Equilibrium in Solution

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

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

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

$$\nu_A\ \mathrm{A}(\mathrm{sol},\ T,\ p) \ +\ \nu_B\ \mathrm{B}(\mathrm{sol},\ T,\ p) \ =\ \nu_C\ \mathrm{C}(\mathrm{sol},\ T,\ p) \ +\ \nu_D\ \mathrm{D}(\mathrm{sol},\ T,\ p)$$

that following the ideal gas analysis in our previous lecture

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

and the equilibrium constant K comes out through

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

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

Temperature dependence of *K (or K_p)*

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

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

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

and from fundamental equation

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

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

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

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 ΔH° independent of T.

$$\Rightarrow \quad \boxed{\ln K(T_2) \approx \ln K(T_1) + \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \ln K(T_1) + \frac{\Delta H^\circ}{R}\left(\frac{T_2 - T_1}{T_1T_2}\right)}$$

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

$$\tfrac{1}{2}\,N_2(g,\ T,\ p)\ +\ 3/2\ H_2(g,\ T,\ p)\ =\ NH_3(g,\ T,\ p)$$

$$\Delta H^\circ_{rxn}(298\ \text{K}) = -46.21\ \text{kJ/mol}$$
$$\Delta G^\circ_{rxn}(298\ \text{K}) = -16.74\ \text{kJ/mol}$$

$$K_p = \frac{p_{NH_3}}{p_{H_2}^{3/2}\,p_{N_2}^{1/2}} = p^{-1}\frac{X_{NH_3}}{X_{H_2}^{3/2}X_{N_2}^{1/2}} = e^{\frac{16{,}740\ \text{J/mol}}{(8.314\ \text{J/K-mol})(298\ \text{K})}} = 860$$

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? ⇒ Note above $K_X = \boxed{p}K_p$

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

$\Rightarrow$ Run reaction at high *T* and high *p*

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

$$K_X = \frac{X_{NH_3}}{X_{H_2}^{3/2} X_{N_2}^{1/2}} = (1) K_p = 0.007$$

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 ΔG.

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

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

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

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

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

$$\therefore \qquad K_p = \left[\frac{p_D^{\nu_D}}{p_B^{\nu_B}}\right]_{Eq.}$$

<u>No A or C involved</u>.

But we still have $\Delta G^\circ_{\text{rxn}} = \nu_C\mu^\circ_C + \nu_D\mu^\circ_D - \nu_A\mu^\circ_A - \nu_B\mu^\circ_B$

and $\ln K_p = -\dfrac{\Delta G^\circ_{\text{rxn}}}{RT}$

<u>e.g.</u> the decomposition of limestone

$CaCO_3$ (s) = CaO (s) + CO_2 (g) T = 25°C

Calculate equilibrium vapor pressure at room T and elevated T.
Data at 25°C:

Substance	$CaCO_3$ (s)	CaO (s)	CO_2 (g)
μ° (kJ/mol)	-1128.8	-604.0	-394.36
$\Delta\bar{H}^\circ_f$ (kJ/mol)	-1206.9	-635.09	-393.51

At equilibrium,

$$\begin{aligned}\Delta G &= \mu(CaO, s) + \mu(CO_2, g) - \mu(CaCO_3, s)\\ &= \mu^\circ(CaO, s) + \mu^\circ(CO_2, g) + RT\ln p_{CO_2} - \mu^\circ(CaCO_3, s)\\ &= \Delta G^\circ + RT\ln K_p \qquad \text{where } K_p = p_{CO_2} \text{ (at eq.)}\end{aligned}$$

The equilibrium constant includes only the gas, but ΔG° includes the solids too.

ΔG° (kJ/mol) = -604.0 – 394.4 – (-1128.8) = 130.4 kJ/mol
ΔH° (kJ/mol) = -635.1 – 393.5 – (-1206.9) = 178.3 kJ/mol

Equilibrium pressure:

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

$$K_p = 1.43x10^{-23} \text{ bar}$$

Nothing there at room T! Try 1100 K:

$$\ln p_{CO_2}(1100 \text{ K}) \approx \ln p_{CO_2}(298 \text{ K}) + \frac{\Delta H^\circ}{R}\left(\frac{1}{1100 \text{ K}} - \frac{1}{298 \text{ K}}\right)$$

$$= -52.50 - \frac{178,300 \text{ J/mol}}{8.314 \text{ J/K-mol}}\left(\frac{1}{1100 \text{ K}} - \frac{1}{298 \text{ K}}\right) = 0.17$$

$$p_{CO_2}(1100 \text{ K}) \approx 0.84 \text{ bar}$$

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