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Class ⇒ B.Sc. (Hons.) Part-II
Subject ⇒ Chemistry
Chapter ⇒ Thermodynamics
Topic ⇒ Variation of work function and free energy with temperature and pressure.

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Variation of work function with Temperature and Pressure

The work function is given by the equation

$$A = U - TS \quad \text{——— (1)}$$

Complete differentiation of this equation gives

$$dA = dU - TdS - SdT \quad \text{——— (2)}$$

Entropy change is given by

$$dS = \frac{\delta q_{rev}}{T} \quad \text{——— (3)}$$

from 1st law of thermodynamics

$$\delta q_{rev} = dU - \delta w \quad \text{——— (4)}$$

and if the work is restricted to the work of expansion only

$$-\delta w = PdV \quad \text{——— (5)}$$

Putting this value in equation (4), we get

$$\delta q_{rev} = dU + PdV \quad \text{——— (6)}$$

Putting this value in equation (3), we get

$$dS = \frac{dU + PdV}{T}$$

or $$TdS = dU + PdV \quad \text{——— (7)}$$

Putting this value in equation (2) we get

$$dA = dU - dU - PdV - SdT$$

or $$dA = -PdV - SdT \quad \text{——— (8)}$$

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ⓐ If temperature is kept constant, $dT=0$, equation ⑧ takes the form

$$(dA)_T = -(PdV)_T \quad \text{——— ⑨}$$

or $$\left(\frac{\partial A}{\partial V}\right)_T = -P \quad \text{——— ⑩}$$

ⓑ If volume is kept constant, $dV=0$, equation ⑧ becomes

$$(dA)_V = -(SdT)_V$$

or, $$\left(\frac{\partial A}{\partial T}\right)_V = -S \quad \text{——— ⑪}$$

Thus variation of work function with temperature and volume is given by eqn. ⑩ and ⑪.

Variation of free energy with Temperature and Pressure

The free energy is given by the equation

$$G = H - TS \quad \text{——— ①}$$

But, $$H = U + PV \quad \text{——— ②}$$

substituting this value in equation ①, we get.

$$G = U + PV - TS \quad \text{——— ③}$$

Complete differentiation of this equation gives

$$dG = dU + PdV + VdP - TdS - SdT \quad \text{——— ④}$$

But,

$$dS = \frac{\delta q_{rev}}{T} = \frac{dU + PdV}{T}$$

or, $$TdS = dU + PdV \quad \text{——— ⑤}$$

Substituting this value in eqn. ④ we get

$$dG = dU + PdV + VdP - (dU + PdV) - SdT = VdP - SdT \quad \text{——— ⑥}$$

This expression gives the change in free energy with change in pressure and change in temperature

In a reversible process. Equation (6) is called Total differential equation.

(a) If temperature is kept constant, $dT=0$ equation (6) takes the form

$$(dG)_T = (VdP)_T \quad \text{———} \quad (7)$$

or, $$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{———} \quad (8)$$

(b) If pressure is kept constant, $dP=0$, equation (6) becomes

$$(dG)_P = -(SdT)_P$$

or, $$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \text{———} \quad (9)$$

Thus variation of free energy with pressure and temperature is given by equations (8) and (9).

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