

**Temperature dependence of  $K$  ( $p$  fixed)**

$$\ln K(T) = -\frac{\Delta G^0}{RT} \Rightarrow \frac{d \ln K(T)}{dT} = \frac{d}{dT} \left( -\frac{\Delta G^0}{RT} \right) = \frac{\Delta G^0}{RT^2} - \frac{1}{RT} \frac{d\Delta G^0}{dT} = \frac{\Delta G^0}{RT^2} - \frac{1}{RT} \left( \frac{\partial \Delta G^0}{\partial T} \right)_p$$

$$\therefore \frac{d \ln K(T)}{dT} = \frac{\Delta H^0(T) - T\Delta S^0(T)}{RT^2} + \frac{1}{RT} \Delta S^0(T) = \frac{\Delta H^0(T)}{RT^2} \quad \text{van't Hoff equation}$$

Integrate:

$$\ln K(T_2) = \ln K(T_1) + \int_{T_1}^{T_2} \frac{\Delta H^0(T)}{RT^2} dT$$

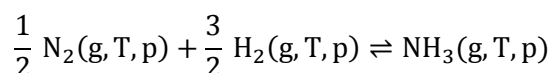
At constant  $p$ ,

$$\Delta H^0(T) = \Delta H^0(T_1) + \Delta C_p(T - T_1)$$

$$\therefore \ln K(T_2) = \ln K(T_1) + \int_{T_1}^{T_2} \frac{\Delta H^0(T_1) + \Delta C_p(T - T_1)}{RT^2} dT$$

Over small  $T$  ranges assume  $\Delta C_p(T - T_1)$  to be small. So  $\Delta H^0$  is independent of  $T$ .

$$\ln K(T_2) \sim \ln K(T_1) + \frac{\Delta H^0}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \ln K(T_1) + \frac{\Delta H^0}{R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$

This gives the **Le Chatelier's principle** for Temperature**Example : The Haber process**

$$\Delta H_{rxn}^0(298 \text{ K}) = -46.21 \text{ kJ mol}^{-1}; \quad \Delta G_{rxn}^0(298 \text{ K}) = -16.74 \text{ kJ mol}^{-1}$$

$$K_p = \frac{p_{\text{NH}_3}}{p_{\text{H}_2}^{3/2} p_{\text{N}_2}^{1/2}} = p^{-1} \frac{X_{\text{NH}_3}}{X_{\text{H}_2}^{3/2} X_{\text{N}_2}^{1/2}} = \exp \left( \frac{16740 \text{ J mol}^{-1}}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})} \right) = 860$$

This value is at 1 bar. Still the two gases do not react. The reaction is very slow (kinetics). Raising the temperature to 800 K can speed it up, but the reaction is exothermic and the value of the equilibrium constant will come down.  $K_p(800 \text{ K}) = 0.007$

But,  $K_X = pK_p$ . At 1 bar  $K_X = 0.007$ . So increase the pressure to 100 bar.  $K_X = 0.7$

**Solutions, heterogeneous equilibria**

Standard states need to be defined.

E.g. reference for concentration could be  $1 \text{ mol L}^{-1}$ . Then,  $K = \frac{[C]^{\nu_C} [D]^{\nu_D}}{[A]^{\nu_A} [B]^{\nu_B}}$

pH, salt concentrations might be required for certain reactions.

Solids or liquids are pure states and not mixed. They do not enter the equilibrium constant. Moreover, they do not have any pressure dependence  $\rightarrow \mu(\text{pure}, p) = \mu^0(\text{pure})$

If,  $\nu_A A(s) + \nu_B B(g) \rightleftharpoons \nu_C C(l) + \nu_D D(g)$

$$\Delta G = \{\nu_C \mu_C^0(T) + \nu_D \mu_D^0(T)\} - \{\nu_A \mu_A^0(T) + \nu_B \mu_B^0(T)\} + RT \ln \left( \frac{p_D^{\nu_D}}{p_B^{\nu_B}} \right) = \Delta G^0 + RT \ln Q$$