# Assignmen - 1 Solution

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CHM - 421/621

1.
$$u = \left(\frac{\theta}{R}\right) s^2 - \left(\frac{R\theta}{v_0^2}\right) v^2 \qquad \text{— (1)}$$

$$\Rightarrow u \equiv \frac{U}{N} = \left(\frac{\theta}{R}\right) \frac{S^2}{N^2} - \left(\frac{R\theta}{v_0^2}\right) \frac{V^2}{N^2}$$

Or,
$$U = \left(\frac{\theta}{R}\right) \frac{S^2}{N} - \left(\frac{R\theta}{v_0^2}\right) \frac{V^2}{N} \qquad \text{— (2)}$$

(a)
$$T \equiv \left(\frac{\partial U}{\partial S}\right)_{V,N} = \left(\frac{\theta}{R}\right) \frac{2S}{N} \qquad \text{— (3)}$$

$$P \equiv -\left(\frac{\partial U}{\partial V}\right)_{S,N} = \left(\frac{R\theta}{v_0^2}\right) \frac{2V}{N} \qquad \text{— (4)}$$

$$\mu \equiv \left(\frac{\partial U}{\partial N}\right)_{V,S} = -\left(\frac{\theta}{R}\right) \frac{S^2}{N^2} + \left(\frac{R\theta}{v_0^2}\right) \frac{V^2}{N^2} \qquad \text{— (5)}$$

(b) Substitute $S = \lambda S$, $V = \lambda V$, $N = \lambda N$ in eq. (3), (4) & (5).

$$T = \left(\frac{\theta}{R}\right) \frac{2(\lambda S)}{(\lambda N)}$$

$$= \left(\frac{\theta}{R}\right)\left(\frac{2S}{N}\right)$$

$\Rightarrow$ T is an intensive parameter (homogeneous of order zero).

Similarly,

$$P = \left(\frac{R\theta}{v_0^2}\right) \frac{2(\lambda V)}{\lambda N} = \left(\frac{R\theta}{v_0^2}\right) \frac{2V}{N}$$

i.e. homogeneous of order zero.

and,
$$\mu = -\left(\frac{\theta}{R}\right) \frac{\lambda^2 S^2}{\lambda^2 N^2} + \left(\frac{R\theta}{v_0^2}\right) \frac{\lambda^2 V^2}{\lambda^2 N^2}$$

$$= -\left(\frac{\theta}{R}\right) \frac{S^2}{N^2} + \left(\frac{R\theta}{v_0^2}\right) \frac{V^2}{N^2}$$

$\Rightarrow$ $\mu$ is an intensive parameter.

(c) from eq. (5),

$$\mu = -\left(\frac{\theta}{R}\right) \frac{S^2}{N^2} + \left(\frac{R\theta}{v_0^2}\right) \frac{V^2}{N^2} \quad \text{--- (6)}$$

$\because$ $s = \frac{S}{N}$, $v = \frac{V}{N}$

$$\mu \equiv -\left(\frac{\theta}{R}\right) s^2 + \left(\frac{R\theta}{v_0^2}\right) v^2 = -u \quad \text{--- (7)}$$

(d) From fundamental equations, we know that,

$$d\mu = -s\,dT + v\,dP \quad \text{--- (8)}$$

from eq. (3) & (4),

$$s = \frac{RT}{2\theta} \quad , \quad v = \frac{P v_0^2}{2R\theta}$$

Substituting $s$ & $v$ in eq. (8), we get,

$$d\mu = -\frac{RT}{2\theta}\,dT + \frac{Pv_0^2}{2R\theta}\,dP$$

$$\Rightarrow \boxed{\mu = \mu_0 - \frac{R}{4\theta}\left(T^2 - T_0^2\right) + \frac{v_0}{4R\theta}\left(P^2 - P_0^2\right)} \quad (9)$$

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(2.) Given,

$$u = Av^{-2}\exp(s/R) \qquad (10)$$

$$U = \frac{AN^3}{V^2}\exp(S/NR)$$

$$T \equiv \left(\frac{\partial U}{\partial S}\right)_{N,V} = \frac{AN^3}{V^2}\left(\frac{1}{NR}\right)\exp\left(S/NR\right) = \frac{u}{R} \qquad (11)$$

$$P \equiv -\left(\frac{\partial U}{\partial V}\right)_{S,N} = \frac{2AN^3}{V^3}\exp\left(S/NR\right) = \frac{2u}{v} \qquad (12)$$

from eq. (11) & (12)

$$\frac{T}{P} = \frac{v}{2R}$$

$$T = \frac{v}{2R}P$$

when $P = \frac{P_0}{2}$,

$$\boxed{T_f = \frac{vP_0}{4R}}$$

(3.) Given,

$$PV^k = \text{constant} = c \text{ (say)}$$

$$P = \frac{c}{V^k}$$

also,

$$P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$$

at constant $S, N$,

$$dU = -P\,dV$$

$$\Rightarrow \quad dU = -\frac{c}{V^k}\,dV$$

$$\Rightarrow \quad U = \frac{cV^{-k+1}}{k-1} + U_0$$

or,

$$U = \frac{PV}{k-1} + U_0$$

$$\boxed{U = \frac{PV}{k-1} + Nf\left(\frac{PV^k}{N^k}\right)}$$

(4) Given,

$$\frac{1}{T^{(1)}} = \frac{3}{2} R \frac{N^{(1)}}{U^{(1)}} \quad \text{--- (13)}$$

$$\frac{1}{T^{(2)}} = \frac{5}{2} R \frac{N^{(2)}}{U^{(2)}} \quad \text{--- (14)}$$

at equilibrium,

$$T^{(1)} = T^{(2)}$$

$$\Rightarrow \quad \frac{2}{3} \frac{U^{(1)}}{RN^{(1)}} = \frac{2}{5} \frac{U^{(2)}}{RN^{(2)}}$$

$\because \quad N^{(1)} = 2 \quad , \quad N^{(2)} = 3$ (Given)

$\therefore \quad 5U^{(1)} = 2U^{(2)}$ — (15)

$U \equiv U^{(1)} + U^{(2)} = 2.5 \times 10^3 \text{ J}$ — (16)

by eq. (15) & (16),

$$\boxed{\begin{aligned} U^{(1)} &= 714.28 \text{ J} \\ U^{(2)} &= 1785.71 \text{ J} \end{aligned}}$$

(5) $S = NA + NR \ln \frac{U^{3/2} V}{N^{5/2}} - N_1 R \ln \frac{N_1}{N} - N_2 R \ln \frac{N_2}{N}$ — (17)

& $N = N_1 + N_2$ — (18)

for chamber 1,

$N_1^{(1)} = 0.5 \quad , \quad N_2^{(1)} = 0.75 \quad , \quad T^{(1)} = 300 \text{ K}$

for chamber 2,

$N_1^{(2)} = 1 \quad , \quad N_2^{(2)} = 0.5 \quad , \quad T^{(2)} = 250 \text{ K}$

$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{3}{2} \frac{NR}{U}$ — (19)

$\Rightarrow \quad \frac{1}{T^{(1)}} = \frac{3}{2} \frac{N^{(1)}R}{U^{(1)}}$

$\frac{U^{(1)}}{300} = \frac{3}{2} \times 1.25 \times 8.31$

$\Rightarrow \quad U^{(1)} = 4674.375 \text{ J}$

Similarly,

$$U^{(2)} = \frac{3}{2} N^{(2)} R T^{(2)}$$

$$U^{(2)} = \frac{3}{2} \times 1.5 \times 8.31 \times 250$$

$$U^{(2)} = \cancel{4674} \; 4674.375 \text{ J}$$

$$\therefore \quad U = U^{(1)} + U^{(2)}$$

$$U = 9348.75 \text{ J}$$

$\Rightarrow$ Temperature at equilibrium,

$$T = \frac{2}{3} \frac{U}{NR}$$

or
$$T = \frac{2}{3} \times \frac{9348.75}{2.75 \times 8.31} = \underline{\underline{272.72 \text{ K}}}$$

Also we know,

$$\frac{P}{T} \equiv \left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{NR}{V}$$

at equilibrium,

$$\left.\begin{aligned} p^{(1)} &= \frac{N^{(1)} R T}{V^{(1)}} \\ \text{similarly, } p^{(2)} &= \frac{N^{(2)} R T}{V^{(2)}} \end{aligned}\right\} \text{— (20)}$$

Also, $$-\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{V,U}$$

$$-\frac{\mu_1^{(1)}}{T^{(1)}} = A + R\ln\left(\frac{U^{(1)3/2}\,V^{(1)}}{N^{(1)5/2}}\right) - \frac{5}{2}R - R\ln\left(\frac{N_1^{(1)}}{N^{(1)}}\right) \quad \text{—(21)}$$

Similarly,

$$-\frac{\mu_1^{(2)}}{T^{(2)}} = A + R\ln\left(\frac{U^{(2)3/2}\,V^{(2)}}{N^{(2)5/2}}\right) - \frac{5}{2}R - R\ln\left(\frac{N_1^{(2)}}{N^{(2)}}\right) \quad \text{—(22)}$$

at equilibrium,

$$\frac{\mu_1^{(1)}}{T^{(1)}} = \frac{\mu_1^{(2)}}{T^{(2)}} \qquad \& \quad T^{(1)} = T^{(2)} = T$$

$$\ln\left(\frac{U^{(1)3/2}\,V^{(1)}}{N^{(1)5/2}}\right) - \ln\frac{N_1^{(1)}}{N^{(1)}} = \ln\left(\frac{U^{(2)3/2}\,V^{(2)}}{N^{(2)5/2}}\right) - \ln\left(\frac{N_1^{(2)}}{N^{(2)}}\right)$$

$$\Rightarrow \left(\frac{U^{(1)}}{N^{(1)}}\right)^{3/2}\left(\frac{V^{(1)}}{N_1^{(1)}}\right) = \left(\frac{U^{(2)}}{N^{(2)}}\right)^{3/2}\left(\frac{V^{(2)}}{N_1^{(2)}}\right)$$

$$\because \quad T^{(1)} = T^{(2)}$$

$$\therefore \quad \frac{U^{(1)}}{N^{(1)}} = \frac{U^{(2)}}{N^{(2)}}$$

$$\Rightarrow \quad \frac{V^{(1)}}{N_1^{(1)}} = \frac{V^{(2)}}{N_1^{(2)}}$$

$$\Rightarrow \quad N_1^{(1)} = N_1^{(2)} \qquad (\because V^{(1)} = V^{(2)} = SL)$$

$\because \quad N_1 \equiv N_1^{(1)} + N_1^{(2)} = 1.5$

$$\therefore \quad \boxed{N_1^{(1)} = N_1^{(2)} = 0.75}$$

$$\therefore \quad P_{eq}^{(1)} = \frac{1.5\,\text{mol} \times 8.31\times10^{-2}\,\text{L.bar.K}^{-1}\text{mol}^{-1} \times 272.72\,\text{K}}{5\,\text{L}} = 679.91\times10^{-2}\ \text{bar}$$

and $$P_{eq.}^{(2)} = \frac{1.25\,\text{mol} \times 8.31\times10^{-2}\,\text{L.bar.K}^{-1}\text{mol}^{-1} \times 272.72\,\text{K}}{5\,\text{L}} = 5.66\ \text{bar}$$