Assignment-3 Solution

Ans 1: We need $\Delta_f H^\circ$ for the reaction

$$2B(s) + 3H_2(g) \longrightarrow B_2H_6(g)$$

reaction (4) = reaction (2) + 3 x reaction (3) - reaction (1)

Thus, $\Delta_r H^\circ = \Delta_r H^\circ[\text{reaction}(2)] + 3 \times \Delta_r H^\circ[\text{reaction}(3)] - \Delta_r H^\circ[\text{reaction}(1)]$

$$= [-2368 + 3\times(-241.8) - (-194)]\ \text{kJ mol}^{-1}$$

$$= -1152\ \text{kJ mol}^{-1}$$

Ans2: $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ (expression for expansion coefficient)

As $V = V'\left[0.77 + 3.7\times10^{-4}\left(\frac{T}{K}\right) + 1.52\times10^{-6}\left(\frac{T^2}{K^2}\right)\right]$

$$\left(\frac{\partial V}{\partial T}\right)_p = V'\left[0 + 3.7\times10^{-4}\,K^{-1} + 2\times1.52\times10^{-6}\,T\,K^{-2}\right]$$

$$\alpha = \frac{\cancel{V'}[3.7\times10^{-4}K^{-1} + 2\times1.52\times10^{-6}\,T\,K^{-2}]}{\cancel{V'}[0.77 + 3.77\times10^{-4}(T/K) + 1.52\times10^{-6}(T^2/K^2)]}$$

at T = 310

$$\alpha = \frac{3.7\times10^{-4}K^{-1} + 2\times1.52\times10^{-6}(310)K^{-1}}{0.77 + 3.77\times10^{-4}(310\cancel{K})\cancel{K} + 1.52\times10^{-6}(310\cancel{K})^2 \cancel{K^2}}$$

$$\boxed{\alpha = 1.27\times10^{-3}\,K^{-1}}$$

Ans3: To prove $\left(\frac{\partial U}{\partial T}\right)_p = C_v + \pi V\alpha$

As, $U = U(T,V)$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

From above equation, divide both sides by dT

$$\frac{dU}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)$$

At constant pressure,

$$\left(\frac{dU}{dT}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

$$\left(\frac{dU}{dT}\right)_p = C_V + \pi_p \left(\frac{\partial V}{\partial T}\right)_p$$

Since, $\left(\frac{\partial V}{\partial T}\right)_p \cdot \frac{1}{V} = \alpha$

$$\Rightarrow \left(\frac{\partial V}{\partial T}\right)_p = \alpha V$$

$$\boxed{\left(\frac{dU}{dT}\right)_p = C_V + \pi_p \alpha V}$$

Ans4: $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V\left(\frac{\partial T}{\partial V}\right)_P}$ (reciprocal Identity) — (1)

$P = \frac{nRT}{V-nb} - \frac{n^2a}{V^2}$ (Van der Waal's equation) — (2)

$T = \left(\frac{P}{nR}\right)(V-nb) + \left(\frac{na}{RV^2}\right)(V-nb)$ — (3)

$\left(\frac{\partial T}{\partial P}\right)_V = \frac{V-nb}{nR}$ — (4)

$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ — (5)

from (1) & (5)

$\frac{\beta}{\alpha} = \frac{-(\partial V/\partial P)_T}{(\partial V/\partial T)_P} = \frac{-1}{(\partial P/\partial V)_T(\partial V/\partial T)_P}$ (reciprocal Identity)

$= \left(\frac{\partial T}{\partial P}\right)_V$ (Euler chain relation)

$\frac{\beta}{\alpha} = \frac{V-nb}{nR}$

$$\boxed{\beta \cdot R = \frac{\alpha(V-nb)}{n}}$$

Ans5 $C_V = \left(\frac{dU}{dT}\right)_V$

$\left(\frac{dC_V}{dV}\right)_T = \left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_V$ (derivatives can be taken in any order)

$\left(\frac{\partial U}{\partial T}\right)_T = 0$ for a perfect gas

Likewise, $C_p = \left(\frac{\partial H}{\partial T}\right)_p$

$$\left(\frac{\partial C_p}{\partial P}\right)_T = \left(\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial T}\right)_P\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial P}\right)_T\right)_P$$

$\left(\frac{\partial H}{\partial P}\right)_T = 0$ for perfect gas

Hence $\left(\frac{\partial C_p}{\partial P}\right)_T = 0$