

E-Content

Topic: Chemical Equilibrium (part II)
Physical Chemistry
B. Sc. Chemistry (H) 2nd Year

By

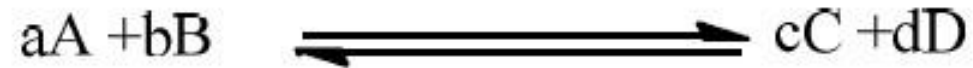
Miss Ipsha Shruti

Department of Chemistry

A.s. College, Bikramganj

Thermodynamics of Law of Chemical Equilibrium:

Let us consider a general reaction,



The chemical potential of a substance in a mixture is

$$\mu = \mu^{\ominus} + RT \ln a \dots \dots \dots (i)$$

Where μ^{\ominus} is the chemical potential of pure substance in standard state of unit activity, (a)

R is the gas constant and T is the absolute temperature.

For a mole of the substance A we can write using the equation (i)

$$a\mu_A = a(\mu^{\ominus} + RT \ln a_A)$$

And similarly,

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

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

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

The change in free energy for the reaction is given by

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

On substitution we get

$$= [\Delta G^\circ + RT \ln Q] - [\Delta G^\circ - RT \ln K] = RT \ln \frac{Q}{K}$$

$$= [c\mu_C^\circ + d\mu_D^\circ] - [a\mu_A^\circ + b\mu_B^\circ] + RT \ln \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b}$$

Where ΔG° is the difference in free energy of the reaction when all reactants and products are in their standard state. It is given by

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

Or, equation (ii) can be written as,

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \dots \dots \dots \text{(ii1)}$$

Where Q is the reaction quotient of activities of the product and reactants.

As BG' is constant at given temperature. Also, the gas constant R and T are constant, the factor Q is &so constant

So,

$$\frac{C}{D}$$

From equation (iii) we have

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

The equation (iv) is called van't Hoff Isotherm. It may be used to calculate the change in free energy of a reaction in the standard (ΔG°) from its equilibrium constant and vice versa.

The sign of ΔG° indicates whether the forward or reverse reaction is spontaneous. Considering the equation (iv), we can have three possibilities depending on the sign of ΔG° for the reaction.

- (1) If ΔG° is negative, $\log K$ must be positive and the reaction proceeds spontaneously in the forward reaction.
- (2) If ΔG° is positive, $\log K$ must be negative and K is less than one. The reverse reaction is then spontaneous.
- (3) If $\Delta G^\circ = 0$, $\log K = 0$ and $K = 1$. The reaction is at equilibrium.

Some exercises related to previous part:

- 1. Determine whether the following reactions favor high or low pressures?
 - (a) $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g})$;
 - (b) $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$;
 - (c) $\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g})$;
 - (d) $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$;
 - (e) $\text{H}_2(\text{g}) + \text{F}_2(\text{g}) \rightleftharpoons 2 \text{HF}(\text{g})$;
- 2. Determine whether the following reactions favors high or low temperature?
 - (a) $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g})$; $\Delta H^\circ = -180 \text{ kJ}$
 - (b) $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$; $\Delta H^\circ = -46 \text{ kJ}$
 - (c) $\text{CO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{COCl}_2(\text{g})$; $\Delta H^\circ = -108.3 \text{ kJ}$
 - (d) $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$; $\Delta H^\circ = +57.3 \text{ kJ}$
 - (e) $\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g})$; $\Delta H^\circ = -270 \text{ kJ}$

References

- Physical chemistry: K.L Kapoor
- Physical chemistry By Atkins.
- Physical chemistry By P.C. Rakshit.
- Principles of chemistry By Puri, Sharma and Pathania.
- NPTEL online materials