

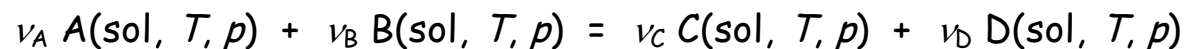
Equilibrium in Solution

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 ($p = 1 \text{ bar}$, 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 ΔH° independent of T .

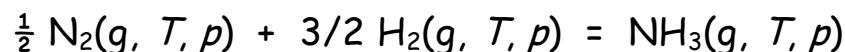
$$\Rightarrow \boxed{\ln K(T_2) \approx \ln K(T_1) + \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) = \ln K(T_1) + \frac{\Delta H^\circ}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)}$$

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 ΔG .

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)

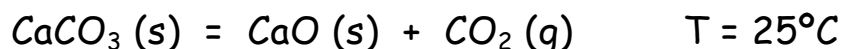
$$\Rightarrow \Delta G = \nu_C \mu_C^\circ + \nu_D \mu_D^\circ - \nu_A \mu_A^\circ - \nu_B \mu_B^\circ + RT \ln \frac{p_D^{\nu_D}}{p_B^{\nu_B}} = \Delta G^\circ + RT \ln Q$$

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

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°C :

Substance	CaCO ₃ (s)	CaO (s)	CO ₂ (g)
μ° (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 ΔG° 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.