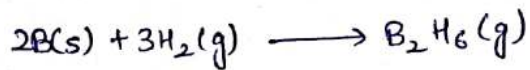


Ans 1: We need  $\Delta_f H^\circ$  for the reaction



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

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

Ans 2:  $\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$  (expression for expansion coefficient)

$$\Rightarrow V = V \left[ 0.77 + 3.7 \times 10^{-4} \left( \frac{T}{K} \right) + 1.52 \times 10^{-6} \left( \frac{T^2}{K^2} \right) \right]$$

$$\left( \frac{\partial V}{\partial T} \right)_P = V \left[ 0 + 3.7 \times 10^{-4} K^{-1} + 2 \times 1.52 \times 10^{-6} T K^{-2} \right]$$

$$\alpha = \frac{V \left[ 3.7 \times 10^{-4} K^{-1} + 2 \times 1.52 \times 10^{-6} T K^{-2} \right]}{V \left[ 0.77 + 3.77 \times 10^{-4} (T/K) + 1.52 \times 10^{-6} (T^2/K^2) \right]}$$

at  $T = 310$

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

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

Ans 3: 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,

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

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

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

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

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

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)

$\frac{\beta}{\alpha} = \frac{-(\partial V / \partial P)_T}{\left( \frac{\partial V}{\partial T} \right)_P} = \frac{-1}{\left( \frac{\partial P}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P}$  (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,  $C_p = \left( \frac{\partial H}{\partial T} \right)_p$

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

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

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