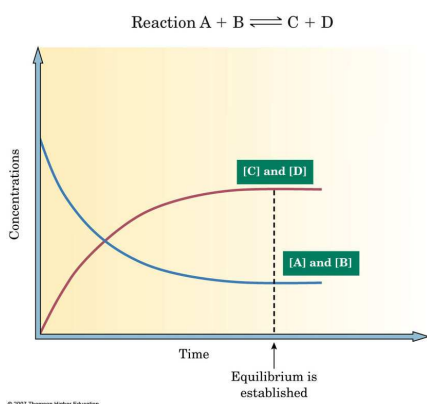


# Chapter 13

## Chemical Equilibrium – General Concepts

### Equilibrium



#### At Equilibrium:

- the rate at which products are consumed equals the rate at which products are produced.
- concentration of reactants and products remain constant with time (steady state)

#### Viewed at a submicroscopic level:

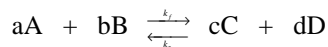
- both reactions (forward and reverse reactions) are still going on like crazy, just occurring at the same rate!!

#### Viewed at the human level

- No changes in concentration with time i.e. a steady state situation.

## Equilibrium

For the general elementary step:



Write the rate laws for the forward and reverse reactions.

Rate for forward reaction =

Rate for reverse reaction =

At equilibrium... rate of forward reaction = rate of reverse reaction.

Rearrangement leads to the *Equilibrium Constant* and the *Equilibrium Constant Expression*.

On what does the value of the Equilibrium Constant depend?

## Sample Questions

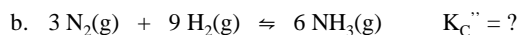
- What does the value of  $K_c$  tell you about the concentrations of the products relative to the concentration of the reactants at equilibrium for the following reactions.
  - $N_2(g) + 3 H_2(g) \rightleftharpoons 2NH_3(g)$ ;  $K_c = 1.7 \times 10^2$  at 500 K.
  - $N_2O_4(g) \rightleftharpoons 2 NO_2(g)$ ;  $K_c = 4.64 \times 10^{-3}$  at 25 °C.
- In general if  $K_c \gg 10^3$ , what does this tell you about the concentrations of reactants and products at equilibrium? if  $K_c \ll 10^{-3}$ ? if  $10^{-3} < K_c < 10^3$ ?
- For each of the following reactions, write the equilibrium constant expression.
  - $4 NH_3(g) + 5 O_2(g) \rightleftharpoons 4 NO(g) + 6 H_2O(g)$
  - $3 Fe(s) + 4 H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4 H_2(g)$
  - $2 H_2O(l) \rightleftharpoons 2 H_2(g) + O_2(g)$
  - $SiCl_4(g) + 2 H_2(g) \rightleftharpoons Si(s) + 4 HCl(g)$
  - $2 H_2O(g) \rightleftharpoons 2 H_2(g) + O_2(g)$
  - $Hg_2^{2+}(aq) + 2 Cl^-(aq) \rightleftharpoons Hg_2Cl_2(s)$
  - $2 NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + H_2O(l) + CO_2(g)$
- An equilibrium mixture of  $N_2$ ,  $H_2$ , and  $NH_3$  at 700 K contains 0.036 M  $N_2$  and 0.15 M  $H_2$ . At this temperature,  $K_c = 0.29$ , for the reaction
$$N_2(g) + 3 H_2(g) \rightleftharpoons 2NH_3(g)$$
What is the concentration of  $NH_3$ ? ( $5.9 \times 10^{-2} M$ )

## Mathematical Manipulation of $K_c$

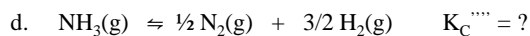
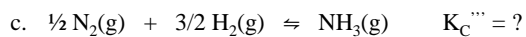
Calculate the numerical value of the equilibrium constant for each reaction below given the following:  $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$   $K_c = 4.1 \times 10^8$  at  $25^\circ\text{C}$



*What happens to the value of  $K_c$  when the reaction is reversed?*

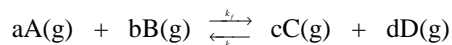


*What happens to the value of  $K_c$  when the coefficients are multiplied?*



## For Gas Phase Reactions...

*One can write the equilibrium constant ( $K_p$ ) in terms of partial pressure*



$$K_p = ??$$

$$P_{\text{total}} = \sum P_i = P_a + P_b + P_c + P_d$$

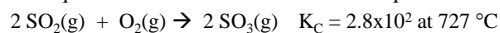
Write the equilibrium constant expression in terms of partial pressures ( $K_p$ ) for the following reactions:

- $\text{CH}_4(\text{g}) + 2 \text{H}_2\text{S}(\text{g}) \rightleftharpoons \text{CS}_2(\text{g}) + 4 \text{H}_2(\text{g})$
- $2 \text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$
- $4 \text{NH}_3(\text{g}) + 5 \text{O}_2(\text{g}) \rightleftharpoons 4 \text{NO}(\text{g}) + 6 \text{H}_2\text{O}(\text{g})$
- $3 \text{F}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2 \text{ClF}_3(\text{g})$
- $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3 \text{H}_2(\text{g})$

## Relationship between $K_c$ and $K_p$

*The pressure of each component in a mixture of ideal gases is directly proportional to its molar concentration*

1. Use the equilibrium shown below to derive an equation relating  $K_c$  to  $K_p$ .

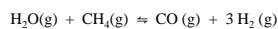


For this reaction, what is the numerical value of  $K_p$  at  $727^\circ\text{C}$ ?

2. What is the general form of the equation relating  $K_p$  to  $K_c$ ?

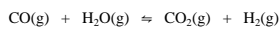
## Sample Questions

1. Hydrogen is produced industrially by the steam-hydrocarbon re-forming process. The reaction that takes place in the first step of this process is:



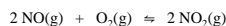
- a. If  $K_c = 3.8 \times 10^{-3}$  at 1000 K, what is the value of  $K_p$  at the same temperature?  
b. If  $K_p = 6.1 \times 10^4$  at  $1125^\circ\text{C}$ , what is the value of  $K_c$  at the same temperature?

2. In the industrial synthesis of hydrogen, mixtures of CO and  $\text{H}_2$  are enriched in  $\text{H}_2$  by allowing the CO to react with steam. The chemical equation for this so-called water-gas shift reaction is



What is the value of  $K_c$  at 700 K if the partial pressures in an equilibrium mixture at 700 K are 1.31 atm of CO, 10.0 atm of  $\text{H}_2\text{O}$ , 6.12 atm of  $\text{CO}_2$ , and 20.3 atm of  $\text{H}_2$ ? (9.48)

3. Nitric oxide reacts with oxygen to give nitrogen dioxide, an important reaction in the Ostwald process for the industrial synthesis of nitric acid:



If  $K_c = 6.9 \times 10^5$  at  $227^\circ\text{C}$ , what is the value of  $K_p$  at this temperature? If  $K_p = 1.3 \times 10^{-2}$  at 1000 K, what is the value of  $K_c$  at 1000K? (at 500 K:  $K_p = 1.7 \times 10^4$ ; at 1000 K:  $K_c = 1.1$ )