\circ} = v_C \mu_C^{\circ} + v_D \mu_D^{\circ} - v_A \mu_A^{\circ} - v_B \mu_B^{\circ}$

and  $\ln K_p = -\frac{\Delta G_{\text{rxn}}^{\circ}}{RT}$

e.g. the decomposition of limestone



Calculate equilibrium vapor pressure at room  $T$  and elevated  $T$ .  
 Data at  $25^{\circ}\text{C}$ :

Substance	CaCO <sub>3</sub> (s)	CaO (s)	CO <sub>2</sub> (g)
$\mu^{\circ}$ (kJ/mol)	-1128.8	-604.0	-394.36
$\Delta \bar{H}_f^{\circ}$ (kJ/mol)	-1206.9	-635.09	-393.51

At equilibrium,

$$\begin{aligned} \Delta G &= \mu(\text{CaO}, s) + \mu(\text{CO}_2, g) - \mu(\text{CaCO}_3, s) \\ &= \mu^{\circ}(\text{CaO}, s) + \mu^{\circ}(\text{CO}_2, g) + RT \ln p_{\text{CO}_2} - \mu^{\circ}(\text{CaCO}_3, s) \\ &= \Delta G^{\circ} + RT \ln K_p \quad \text{where } K_p = p_{\text{CO}_2} \text{ (at eq.)} \end{aligned}$$

The equilibrium constant includes only the gas, but  $\Delta G^{\circ}$  includes the solids too.

$$\Delta G^{\circ} \text{ (kJ/mol)} = -604.0 - 394.4 - (-1128.8) = 130.4 \text{ kJ/mol}$$

$$\Delta H^{\circ} \text{ (kJ/mol)} = -635.1 - 393.5 - (-1206.9) = 178.3 \text{ kJ/mol}$$

Equilibrium pressure:

$$\ln K_p = -\frac{\Delta G^\circ}{RT} = -\frac{130,400 \text{ J/mol}}{(8.314 \text{ J/K-mol})(298.15 \text{ K})} = -52.50$$

$$K_p = 1.43 \times 10^{-23} \text{ bar}$$

Nothing there at room  $T$ ! Try 1100 K:

$$\begin{aligned} \ln p_{\text{CO}_2} (1100 \text{ K}) &\approx \ln p_{\text{CO}_2} (298 \text{ K}) + \frac{\Delta H^\circ}{R} \left( \frac{1}{1100 \text{ K}} - \frac{1}{298 \text{ K}} \right) \\ &= -52.50 - \frac{178,300 \text{ J/mol}}{8.314 \text{ J/K-mol}} \left( \frac{1}{1100 \text{ K}} - \frac{1}{298 \text{ K}} \right) = 0.17 \end{aligned}$$

$$p_{\text{CO}_2} (1100 \text{ K}) \approx 0.84 \text{ bar}$$

There's probably some change in  $\Delta \bar{H}_f^\circ$  over such a wide  $T$  range, but clearly the equilibrium shifts dramatically.