

# lecture one

Chemistry

30/09/2025

## chapter i: solution chemistry

### 0.1 General information Free energy (G) and equilibrium constant (k)

#### 0.1.1 spontaneity criteria: "second law of thermodynamic"

$$\Delta S = \Delta S_{tot} = \Delta S_{sys} + \Delta S_{exch} / \Delta S_{exch} = -\Delta S_{surr} \text{ where } \Delta$$

$$\Delta S_{tot} \geq 0 \rightarrow \Delta S_{tot} = 0 \rightarrow \text{reversible (ideal)}$$

$$\Delta S_{tot} > 0 \rightarrow \text{irreversible (real)}$$

$$\Delta S_{tot} \rightarrow \text{process is impossible (non-spontaneous)}$$

However, in practice, the calculation of  $\Delta S_{exch}$  is not always possible  $\rightarrow$  limitation

$\rightarrow$  We introduce a new concept: Free energy or Gibbs energy with

$$G = H - TS \quad , \quad dG = dH - TdS$$

$$\Delta G = \Delta H - T\Delta S$$

where  $\Delta H = \text{enthalpy}$

$\Delta S$ : entropy

G is very used for open systems (i.e. chemical reaction)

G is a state function

then, the spontaneity criteria are:

$\Delta G < 0$ , the process is spontaneous, G decreases  $\Delta G > 0$ , the process is non-spontaneous, it could not take place  $\Delta G = 0$ , (G = const), we are at equilibrium in the studied conditions

Example: Chemical reaction:

$A + B \rightarrow C + D$   $\Delta G < 0$  to the forward reaction is spontaneous  $\rightarrow$ : forward direction

$\Delta G > 0$  to the reverse reaction is spontaneous  $\leftarrow$ : reverse direction

## 0.2 Calculation of free energy:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$\Delta H^0 \Delta S^0 (S^0) \rightarrow$  thermodynamic data

Example: The vaporization of water at room temperature :



Data:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ(H_2(g)) - \Delta H_f^\circ(H_2(l)) \\ &= -241.82 - (-285.083) = 44.01 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= S_{298 \text{ H}_2\text{O}(g)}^\circ - S_{298 \text{ H}_2\text{O}(l)}^\circ \\ &= 118.8 \text{ J mol}^{-1}\text{K}^{-1}\end{aligned}$$

## 0.3 Free energy for chemical reaction

Let's have the following reaction:  $aA + bB \xrightarrow{\Delta g_R} cC + dD$

$$\Delta G_R^\circ = \sum n, \Delta G_f^\circ(\text{Products}) - \sum n, \Delta G_f^\circ(\text{reagents}) / F = \text{formation}$$

The Hess's law

## 0.4 Chemical equilibrium:

The chemical reactions are not always complete, they are not always accompanied by total disappearance of reagents.

Too many reactions are partial, reagents and products are present simultaneously

During equilibrium, the rate of forward reaction equals the rate of reverse reaction.



Reagents and products are present at the same proportion  $\rightarrow$  the mass action law

## 0.5 The mass action law:

This law is represented by a constant ( $K$ ) called equilibrium constant =  $K_{eq}$

$$\text{with: } K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

It was proved that  $\Delta G(i) = \Delta G^\circ + RT \ln K$

$\rightarrow$  equilibrium  $\rightarrow \Delta G = 0 \rightarrow \Delta G^\circ = -RT \ln K$