

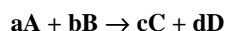
## CHAPTER 17 CHEMICAL EQUILIBRIUM

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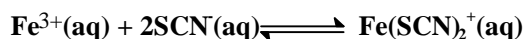
### THE EQUILIBRIUM CONSTANT, K

- At equilibrium, [reactants] is not necessarily equal to [products]
- Relationship between concentrations of reactants and products is called the **equilibrium constant expression**

- For the general reaction

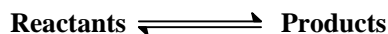


$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

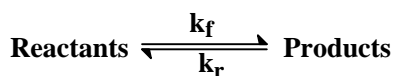


$$K_c = \frac{[\text{Fe}(\text{SCN})_2^+]}{[\text{Fe}^{3+}][\text{SCN}]^2}$$

- Reactions that do not go to completion are called **reversible** reactions



- **Chemical equilibrium**: exists when two opposing reactions occur simultaneously at the same rate
- **Dynamic** equilibrium: overall concentrations of species is constant but reactions does not stop



- For the forward reaction; rate =  $k_f[\text{reactants}]$
- For the reverse reaction; rate =  $k_r[\text{products}]$
- At equilibrium,  $k_f[\text{reactants}] = k_r[\text{products}]$   
 $k_f/k_r = [\text{Products}]/[\text{Reactants}]$
- The ratio  $k_f/k_r$  is called the **equilibrium constant,  $K_c$**

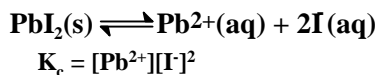
$$K_c = [\text{Products}]/[\text{Reactants}]$$

- In discussing  $K_c$  **activities** are used in preference to concentrations
- The **activity** of a compound is the ratio of its concentration (or partial pressure) to a standard concentration (1 M or 1 atm)
- The values used to calculate the equilibrium constant are numerically equal to concentration but has no units
- The equilibrium constant has no units

- For activities

1. For *pure* liquids and solids, the activity is taken as 1
2. For components in an ideal solution, the activity of each component is taken to be equal to its molar concentration
3. For gases, activity equals the partial pressure

- The larger the value of  $K_c$  ( $K_c > 1$ ) the more product-favored is the reaction
- The smaller the value of  $K_c$  ( $K_c \ll 1$ ) indicates the reaction does not proceed to any extent
- The reaction is reactant-favored



- Recall activity of solids and solvents is 1
- They are not involved in the  $K_c$  expression

- In general when two or more equations are added to produce a new equation, the equilibrium constant for the net equation is the product of the equilibrium constants for the added reactions

#### For $K_c$

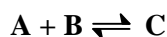
- The numerical value of  $K_c$  indicates the extent to which the reaction has proceeded
- Can be used to predict if a reaction is product- or reactant-favored
- The value varies with only with temperature
- It is constant at a given temperature
- It is independent of the initial concentration

### Variation of $K_c$

- The equilibrium constants for a reaction and its reverse are reciprocals of each other
- When stoichiometric coefficients of a balanced equation are multiplied by some factor  $f$ , the equilibrium constant for the new equation ( $K_{\text{new}}$ ) is the equilibrium constant for the old reaction ( $K_{\text{old}}$ ) raised to the power of the factor,  $f$

- **Q** is used to determine direction the reaction has to move to reach equilibrium
- **Q < K: Forward reaction predominates until equilibrium is reached**
- **Q = K: Equilibrium is established**
- **Q > K: Reverse reaction predominates until equilibrium is established**

## 1. Concentration



- **Addition** of more reactants or products causes the system to shift the equilibrium in the direction that uses up the added species
- Reactants added =  $Q < K$ . Forward reaction will dominate to re-establish equilibrium
- Products added =  $Q > K$ . Reverse reaction will dominate to re-establish equilibrium

## 2. Pressure/Volume changes

- Important only for gas phase reactions
- A volume decrease (pressure increase) is counter-balanced by shifting the equilibrium position to the side with fewer gas molecules
- The reverse is true
- No change in the number of moles means volume (pressure) change does not affect the equilibrium position

## Factors affecting equilibrium

- Systems at equilibrium are governed by **LeChateliers' Principle**: If a change of conditions is applied to a system at equilibrium, the system responds in such a way as to reduce the effect of the change in attaining a new equilibrium
- The reaction quotient helps
- Four factors: concentration, temperature, volume and catalysis

Stress	Q	Shift of $A + B \leftrightarrow C + D$
Increase in [A] or [B]	$Q < K$	→ right
Increase in [C] or [D]	$Q > K$	← left
Decrease in [A] or [B]	$Q > K$	← left
Decrease in [C] or [D]	$Q < K$	→ right

## 3. Temperature

Generally,

- Increasing in temperature moves the reaction in a direction that absorbs energy
- Decreasing in temperature moves the reaction in a direction that releases energy
- Depends on the type of reaction
- Temperature **increase** favors **endothermic** rxns
- Temperature **decrease** favors **exothermic** rxns

#### 4. Catalyst

- Introduction of a catalyst has **NO** effect on the equilibrium position
- Equilibrium is established faster
- A catalyst only speeds up a reaction. Both forward and reverse reactions are affected equally

#### Free energy and the equilibrium constant

- Standard free energy change is  $\Delta G^\circ$
- For other concentrations free energy change is  $\Delta G$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

At equilibrium,  $\Delta G = 0$ , and  $Q = K$

$$0 = \Delta G^\circ + RT \ln K$$

$$\Delta G^\circ = -RT \ln K$$

#### Temperature - $K_c$ relationship

- Equilibrium constants can be calculated at different temperatures from the **van't Hoff equation**
- Must know  $\Delta H^\circ$  for the reaction

$$\ln (K_1/K_2) = \Delta H^\circ/R(1/T_1 - 1/T_2)$$

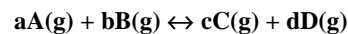
$K_1$  = equilibrium constant at temperature  $T_1$

$K_2$  = equilibrium constant at temperature  $T_2$

#### Pressure and the equilibrium constant

- For a gas phase reaction

$$P = (n/V)RT = MRT$$



$$K_p = (P_C)^c (P_D)^d / (P_A)^a (P_B)^b$$

$P_C, P_D, \dots$  are partial pressures in atmospheres

- As with  $K_c$ ,  $K_p$  has no units

$$K_c = K_p (RT)^{-\Delta n}$$

$$\Delta n = n_{\text{gas prod}} - n_{\text{gas react}}$$

- For  $\Delta G^\circ < 0$ ,  $\ln K > 0$ ,  $K > 1$  : Products are favored over reaction (spontaneous reaction)
- $\Delta G^\circ > 0$ : Reactants are favored and reaction is nonspontaneous
- The magnitude of  $K$  relates directly to  $\Delta G^\circ$
- A very negative  $\Delta G^\circ$  means  $K$  is large and the reaction goes to "completion"