E-Content

Topic: Chemical Equilibrium (part II)

Physical Chemistry

B. Sc. Chemistry (H) 2nd Year

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Thermodynamics of Law of Chemical Equilibrium:

Let us consider a general reaction,

$$aA + bB \rightleftharpoons cC + dD$$

The chemical potential of a substance in a mixture is

$$\mu = \mu^0 + RT \ln a \ldots\ldots\ldots\ldots\ldots (i)$$

Where μ^0 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)

$$a\mu_A = a(\mu^0 + RT \ln a_A)$$

And similarly,

bpg = b(jz° 4 £1Inep)

cJzg = r(jz° -1- APIn op)

dpp = (yr° 4 fifilnnp)

The change in hee energy for ie reaction is given by

pe'ndn rt:e 'e'rnr0nxPo

On subshtution we get

=f[js'g+RT A op] •J- d Qr$ + fifiln up] - [a(jsp -J- 2t rfnng} I fi[jt$+RT ln og)]

$$= [\{c\mu_C^0 + d\mu_D^0\} - \{a\mu_A^0 + \mu_B^0\}] + RT \ln \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b}$$

Where fiP' is the difference in free energy of the reaction wheu all reactauts aud products are in theii standard state. It is given by

= –

Or, equation (ii) can be written as,

A G = fi G° + RT O Q ••• •••• • (ii1)

Where Q 1s the reaction quotieut of activities of the product and reactauts.

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

So,

$$\frac{"C \quad *'D \quad ``'}{}$$

From equation (iii) we have

$$A\,G° = -RT\,A K$$

The equation (iv) is called van't Hoff Isotherm. It may be used to calculate the change in fiee energy of a reaction in the standard (fiG^{i3}) from ie equilibrium constant and vive —versa. 1

The sign of fiti° indicates whether the forward or reverse reachon is spontaneous. 1
Considering the equation (iv), we can have three possibilities depending on the 1
sign of fiti° for the reaction. 1

(1) If AG° is negative, log K must be positive and the reaction proceeds spontaneously in the forward reaction.

(2) If *fiG'* is positive, log K must be negative and K is less than one. The reverse reaction is then spontaneous.

(3) If *fiG'* - *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) $2SO_2(g) + O_2(g) \rightleftarrows 2\ SO_3(g)$;
- (b) $PCl_5(g) \rightleftarrows PCl_3(g) + Cl_2(g)$;
- (c) $CO(g) + 2H_2(g) \rightleftarrows CH_3OH(g)$;
- (d) $N_2O_4(g) \rightleftarrows 2\ NO_2(g)$;
- (e) $H_2(g) + F_2(g) \rightleftarrows 2\ HF(g)$;
- 2. Determine whether the following reactions favors high or low temperature?
- (a) $2SO_2(g) + O_2(g) \rightleftarrows 2\ SO_3(g)$; $\Delta H^o = -180$ kJ
- (b) $CO(g) + H_2O(g) \rightleftarrows CO_2(g) + H_2(g)$; $\Delta H^o = -46$ kJ
- (c) $CO(g) + Cl_2(g) \rightleftarrows COCl_2(g)$; $\Delta H^o = -108.3$ kJ
- (d) $N_2O_4(g) \rightleftarrows 2\ NO_2(g)$; $\Delta H^o = +57.3$ kJ
- (e) $CO(g) + 2H_2(g) \rightleftarrows CH_3OH(g)$; $\Delta H^o = -270$ kJ

References

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- Physical chemistry By P.C. Rakshit.
- Principles of chemistry By Puri, Sharma and Pathania.
- NPTEL online materials