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

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

Putting this value in equation (4), we get

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

Putting this value in equation (3), we get

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

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

Putting this value in equation (2) we get

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

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

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

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

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

(b) 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

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

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

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

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

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

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

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