Chemical Equilibria & the Application of Le Châtelier's Principle to General Equilibria

CHEM 102

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Example of Equilibrium

$$N_2(g) + 3H_2(g) \rightleftharpoons 2\,NH_3(g)$$

- Reactions can occur, in principle, in either direction.
- When the rate of the forward and reverse reactions become equal, the system is said to be in (dynamic) equilibrium.
- Set up an equation to find the equilibrium concentrations.

$$\alpha A(g) + \beta B(g) \rightleftharpoons \gamma C(g) + \delta D(g)$$

- Recall that for gas-phase equilibria:

$$G_m(J) = G^\circ(J) + RT \ln P_J$$

- for each gas (J = A, B, C, or D) involved

- We can use separate expressions for each gas to derive

$$\Delta G_{rxn} = \Delta G^\circ_{rxn} + RT\ln Q$$

- where Q is the reaction quotient:

$$Q = \frac{P_C^\gamma\, P_D^\delta}{P_A^\alpha\, P_B^\beta}$$

$$\alpha A(g) + \beta B(g) \rightleftharpoons \gamma C(g) + \delta D(g)$$

$$\Delta G_{rxn} = \Delta G^\circ_{rxn} + RT\ln Q$$

When the reaction has "come to equilibrium", no net changes in pressures of reactants or products occur. At that point, $\Delta G_{rxn} = 0$, and Q becomes equal to K_{eq}.

$$\Delta G^\circ_{rxn} = -RT\ln K_{eq}$$

- where K_{eq} has the same form as the reaction quotient, but <u>the pressures must satisfy the constraint</u>:

$$K_{eq} = \frac{P_C^\gamma\, P_D^\delta}{P_A^\alpha\, P_B^\beta}$$

pressures are values *at equilibrium*

General Expressions for K_{eq}

$$\alpha A(g) + \beta B(g) \rightleftharpoons \gamma C(g) + \delta D(g)$$

- In general, the equilibrium constant is defined using *activities* (<u>no units</u>):

$$Q = \frac{a_C^\gamma\, a_D^\delta}{a_A^\alpha\, a_B^\beta} \qquad K_{eq} = \frac{a_C^\gamma\, a_D^\delta}{a_A^\alpha\, a_B^\beta} \quad \textit{equilibrium} \text{ values}$$

for *gases*, **pressures** (bars) **≈ activities**. For species in *dilute solutions* **concentrations** (M) **≈ activities**:

$$K_{eq} \approx \frac{[C]^\gamma[D]^\delta}{[A]^\alpha[B]^\beta}, \text{ but w/o units}$$

Equilibrium Probs - General Approach

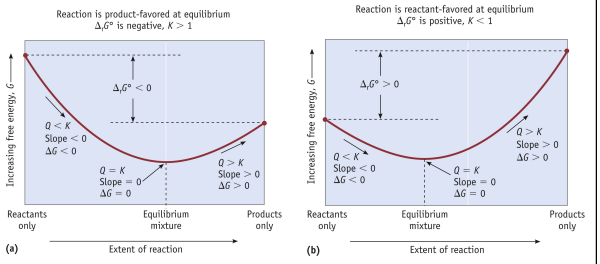
$$Q = \frac{\text{activities of products}}{\text{activities of reactants}}$$

$$\Delta G_{rxn} = \Delta G^\circ_{rxn} + RT\ln Q$$

- If ΔG_{rxn} is negative, the reaction will "go forward" to form more products. Q will therefore get bigger (until it reaches K_{eq}).
- If ΔG_{rxn} is positive, the reaction will "go in reverse" to form more reactants. Q will therefore get smaller (until it reaches Keq).

ΔG, ΔG°, and approach to equilibrium

$$Q = \frac{\text{activities of products}}{\text{activities of reactants}} \qquad \Delta G_{rxn} = \Delta G^\circ_{rxn} + RT\ln Q$$



Standard States $\alpha A + \beta B \rightleftharpoons \gamma C + \delta D$

- 298 K, 1 atm. Each gas phase reactant and product considered to be at 1 atm. pressure under standard conditions. (eg., if A & C are gases, $P_A = P_C = 1$atm)

Example: $NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(s)$

from data in Appendix 2 (all in kJ):

$\Delta G^\circ_{rxn} = -202.87 - (-16.45) - (-95.30) = -91.12$ kJ

This is ΔG for converting 1 mol NH_3 and 1 mol HCl at 1.0 atm. pressure into solid NH_4Cl at 298 K.

Example: Haber Process

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

- 1.00 mol N_2, 3.00 mol H_2, and 0.500 mol NH_3 are placed in a 50.0 L vessel at 400 °C. At this T, $K_C = 0.500$.

1. Will more NH_3 form, or will NH_3 dissociate to form more N_2 and H_2?
2. Set up an equation to find the equilibrium concentrations.

Different Forms of K_{eq}: K_C vs K_P

- In the preceding example we used "K_C" - the eq. constant expressed in concentrations. How is this related to "K_P" - the eq. constant expressed in pressures?
- Ans.: For this example, $K = K_P = (RT)^{-2} K_C$
  $= [(0.08314)(673)]^{-2}(0.5) = 1.6 \times 10^{-4}$
  (Note the value for R was in "L• bar/mol^{-1}K^{-1}")
- In general, $K_P = (RT)^{\Delta n} K_C$
- Remember, K_P is the "thermodynamic equilibrium constant", K

Le Châtelier's Principle

- "When a change is imposed on a system at equilibrium, the system will react in the direction that reduces the amount of change."
- "Changes" include adding or removing material, or changes in pressure or temperature.

Response of Equilibria to Changes

- Easy to predict effect of concentration changes - look at *Q*.
- Example: consider adding 0.05 mol Cl_2 to the to this system, prepared by putting 0.05 mol of PCl_5 into a 1.0 L flask already at equilibrium:

$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$ $\quad K_P = 78.3$ (at 250 °C)

More: Le Châtelier's Principle

$$CO(g) + 3\,H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

- An equilibrium mixture at 1200 K contains 0.613 mol CO, 1.839 mol H_2, 0.387 mol CH_4 and 0.387 mol H_2O, all in a 10.0 L vessel. (What is K_C?)
- All of the H_2O is somehow removed, and equilibrium is re-established.
- What will happen to the amount of CH_4?
- Set up eqn. for final amount of CH_4.

Changes in Temperature

- The equilibrium "constant" is not constant with temperature.

Le Châtelier's Principle would suggest:

- Qualitatively, if a reaction is endothermic then the equilibrium "constant" increases with temperature
- If a reaction is exothermic then the equilibrium "constant" decreases with temperature

Effect of Temperature on Equilibria

We have already seen the key relationship:

$$\Delta G^\circ_{rxn} = -RT\ln K_{eq} \text{ (at T = 298 K)}$$

Solve for $\ln K_{eq}$ and use $\Delta G \approx \Delta H^\circ - T\Delta S^\circ$:

$$\ln K(T) = \frac{-\Delta G}{RT} \cong -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

or, comparing two temperatures:

$$\ln\frac{K_2}{K_1} \cong \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \Leftrightarrow \text{van't Hoff eqn.}$$

Mond Process - Another Look

$$Ni(s) + 4\,CO(g) \rightleftharpoons Ni(CO)_4(g)$$

- From our earlier problem, $\Delta H^\circ = -160.8$ kJ and $\Delta S^\circ = -409.5$ J/K
- Suppose that 0.05 mol of $Ni(CO)_4$ is introduced into a 1.0 L flask.

1. What are the pressures of $Ni(CO)_4$ and CO at 300K?
2. What are the pressures of $Ni(CO)_4$ and CO at 500K?

Changes in Pressure

- Consider (significant at 700 °C):

$$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$$

Le Châtelier's Principle would suggest:

- If the pressure is suddenly increased, say by suddenly compressing the container, more CO_2 would react with CaO to produce more $CaCO_3$.

Changes in Pressure

$$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$$

$$\Delta H^\circ = +178.3 \text{ kJ};\ \Delta S^\circ = -160.59 \text{ J/K}$$

- Estimate the temperature at which $CaCO_3$ decomposes under normal conditions. (Air is 0.03% CO_2 by volume.)
- If $CaCO_3$ is put in a chamber being pumped by a pump capable of maintaining a reduced pressure of 7.6×10^{-4} torr, at what temperature will $CaCO_3$ decompose?

Catalysts - & the Haber Process

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

$$\Delta H^\circ = -92.22 \text{ kJ};\ \Delta S^\circ = -198.75 \text{ J/K}$$

- The role of a catalyst is to increase the rate of reaction (both forward and reverse rates).
- Under a given set of conditions, this has NO EFFECT on the final equilibrium state (though the system can reach equilibrium faster).
- As a practical matter in the Haber process, the catalyst allows one to use lower temperatures because equilibrium can be achieved faster.
- What is the thermodynamic benefit of running the Haber process at a lower temperature?