

① Show that  $C_p = C_v$  for water at  $4^\circ\text{C}$ .

General expression of  $C_p - C_v$  :

$$C_p - C_v = \left[ P + \left( \frac{\partial U}{\partial V} \right)_T \right] \left( \frac{\partial V}{\partial T} \right)_P$$

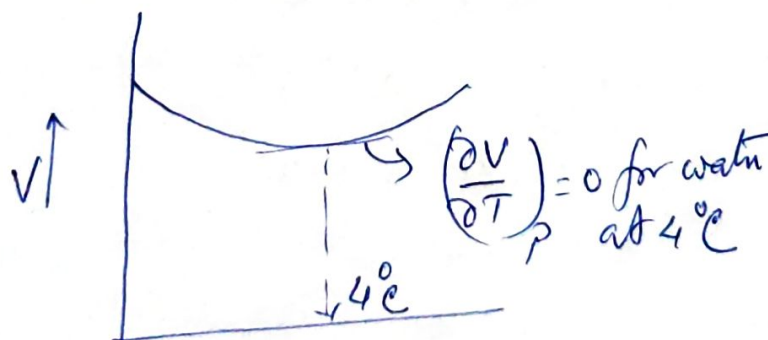
Thermodynamic eq<sup>n</sup> of state :

$$\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P$$

Putting this :

$$C_p - C_v = T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P$$

At  $4^\circ\text{C}$ , density of water is maximum, i.e.



$\therefore C_p - C_v = 0$ ,  
i.e.  $C_p = C_v$  for  
water at  $4^\circ\text{C}$ .

Again,  $\left( \frac{\partial P}{\partial T} \right)_V = \beta = \frac{\alpha}{k} = \frac{\text{Coeff of thermal expansion}}{\text{Coeff of compressibility}}$

$\beta \Rightarrow$  Press. Coeff:  $\frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = \alpha$

Putting this values:

$$C_p - C_v = \frac{\alpha^2 T V}{k}$$

(3)  $N_2$  gas is expanded reversibly and adiabatically from a volume of 1 lit at  $0^\circ C$  and 1 atm to a volume of 2 lit.  $C_v = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$ .

Assuming ideal behaviour, calculate the final  $T, P$ . What are  $q, w, \Delta U$  and  $\Delta H$ ?

Soln

$$\bar{C}_v = 20.8 \text{ J K}^{-1} \text{ mol}^{-1} \quad \left| \quad \text{For ideal gas -} \right.$$

$$\bar{C}_p - \bar{C}_v = R = 8.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\therefore \frac{\bar{C}_p}{\bar{C}_v} = \frac{29.1}{20.8} = 1.4 \quad \therefore \bar{C}_p = (R + C_v) = \underline{29.1 \text{ J K}^{-1} \text{ mol}^{-1}}$$

For adiabatic change involving ideal gas:

$$P_1 V_1^\gamma = P_2 V_2^\gamma \quad \Rightarrow \quad 1 \times 1^{1.4} = P_2 \times 2^{1.4}$$

$$P_1 = 1 \text{ atm}, V_1 = 1 \text{ lit} \quad \left| \quad \text{or, } \underline{P_2 = 0.38 \text{ atm.}} \right.$$

$$V_2 = 2 \text{ lit}$$

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$T_1 = 273 \text{ K} \quad \therefore \underline{T_2 = 206.9 \text{ K}}$$

For adiabatic process,  $q = 0$ .

$$\Delta U = q + w$$

$$n \bar{C}_v (T_2 - T_1)$$

On this problem  $\eta = 1$

$$\left\{ \begin{aligned} w &= n \bar{C}_v (T_2 - T_1) = 20.8 (206.9 - 273) = -1381.5 \text{ J mol}^{-1} \\ &\quad (\text{negative sign} \Rightarrow \text{work done by the system}) \\ \Delta U &= n \bar{C}_v (T_2 - T_1) = -1381.5 \text{ J mol}^{-1} \\ \Delta H &= n \bar{C}_p (T_2 - T_1) = -1923.5 \text{ J mol}^{-1} \end{aligned} \right.$$

- ④ For a certain ideal gas  $C_p = 8.58 \text{ Cal K}^{-1} \text{ mol}^{-1}$ . Two moles of the gas is expanded adiabatically and reversibly from an initial temp of  $20^\circ\text{C}$  to a final temp of  $-45.4^\circ\text{C}$ . Calculate the work done. [Note: for adiabatic expansion temp drops]

Soln:

$$w_{\text{rev, Adiabatic, ideal gas}} = \frac{(P_2 V_2 - P_1 V_1)}{(\gamma - 1)} \quad \left| \gamma = \frac{\bar{C}_p}{\bar{C}_v} \right.$$
$$= \frac{nR(T_2 - T_1)}{\gamma - 1}$$

$$\bar{C}_p = 8.58; \quad \bar{C}_p - \bar{C}_v = R \approx 2 \text{ Cal}$$

$$\therefore \bar{C}_v = 8.58 - 2 = 6.58 \text{ Cal mol}^{-1} \text{ K}^{-1}$$

$$\therefore \gamma = \bar{C}_p / \bar{C}_v = 1.3$$

$$n = 2 \text{ moles}$$

$$\therefore w = \frac{2 \times 8.314 (-65.4)}{(1.3 - 1)} \text{ J}$$

$$= -3624.9 \text{ J}$$



Calculate the work done by 2 moles of an ideal gas during expansion from 2 atm at  $0^\circ\text{C}$  to 1 atm at  $27^\circ\text{C}$  against a constant pressure of 1 atm. If for the gas  $\bar{C}_p = 5 \text{ cal mol}^{-1}$ , find  $\Delta U$ ,  $\Delta H$  and  $q$ .

Soln: Expansion against a constant opposing pressure  $\Rightarrow$  Irreversible process  
 [For a reversible change opposing pressure will vary continuously by very very small amount]

$$W_{\text{irrev}} = -P_{\text{op}}(V_2 - V_1) = -P_{\text{op}} \left( \frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right)$$

$$P_{\text{op}} = 1 \text{ atm}; R = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}; T_1 = 273 \text{ K}, T_2 = 300 \text{ K}$$

$$P_1 = 2 \text{ atm}; P_2 = 1 \text{ atm}.$$

$$\text{Putting the values: } W_{\text{irrev}} = -649.4 \text{ Cal.}$$

$$\Delta H = n \bar{C}_p (T_2 - T_1) = 2 \times 5 (300 - 273) = 270 \text{ Cal}$$

$$\left[ \text{As } C_p = \left( \frac{\partial q}{\partial T} \right)_P = \left( \frac{\partial H}{\partial T} \right)_P \right] \quad \& \quad H = U + PV$$

$$\therefore \Delta H = \Delta U + (P_2 V_2 - P_1 V_1)$$

$$\therefore \Delta U = \Delta H - (P_2 V_2 - P_1 V_1) \\ = \Delta H - nR(T_2 - T_1)$$

$$\therefore \Delta U = 162.7 \text{ Cal}$$

1st law:

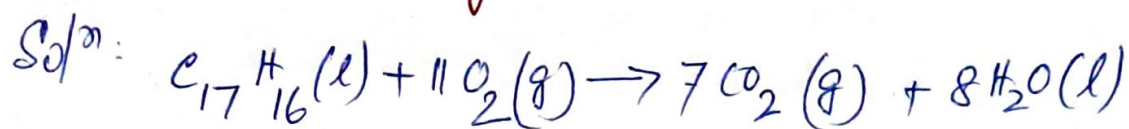
$$\Delta U = q + w; \quad q = \Delta U - w = (162.7 + 649.4) \\ q = 812.1 \text{ Cal.}$$

Here,  $\Delta H \neq q$ , as its an irreversible process.

$$\Delta H = (q_{\text{rev}})_{\text{const } P}$$

- ⑤ Combustion of Heptane  $C_7H_{16}$  in a constant volume calorimeter gave the value:

$$\Delta U = q_v = -4793 \text{ kJ at } 298\text{K} \cdot \Delta H = ?$$



$$\Delta n_g = 7 - 11 = -4$$

$$\Delta H = \Delta U + (\Delta n_g) \cdot RT \quad ; \quad R = 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{K}^{-1}$$

$$= -4802 \text{ kJ}.$$

- ⑥ Coefficient of Compressibility ( $k$ ) of water at  $298\text{K}$  is  $4.9 \times 10^{-6} \text{ atm}^{-1}$  over a range of 1 to 25 atm. Calculate the work attending the compression of 1 mol of liq. water from 1 to 25 atm at  $298\text{K}$ . Compare the same process for 1 mole of ideal gas.

Soln:  $k = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \quad ; \quad \therefore dV = -k \cdot V \cdot dP$

Work done,  $dW = -P \cdot dV = kV \cdot P \cdot dP$

Integrating,  $W = \int_{P_1}^{P_2} kV P dP = kV \left[ \frac{P_2^2}{2} - \frac{P_1^2}{2} \right]$

Here,  $V = 18 \text{ cc mol}^{-1}$  (for liq. water)  $= 18 \times 10^{-3} \text{ lit mol}^{-1}$

$2.082 \text{ lit-atm}$   
 $= 8.314 \text{ J}$

$$\therefore W = 4.9 \times 10^{-6} \times 18 \times 10^{-3} \left[ \frac{25^2}{2} - \frac{1^2}{2} \right] \text{ lit-atm mol}^{-1}$$

$$= 0.00279 \text{ J mol}^{-1}$$

For ideal gas  
under isothermal condn:

$$W = -nRT \ln \left( \frac{V_2}{V_1} \right) = -nRT \ln \left( \frac{P_1}{P_2} \right)$$

$$= 7.97 \times 10^7 \text{ J mol}^{-1}$$



How to prove  $PV^\gamma$  or  $TV^{\gamma-1} = \text{const}$  for  
Adiabatic process involving ideal gas:

1st law:

$$dU = dq - P.dV$$

For Adiabatic process:  $dq = 0$ .

[P-V work done by the system.]

$$\therefore dU = -P.dV$$

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$$\text{or, } n\bar{C}_V dT = -P.dV$$

$$\left| \bar{C}_V = \left( \frac{dU}{dT} \right)_V \right.$$

$$\text{or, } n\bar{C}_V dT = - \frac{nRT}{V}.dV \quad (\text{for ideal gas})$$

$$\text{or, } \bar{C}_V \int_{T_1}^{T_2} \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\text{or, } \bar{C}_V \ln(T_2/T_1) = R \ln(V_1/V_2)$$

$$\text{or, } \ln(T_2/T_1) = \frac{R}{\bar{C}_V} \ln(V_1/V_2) = \ln(V_1/V_2)^{R/\bar{C}_V}$$

For ideal gas,  $\bar{C}_P - \bar{C}_V = R$

$$\therefore \frac{R}{\bar{C}_V} = \frac{\bar{C}_P}{\bar{C}_V} - 1 = (\gamma - 1)$$

$$\therefore \ln(T_2/T_1) = \ln(V_1/V_2)^{\gamma-1}$$

$$\text{or, } \frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{\gamma-1}$$

$$\therefore T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1} \quad \parallel \quad \boxed{TV^{\gamma-1} = \text{const}}$$