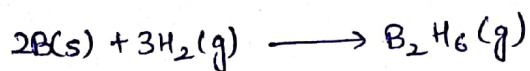


Assignment-3 Solution

1.

Ans1: We need $\Delta_f H^\circ$ for the reaction



$$\text{reaction (4)} = \text{reaction (2)} + 3 \times \text{reaction (3)} - \text{reaction (1)}$$

$$\begin{aligned} \text{Thus, } \Delta_r H^\circ &= \Delta_r H^\circ[\text{reaction (2)}] + 3 \times \Delta_r H^\circ[\text{reaction (3)}] - \Delta_r H^\circ[\text{reaction (1)}] \\ &= [-2368 + 3 \times (-241.8) - (-194)] \text{ kJ mol}^{-1} \\ &= -1152 \text{ kJ mol}^{-1} \end{aligned}$$

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

$$V = V' \left[0.77 + 3.7 \times 10^{-4} \left(\frac{T}{K} \right) + 1.52 \times 10^{-6} \left(\frac{T^2}{K^2} \right) \right]$$

$$\left(\frac{\partial V}{\partial T} \right)_P = V' \left[0 + 3.7 \times 10^{-4} K^{-1} + 2 \times 1.52 \times 10^{-6} T K^{-2} \right]$$

$$\alpha = \frac{V' [3.7 \times 10^{-4} K^{-1} + 2 \times 1.52 \times 10^{-6} T K^{-2}]}{V' [0.77 + 3.77 \times 10^{-4} (T/K) + 1.52 \times 10^{-6} (T^2/K^2)]}$$

at $T = 310$

$$\alpha = \frac{3.7 \times 10^{-4} K^{-1} + 2 \times 1.52 \times 10^{-6} (310) K^{-1}}{0.77 + 3.77 \times 10^{-4} (310) K + 1.52 \times 10^{-6} (310)^2 K^2 / K^2}$$

$$\boxed{\alpha = 1.27 \times 10^{-3} K^{-1}}$$

Ans3: To prove $\left(\frac{\partial U}{\partial T} \right)_P = C_V + P V \alpha$

$$\text{As, } U = U(T, V)$$

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

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,

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

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

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

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

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

Ans 4: $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{V} \left(\frac{\partial T}{\partial V} \right)_P$ (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)

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

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

Ans 5

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

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

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

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

$$\left(\frac{\partial C_p}{\partial p} \right)_T = \left(\frac{\partial}{\partial p} \left(\frac{\partial H}{\partial T} \right)_p \right)_T = \left(\frac{\partial}{\partial T} \left(\frac{\partial H}{\partial p} \right)_T \right)_p$$

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

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