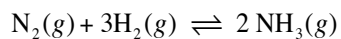


*Chemical Equilibria
& the Application of Le Châtelier's
Principle to General Equilibria*

CHEM 102H
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Example of Equilibrium



- 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.



- Recall our “thin-air” equation (page 335):

$$G_{\text{m}}(\text{J}) = G^{\circ}(\text{J}) + RT \ln P$$

- applies to each gas (J) involved in the equilibrium

- We can use separate expressions for each gas to derive

$$\Delta G_{\text{rxn}} = \Delta G^{\circ}_{\text{rxn}} + RT \ln Q$$

- where Q is the reaction quotient:

$$Q = \frac{P_{\text{C}}^{\gamma} P_{\text{D}}^{\delta}}{P_{\text{A}}^{\alpha} P_{\text{B}}^{\beta}}$$



$$\Delta G_{\text{rxn}} = \Delta G^{\circ}_{\text{rxn}} + RT \ln Q$$

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

$$\Delta G^{\circ}_{\text{rxn}} = -RT \ln K_{\text{eq}}$$

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

$$K_{\text{eq}} = \frac{P_C^{\gamma} P_D^{\delta}}{P_A^{\alpha} P_B^{\beta}} \quad \begin{array}{l} \text{pressures are values} \\ \text{at equilibrium} \end{array}$$

General Expressions for K_{eq}



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

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

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

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

Equilibrium Probs - General Approach

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

$$\Delta G_{\text{rxn}} = \Delta G^{\circ}_{\text{rxn}} + RT \ln Q$$

- 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 K_{eq}).

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, $P_A = P_C = 1\text{atm}$)

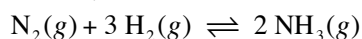


from data in Appendix 2 (all in kJ):

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

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



- 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.

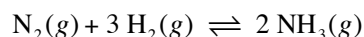
Haber Process - answer, 1st part

- Compare the value of Q with K_C

$$Q = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(0.01)^2}{(0.02)(0.06)^3} = 23.15$$

- This is larger than 0.50 so rxn. shifts left
- $[\text{NH}_3]$ will decrease from its initial value, $[\text{H}_2]$ and $[\text{N}_2]$ will increase.

Haber Process - answer, 2nd part



define x as the amount that $[\text{NH}_3]$ decreases:

initial: 0.02M 0.06M 0.01M

change: $+(1/2)x$ $+(3/2)x$ $-x$

$$K_C = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(0.01 - x)^2}{(0.02 + x/2)(0.06 + 3x/2)^3}$$

$$0.500 = \frac{(0.01 - x)^2}{(0.02 + x/2)(0.06 + 3x/2)^3} \Rightarrow x \approx .0079$$

(Solution found graphically)

Different Forms of K_{eq} : K_C vs K_P

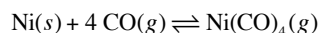
- In the preceding example we used " K_C " - the eq. constant expressed in concentrations. How is this related to " K_P " - the eq. constant expressed in pressures?

■ 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 " $\text{L} \cdot \text{bar}/\text{mol} \cdot \text{K}$ ")

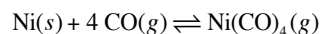
- In general, $K_P = (RT)^{\Delta n} K_C$
- Remember, K_P is the "thermodynamic equilibrium constant", K

Mond Process - Another Look



- From our earlier problem, $\Delta H^\circ = -160.8 \text{ kJ}$ and $\Delta S^\circ = -409.5 \text{ J/K}$
- Suppose that 0.05 mol of $\text{Ni}(\text{CO})_4$ is introduced into a 1.0 L flask.
- 1. What are the pressures of $\text{Ni}(\text{CO})_4$ and CO at 300K?
- 2. What are the pressures of $\text{Ni}(\text{CO})_4$ and CO at 500K?

Mond Process - Another Look



$$K_{300} = \exp\{-[-160,800/300 - (-409.5)]/(8.314)\} \\ = e^{15.21} = 4.05 \times 10^6$$

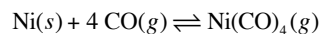
$$K_{500} = \exp\{-[-160,800/500 - (-409.5)]/(8.314)\} \\ = e^{-10.57} = 2.56 \times 10^{-5}$$

Initial pressures:

$$P_{300, \text{Ni}(\text{CO})_4} = 1.25 \text{ bar}$$

$$P_{500, \text{Ni}(\text{CO})_4} = 2.08 \text{ bar}$$

Mond Process - answers, 2nd part



define x as the amount that $P_{\text{Ni}(\text{CO})_4}$ decreases:

initial: 0.0 1.25

change: +4x -x

$$K_p(300) = \frac{P_{\text{Ni}(\text{CO})_4}}{P_{\text{CO}}^4} = \frac{1.25-x}{(4x)^4} ; K_p(500) = \frac{P_{\text{Ni}(\text{CO})_4}}{P_{\text{CO}}^4} = \frac{2.08-x}{(4x)^4}$$

$$4.05 \times 10^6 = \frac{1.25-x}{256x^4} \Rightarrow x \approx .0056 \quad P_{\text{CO}} = .0224 \text{ bar}$$

$$2.56 \times 10^{-5} = \frac{2.08-x}{256x^4} \Rightarrow x \approx 1.9794 \quad P_{\text{Ni}(\text{CO})_4} = 0.1006 \text{ bar}$$

$$P_{\text{CO}} = 7.9176 \text{ bar}$$

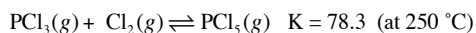
Le Châtelier's Principle

- "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:



P x x 2.174 - x

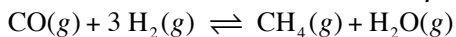
P_{eq} .1799 .1799 2.5341 \Leftrightarrow (x = 0.1799)

+2.714

added pressure

P_{eq} .1799-y 2.8939-y 2.5341+y \Leftrightarrow (x = 0.1799)

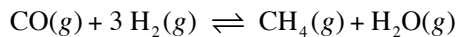
More: Le Châtelier's Principle



- 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 .

Using Le Châtelier's Principle - Set up

$$K_C = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3}$$



init. .0613 .1839 .0387 .0387 M

chg. .0613 .1839 .0387 0.0 M

- Equilibrium is re-established by production of more H_2O (let the final $[\text{H}_2\text{O}] = x$):

fin. .0613-x .1839-3x .0387+x x M

Using Le Châtelier's Principle - Set up

$$K_{eq} = 3.93 = \frac{(.0387 + x)x}{(.1839 - 3x)^3(.0613 - x)}$$

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:

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

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

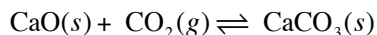
$$\ln K(T) = \frac{-\Delta G}{RT} \approx -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

or, comparing two temperatures:

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

Changes in Pressure

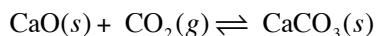
- ◆ Consider (significant at 700 °C):



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 .

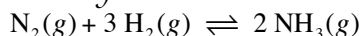
Changes in Pressure



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

- 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



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

- 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?
