

# Section-I Previous Year Problems

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8g of  $N_2$  is expanded reversibly from 1 lit to 10 lit at 300 K. Calculate  $\Delta S$ ,  $\Delta H$  and  $\Delta G$  (At. mass N = 14).

Given Weight = 8 gm  $N_2$

Molecular weight of  $N_2 = 2 \times N = 2 \times 14 = 28 \text{ gm/mol}$

$$(n) \text{ no. of moles of } N_2 = \frac{\text{given weight}}{\text{Molecular weight}} = \frac{8 \text{ gm}}{28 \text{ gm/mol}}$$

$$\rightarrow = 0.2857 \text{ moles}$$

$$V_1 = \text{Initial vol} = 1 \text{ Lit}$$

$$V_2 = \text{final vol} = 10 \text{ Lit}$$

$$T = 300 \text{ K}$$

formula for  $\Delta S$

$$S = \frac{q}{T}$$

from 1st law

$$U = q + w$$

$$\Delta U = q + (-P_{\text{ext}} dv)$$

at constant temp

$$\Delta U = 0$$

$$\therefore q = P_{\text{ext}} dv$$

from ideal gas eq<sup>n</sup>

$$P_{\text{ext}} = \frac{nRT}{V}$$

$$\therefore q = nRT \frac{dv}{V}$$

formula for  $\Delta G$

from maxwell eq<sup>n</sup>

$$dG = v dp - S dT$$

at constant temp.

$$dT = 0$$

$$\therefore dG = v dp$$

from ideal gas eq<sup>n</sup>

$$v = \frac{nRT}{P}$$

$$\therefore dG = \frac{nRT}{P} dp$$

$$\int_{G_1}^{G_2} dG = nRT \int_{P_1}^{P_2} \frac{dp}{P}$$

$$\Delta G = nRT \ln \left( \frac{P_2}{P_1} \right)$$

$$\therefore q = nRT \frac{dv}{v}$$

$$\therefore s = \frac{q}{T}$$

$$s = \frac{nRT \frac{dv}{v}}{T}$$

$$\int_{s_1}^{s_2} ds = nR \int_{v_1}^{v_2} \frac{dv}{v}$$

$$\Delta S = nR \ln \frac{v_2}{v_1}$$

$$\Delta S = 0.2857 \times 8.314 \times \ln\left(\frac{10}{1}\right)$$

$\begin{matrix} \uparrow & \uparrow & \uparrow \\ \text{unit} & \text{unit} & \text{Lit} \\ \text{mol} & \text{J K}^{-1} \text{mol}^{-1} & \text{Lit} \end{matrix}$

$$\Delta S = 5.494 \text{ J K}^{-1}$$

Comment =  $\Delta S$  +ve spontaneous

$$\Delta G = nRT \ln \left( \frac{P_2}{P_1} \right)$$

as  $PV = nRT$

$$P_1 = \frac{nRT}{V_1}$$

$$P_2 = \frac{nRT}{V_2}$$

At constant temp.

Put  $P_1$  &  $P_2$  in  $\Delta G$

$$\therefore \Delta G = nRT \ln \left( \frac{nRT/V_2}{nRT/V_1} \right)$$

$$\therefore \Delta G = nRT \ln \left( \frac{V_1}{V_2} \right)$$

$$\therefore \Delta G = 0.2857 \times 8.314 \times \ln\left(\frac{1}{10}\right) \times 300 \text{ K}$$

$\begin{matrix} \downarrow & \downarrow & \downarrow \\ \text{mol} & \text{J K}^{-1} \text{mol}^{-1} & \text{Lit} \\ & & \text{Lit} \end{matrix}$

$$\Delta G = -1640.80 \text{ J}$$

Comment =  $\Delta G = -ve$  spontaneous

Now for  $\Delta H$

$$\Delta G = \Delta H - T \Delta S$$

$\uparrow$   
 300 K

$$\therefore \Delta H = \Delta G + T \Delta S$$

$$= -1640.80 \text{ J} + 300 \text{ K} \times 5.494 \text{ J K}^{-1}$$

$$\Delta H = 7.394 \text{ J}$$

Three moles of hydrogen are compressed isothermally and reversibly from  $60 \text{ dm}^3$  to  $20 \text{ dm}^3$  and  $8.22 \text{ KJ}$  of work is done on it. Assuming ideal behaviour, calculate the temperature of the gas.

$$n = \text{no. of moles} = 3$$

$$V_1 = 60 \text{ dm}^3 \quad \text{for compression } V_2 < V_1$$

$$V_2 = 20 \text{ dm}^3$$

$$W = 8.22 \text{ KJ} = 8.22 \times 10^3 \text{ J}$$

Formula; reversible Process

$$W = -P_{\text{ext}} dv$$

from ideal gas eq<sup>n</sup>

$$P_{\text{ext}} = \frac{nRT}{V}$$

$$\therefore W = -nRT \frac{dv}{V}$$

$$W = -nRT \int_{V_1}^{V_2} \frac{dv}{V}$$

$$W = -nRT \ln \frac{V_2}{V_1}$$

$$\therefore T = \frac{W}{-nR \ln \left( \frac{V_2}{V_1} \right)} = \frac{8.22 \times 10^3 \text{ J}}{-3 \times 8.314 \text{ J K}^{-1} \times \ln \left( \frac{20 \text{ dm}^3}{60 \text{ dm}^3} \right)}$$

$$T = 299.98 \text{ K} \approx 300 \text{ K}$$

Calculate the work done during adiabatic reversible expansion of 0.02 mol  
 at 25°C expanded from 0.5 L to 1.0 L.

[Given :  $C_{v,m}$  of Ar =  $12.48 \text{ J K}^{-1} \text{ mol}^{-1}$ ]

$$V_1 = 0.5 \text{ L}$$

$$V_2 = 1.0 \text{ L}$$

$$T = 25^\circ\text{C} = 298 \text{ K}$$

$$C_{v,m} = 12.48 \text{ J K}^{-1} \text{ mol}^{-1} \quad \text{ie} \quad n = 1 \text{ mole}$$

formula  $\rightarrow$   $\Delta U = q + w$

$q = 0$  for adiabatic. process

$$\therefore \Delta U = w$$

$$w = -P_{\text{ext}} dV$$

$$w = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\left( P_{\text{ext}} = \frac{nRT}{V} \right)$$

$$\therefore w = -nRT \ln\left(\frac{V_2}{V_1}\right)$$

$$\therefore w = -0.02 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \ln\left(\frac{1}{0.5}\right)$$

$$w = -34.34 \text{ J}$$

Calculate  $\Delta S$ ,  $\Delta G$  and  $\Delta H$  when 20g of methane is mixed with 30g of ethane considering both of them to be ideal at 30°C. comment on your answer.

Formula.

$$\Delta S_{\text{mix}} = -nR \sum x_i \ln x_i = -nR (x_A \ln x_A + x_B \ln x_B)$$

$$\Delta G_{\text{mix}} = nRT \sum x_i \ln x_i = nRT (x_A \ln x_A + x_B \ln x_B)$$

$$\Delta G_{\text{mix}} = nRT \sum x_i \ln x_i = nRT (x_A \ln x_A + x_B \ln x_B)$$

$n$  = Total no. of moles

$x$  = mole fraction.

$x_A$  = mole fraction of methane

$x_B$  = — | ————— ethane

Now first Calculate mole fraction  $x_A$  &  $x_B$  & total no. of moles

given weight of methane = 20 gm

Molecular weight of methane =  $\text{CH}_4 = 12 + (1 \times 4) = 16 \text{ gm mol}^{-1}$

$$\text{no. of moles of methane} = n_A = \frac{\text{given weight}}{\text{Molecular weight}} = \frac{20}{16} = \boxed{1.25 = n_A}$$

given weight of ethane = 30 gm

Molecular — | ————— =  $\text{CH}_3 - \text{CH}_3 = (2 \times 12) + (1 \times 6)$   
 $\rightarrow = 24 + 6 = 30 \text{ gm mol}^{-1}$

$$\text{no. of moles of ethane} = n_B = \frac{\text{given weight}}{\text{M. wt.}} = \frac{30 \text{ gm}}{30 \text{ gm mol}^{-1}} = 1 \text{ mol}$$

$$\therefore x_A = \frac{n_A}{n_A + n_B} = \frac{1.25}{1.25 + 1.0} = 0.55$$

$$x_B = \frac{n_B}{n_A + n_B} = \frac{1.0}{1.25 + 1.0} = 0.44$$

$$n = \text{Total no. of moles} = n_A + n_B = 1 + 1.25 = 2.25$$

$$\therefore \Delta S_{\text{mix}} = -nR (x_A \ln x_A + x_B \ln x_B)$$

$$= -2.25 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} (0.55 \ln(0.55) + 0.44 \ln(0.44))$$

$$= -2.25 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times (0.55 \ln(0.55) + 0.45 \ln(0.45))$$

$$\Delta S_{\text{mix}} = -18.70 \text{ J K}^{-1} \times (-0.3288 + (-0.3612))$$

$$\Delta S_{\text{mix}} = 12.90 \text{ J K}^{-1}$$

$$\text{H}_2 \quad \Delta G_{\text{mix}} = nRT (\chi_A \ln \chi_A + \chi_B \ln \chi_B)$$

$$= 2.25 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times (30 + 273) \text{ K} \times (0.55 \ln(0.55) + 0.45 \ln(0.45))$$

$$\Delta G_{\text{mix}} = -3911.20 \text{ J}$$

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}}$$

$$\therefore \Delta H_{\text{mix}} = \Delta G_{\text{mix}} + T \Delta S$$

$$= -3911.20 + 303 \text{ K} \times 12.90$$

$$\Delta H_{\text{mix}} = 0$$