ASSIGNMENT - 2

MODEL - SOLUTION

(CHE221A)

3.3-3 Given, $P = \dfrac{-NU}{NV - 2AVU}$, $T = \dfrac{2CU^{1/2} \cdot V^{1/2} e^{(AU/N)}}{N - 2AU}$

$$\therefore \frac{1}{T} = \frac{N - 2AU}{2CU^{1/2}V^{1/2}} \cdot e^{-AU/N}$$

→ Rewriting in terms of per mole we get;

$$\boxed{\frac{1}{T} = \left[\left(\frac{u^{-1/2} \cdot v^{-1/2}}{2C}\right) - \left(\frac{A u^{1/2} v^{-1/2}}{C}\right)\right] \cdot e^{-Au}}$$

$$\rightarrow \frac{P}{T} = \left(\frac{-u}{v - 2Avu}\right)\left(\frac{u^{-1/2} \cdot v^{1/2}}{2C} - \frac{A u^{1/2} v^{-1/2}}{C}\right) \cdot e^{-Au}$$

$$= \left(\frac{-u}{v - 2Avu}\right)\left(\frac{1 - 2Au}{2C u^{1/2} v^{1/2}}\right) \cdot e^{-Au}$$

$$= \frac{-u}{v\cancel{(1 - 2Au)}} \cdot \left(\frac{\cancel{1 - 2Au}}{2C u^{1/2} \cdot v^{1/2}}\right) \cdot e^{-Au}$$

$$\boxed{\frac{P}{T} = \frac{-u^{1/2} \cdot v^{-3/2} \cdot e^{-Au}}{2C}}$$

→ Substituting $\frac{1}{T}$ & $\frac{P}{T}$ in eq^n

$$ds = \frac{1}{T} du + \frac{P}{T} dv$$

$$ds = \left\{\left(\frac{1}{2C}\right)\left[u^{-1/2} - 2Au^{1/2}\right] v^{1/2} e^{-Au}\right\} du +$$

$$\left\{\left(-\frac{1}{2C}\right)\left[u^{1/2} \cdot v^{-3/2} \cdot e^{-Au}\right]\right\} dv \quad — (1)$$

→ Now;

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$$s = D u^n v^m e^{-Au}$$

$$\therefore ds = (D v^m)(n u^{n-1} \cdot e^{-Au} - A u^n e^{-Au}) du + D u^n e^{-Au} (m v^{m-1}) dv \quad — (2)$$

→ Comparing (1) & (2) we get;

$$D = \frac{1}{C}, \quad n = \frac{1}{2}, \quad m = \frac{-1}{2}$$

$$\therefore \boxed{s = \left(\frac{1}{C}\right) u^{1/2} v^{-1/2} \cdot e^{-Au} + C_1}$$

[C_1 = Constant of Integration]

~~3.4-5~~ $\boxed{3.4-2}$ For ideal gas;

$$P = \frac{NRT}{V}, \quad U = \frac{3}{2} RT \qquad [\because \text{Monoatomic gas}]$$

→ Fundamental eqⁿ in terms of Internal energy is as follows

$$dU = TdS - PdV$$

But for adiabatic compression, $TdS = 0$

$$\therefore \boxed{dU = -PdV} \quad — (1)$$

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$$U = \frac{3}{2} PV$$

→ Differentiating; $dU = \frac{3}{2} PdV + \frac{3}{2} VdP$

$$\therefore -PdV = \frac{3}{2} PdV + \frac{3}{2} VdP \qquad [\text{From } (1)]$$

$$\therefore \frac{5dV}{V} = 3\frac{dP}{P}$$

Integrating; $\boxed{PV^{5/3} = k = \text{constant}}$

→ Fundamental eqⁿ for Ideal gas:- $\boxed{s = s_0 + \frac{3}{2}R \ln\left(\frac{u}{u_0}\right) + R \ln\left(\frac{v}{v_0}\right)}$

$$\therefore \frac{u}{u_0}\left(\frac{v}{v_0}\right)^{2/3} = e^{\left(\frac{2(s-s_0)}{3R}\right)} \Rightarrow Pv^{5/3} = \frac{2}{3} u_0 v_0^{2/3} e^{2(s-s_0)/3R} \Rightarrow \boxed{Pv^{5/3} = \left(P_0 v_0^{5/3} \cdot e^{-(2s_0/3R)}\right) \cdot \left(e^{2s/3R}\right)}$$

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$\boxed{3.4\text{-}5}$ Given, $T = \left(\frac{V}{V_0}\right)^2 \cdot T_0$

$c = 3/2$ ($\because$ Monoatomic gas)

$\therefore \boxed{U = \frac{3}{2} NRT}$

→ Now,

(a)

$$dW = -PdV$$

$$W = -\int_{V_0}^{V_1} PdV$$

$$= -\int_{V_0}^{V_1} \frac{NRT}{V} dV$$

$$= -\int_{V_0}^{V_1} \frac{NR}{V} \cdot \left(\frac{V}{V_0}\right)^2 \cdot T_0 \, dV$$

$$= \frac{-NRT_0}{V_0^2} \int_{V_0}^{V_1} V^{2-1} dV$$

$$= -\frac{NRT_0}{V_0^2} \left[\frac{V^2}{2}\right]_{V_0}^{V_1}$$ ②

$$= -\frac{NRT_0}{2V_0^2} \left[V_1^2 - V_0^2\right]$$

$$\boxed{W = \frac{NRT_0}{2}\left[1 - \left(\frac{V_1}{V_0}\right)^2\right]} \quad — ①$$

(b)

$$\Delta U = U_1 - U_0$$

$$= \frac{3}{2} NRT_1 - \frac{3}{2} NRT_0$$

$$= \frac{3}{2} NR \left[\left(\frac{V_1}{V_0}\right)^2 T_0 - T_0\right]$$

$$= \frac{3}{2} NRT_0 \left[\left(\frac{V_1}{V_0}\right)^2 - 1\right]$$

~~Let~~ (2)

$$\therefore \boxed{\Delta U = U_0\left[\left(\frac{V_1}{V_0}\right)^2 - 1\right]} \quad -(2)$$

(c) $\Delta Q = -\Delta W + \Delta U$

$$= -\frac{NRT_0}{2}\left[1-\left(\frac{V_1}{V_0}\right)^2\right] + \frac{3}{2}NRT_0\left[1-\left(\frac{V_1}{V_0}\right)^2\right] \quad \left[\text{From (1) \& (2)}\right]$$

$$\boxed{\Delta Q = NRT_0\left[-1+\left(\frac{V_1}{V_0}\right)^2\right]\cdot\left(\frac{1}{2}+\frac{3}{2}\right)} \quad -(3)$$

(2)

(d) $dQ = TdS$

→ Now;

Fundamental eqⁿ for Ideal gas is as follows:-

$$\cancel{S-S_0 = \left(\frac{3}{2}2+1\right)R\ln\left(\frac{V}{V_0}\right)}$$

$$S-S_0 = \frac{N3}{2}R\ln\left(\frac{U}{U_0}\right) + NR\ln\left(\frac{V}{V_0}\right)$$

→ Substituting $\frac{U}{U_0} = \left(\frac{V}{V_0}\right)^2$ in above eqⁿ

$$S-S_0 = \frac{3}{2}NR\ln\left(\frac{V}{V_0}\right)^2 + NR\ln\left(\frac{V}{V_0}\right)$$

$$\therefore \boxed{S-S_0 = NR\ln\left(\frac{V}{V_0}\right)\cdot\left[\frac{3}{2}2+1\right]}$$

Thus; $dQ = TdS$

~~TNRln~~

$$dQ = (T)\left(\frac{3}{2}2+1\right)NR\,d\ln\left(\frac{V}{V_0}\right)$$

→ Integrating;

$$\Delta Q = \int_{V_0}^{V_1} (T)\left(\frac{3}{2}\eta+1\right) NK \, d\ln\left(\frac{V}{V_0}\right)$$

$$= \left(\frac{3}{2}\eta+1\right) NRT_0 \int_{V_0}^{V_1} \left(\frac{V}{V_0}\right)^{\eta} d\ln\left(\frac{V}{V_0}\right)$$

$$= \left(\frac{\cancel{\eta} NRT_0}{\cancel{\eta}}\right)\left(\frac{1}{\eta}+\frac{3}{2}\right)\left[\left(\frac{V_1}{V_0}\right)^{\eta}-1\right]\left(\frac{1}{\cancel{\eta}}\right)$$

$$\boxed{\Delta Q = (NRT_0)\left(\frac{1}{\eta}+\frac{3}{2}\right)\left[\left(\frac{V_1}{V_0}\right)^{\eta}-1\right]} \quad \text{--- (4)} \quad (2)$$

→ Consider ΔQ in either eq^n (3) or (4)

(e) For $\Delta Q = 0$ i.e. Adiabatic process

$$\frac{1}{\eta} + \frac{3}{2} = 0$$

$$\Rightarrow \boxed{\eta = -\frac{2}{3}} \quad (2)$$

3.4-11 Eqn of state for Ideal gas is as below;

$$\frac{P}{T} = \frac{NR}{V}$$

For multicomponent system

$$N = \sum_{i=1}^{r} N_i \quad \text{--- (1)}$$

$$\therefore \frac{P}{T} = \left(\sum_{i=1}^{r} N_i\right)\frac{R}{V} \quad \text{--- (1)}$$

→ For each specie T & V will be equal to the bulk Temp. and volume

$$\therefore \sum_{i=1}^{r} P_i = \left(\sum_{i=1}^{r} N_i\right)\frac{R}{V}$$

$$\therefore \boxed{P = \sum_{i=1}^{r} P_i} \quad \text{--- (1)}$$

$\boxed{3.5-1}$

(c) Given;

$$P = \frac{u}{v} \cdot \frac{c+buv}{a+buv} \;,\; T = \frac{u}{a+buv}$$

$$\therefore \frac{P}{T} = \frac{1}{v} \cdot \frac{c+buv}{\cancel{a+buv}} \times \frac{\cancel{a+buv}}{\cancel{u}}$$

$$\boxed{\frac{P}{T} = \frac{c+buv}{v}}$$

(1)

→ Condition for EOS to be compatible is as follows

$$\frac{\partial}{\partial v}\left(\frac{1}{T}\right)_u = \frac{\partial}{\partial u}\left(\frac{P}{T}\right)_v$$

$$\rightarrow LHS = \frac{\partial}{\partial v}\left(\frac{1}{T}\right)_u = \frac{\partial}{\partial v}\left(\frac{a+buv}{u}\right)_u$$

$$= \frac{bu}{u}$$

(1)

$$\boxed{LHS = b}$$

$$\rightarrow RHS = \frac{\partial}{\partial u}\left(\frac{P}{T}\right)_v = \frac{\partial}{\partial u}\left(\frac{c+buv}{v}\right)_v$$

$$= \frac{b\cancel{v}}{\cancel{v}} \Rightarrow \boxed{RHS = b}$$

$\therefore$ The EOS is compatible

(1)

3.5-1

→ Now to get Fundamental eq^n use;

$$ds = \frac{1}{T}dU + \frac{P}{T}dV \qquad 1$$

$$= \frac{a}{U}dU + bv\,du + \frac{c}{v}dv + bu\,dv$$

→ Integrating;

$$\boxed{S = a\ln\left(\frac{U}{U_0}\right) + c\ln\left(\frac{V}{V_0}\right) + b(uv - u_0v_0) + S_0} \qquad 1$$

5.3.1

From section, 3.4, fundamental equation is given by:

$$S = NS_0 + NR \ln\left[\left(\frac{U}{U_0}\right)^c \left(\frac{V}{V_0}\right)\cdot\left(\frac{N}{N_0}\right)^{-(c+1)}\right]$$

For ideal gas, $U = cNRT$ and for monoatomic gas, $c = \frac{3}{2}$

$$\therefore \frac{U}{U_0} = \frac{\cancel{\frac{3}{2}}N\cancel{R}T}{\cancel{\frac{3}{2}}N_0\cancel{R}T_0} = \frac{NT}{N_0T_0}$$

$$S = NS_0 + NR \ln\left[\left(\frac{NT}{N_0T_0}\right)^{3/2}\cdot\left(\frac{V}{V_0}\right)\left(\frac{N}{N_0}\right)^{-5/2}\right]$$

$$= NS_0 + NR \ln\left[\left(\frac{T}{T_0}\right)^{3/2}\cdot\left(\frac{V}{V_0}\right)\cdot\left(\frac{N_0}{N}\right)\right]$$

$$= NS_0 + \frac{3}{2}NR \ln\left(\frac{T}{T_0}\right) + NR\ln\left(\frac{V}{V_0}\right) - NR\ln\left(\frac{N}{N_0}\right) \quad ✓ \ ①$$

1. Helmholtz free-energy representation:- $A(\cancel{S},T,V,N)$

$$A = U - TS = \frac{3}{2}NRT - NS_0T - \frac{3}{2}NRT\ln\left(\frac{T}{T_0}\right) - NRT\ln\left(\frac{V}{V_0}\right) + NRT\ln\left(\frac{N}{N_0}\right)$$

$$\boxed{A = \left(\frac{3}{2}NR - NS_0\right)T - \frac{3}{2}NRT\ln\left[\left(\frac{T}{T_0}\right)\cdot\left(\frac{V}{V_0}\right)^{2/3}\cdot\left(\frac{N_0}{N}\right)^{2/3}\right]} \quad ✓ \ 2$$

$$-S = \left(\frac{\partial A}{\partial T}\right)\Big|_{V,N} = \left(\frac{3}{2}NR - NS_0\right) - \frac{3}{2}NR - \frac{3}{2}NR\ln\left(\frac{T}{T_0}\right) - NR\ln\left(\frac{V}{V_0}\right) + NR\ln\left(\frac{N}{N_0}\right)$$

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$$= -NS_0 - \frac{3}{2}NR\ln\left[\left(\frac{T}{T_0}\right)\left(\frac{V}{V_0}\right)^{2/3}\cdot\left(\frac{N_0}{N}\right)^{2/3}\right]$$

$$\Rightarrow \boxed{S = NS_0 + \frac{3}{2}NR\ln\left[\left(\frac{T}{T_0}\right)\cdot\left(\frac{V}{V_0}\right)^{2/3}\left(\frac{N_0}{N}\right)^{2/3}\right]} \quad ✓ \ 2$$

$$-P = \left(\frac{\partial A}{\partial V}\right)\Big|_{T,N} = -\frac{NRT}{V} \Rightarrow \boxed{P = \frac{NRT}{V}} \quad ✓ \ 1$$

$$\mu = \left(\frac{\partial A}{\partial N}\right)\Big|_{T,V} = \frac{3}{2}RT - S_0T - \frac{3}{2}RT\ln\left(\frac{T}{T_0}\right) - RT\ln\left(\frac{V}{V_0}\right) + RT\ln\left(\frac{N}{N_0}\right) + RT.\cancel{N}.\frac{1}{\cancel{N}}$$

$$\boxed{\mu = \frac{A}{N} + RT} \quad ✓ \ 1$$

2. Enthalpie representation: $H(S, P, N)$

$$H = U + PV = U + \frac{2}{3}\left(\frac{3}{2}NRT\right) = U\left(1+\frac{2}{3}\right) = \frac{5}{3}U$$ ✓ 1

$$S = NS_0 + NR \ln\left[\left(\frac{U}{U_0}\right)^{3/2} \cdot \left(\frac{V}{V_0}\right) \cdot \left(\frac{N}{N_0}\right)^{-5/2}\right]$$

$$\Rightarrow \left(\frac{S - NS_0}{NR}\right) = \ln\left[\left(\frac{U}{U_0}\right)^{3/2} \cdot \left(\frac{V}{V_0}\right)\left(\frac{N}{N_0}\right)^{-5/2}\right]$$

again, $\frac{U}{U_0} = \frac{\frac{3}{2}PV}{\frac{3}{2}P_0V_0} \Rightarrow V = \frac{P_0 V_0 U}{P U_0} \Rightarrow \frac{V}{V_0} = \frac{P_0 U}{P U_0}$.

$$\Rightarrow \left(\frac{S - NS_0}{NR}\right) = \ln\left[\left(\frac{U}{U_0}\right)^{3/2} \cdot \left(\frac{P_0 \cdot U}{P U_0}\right) \cdot \left(\frac{N}{N_0}\right)^{-5/2}\right]$$

$$\Rightarrow \left(\frac{U}{U_0}\right)^{5/2} \cdot \left(\frac{P_0}{P}\right)\left(\frac{N_0}{N}\right)^{5/2} = \exp\left(\frac{S - NS_0}{NR}\right)$$

$$\Rightarrow U = U_0 \cdot \left(\frac{P}{P_0}\right)^{2/5} \cdot \left(\frac{N}{N_0}\right) \cdot \exp\left(\frac{S - NS_0}{5/2\, NR}\right)$$

$$\Rightarrow \boxed{H = \frac{5}{3} U_0 \left(\frac{P}{P_0}\right)^{2/5} \left(\frac{N}{N_0}\right) \exp\left(\frac{S - NS_0}{5/2\, NR}\right)}$$ ✓ 2

$$V = \left(\frac{\partial H}{\partial P}\right)\Bigg|_{S,N} = \frac{\cancel{5}}{3} U_0 \cdot \frac{N}{N_0} \cdot \frac{1}{P_0^{2/5}} \cdot \frac{2}{\cancel{5}} \frac{1}{P^{3/5}} \exp\left(\frac{S - NS_0}{\frac{5}{2} NR}\right)$$

$$= \frac{2}{3} U_0 \cdot \frac{N}{N_0} \cdot \left(\frac{P}{P_0}\right)^{2/5} \cdot \frac{1}{P} \exp\left(\frac{S - NS_0}{\frac{5}{2} NR}\right)$$

$$= \left\{\frac{5}{3} U_0 \cdot \frac{N}{N_0} \left(\frac{P}{P_0}\right)^{2/5} \exp\left(\frac{S - NS_0}{5/2\, NR}\right)\right\} \cdot \frac{2}{5P}$$

$$\boxed{V = \frac{2H}{5P}}$$ ✓ 1

0.5 → it not being shown from fundamental equation

$$T = \left(\frac{\partial H}{\partial S}\right)\Bigg|_{P,N} = \frac{5}{3} \cdot U_0 \cdot \left(\frac{P}{P_0}\right)^{2/5} \cdot \left(\frac{N}{N_0}\right) \cdot \frac{1}{\frac{5}{2} NR} \cdot \exp\left(\frac{S - NS_0}{5/2\, NR}\right)$$

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$$= H \cdot \frac{2}{5NR}$$

$$\boxed{T = \frac{2H}{5NR}}$$ ✓ 1

$$\mu = \left(\frac{\partial H}{\partial N}\right)\Bigg|_{S,P} = \frac{5}{3} U_0 \left(\frac{P}{P_0}\right)^{2/5} \cdot \frac{1}{N_0} \exp\left(\frac{S - NS_0}{\frac{5}{2} NR}\right)$$

$$+ \frac{5}{3} \cdot U_0 \left(\frac{P}{P_0}\right)^{2/5} \cdot \frac{N}{N_0} \cdot \left\{ - \frac{S \cdot \exp\left(\frac{S - NS_0}{5/2\, NR}\right)}{\frac{5}{2} R N^2} \right\}$$

$$= \frac{H}{N} + \frac{5}{3} \cdot U_0 \cdot \left(\frac{P}{P_0}\right)^{2/5} \cdot \frac{N}{N_0} \cdot \exp\left(\frac{S - NS_0}{\frac{5}{2} NR}\right)\left(-\frac{S}{\frac{5}{2} N^2 R}\right)$$

$$= \frac{H}{N} - \frac{H \cdot S}{\frac{5}{2} R N^2} = \frac{H}{N}\left(1 - \frac{S}{\frac{5}{2} NR}\right)$$

$$\boxed{\mu = \frac{H}{N}\left(1 - \frac{S}{5/2\, NR}\right)}$$ ✓ 2

3. Gibbs' free energy representation:-

$$G = U - TS + PV \qquad G(P,T,N).$$

$$= A + PV$$

$$= A + NRT \quad ✓ 1$$

$$G = \frac{3}{2} NRT - NS_0T + NRT - \frac{3}{2} NRT \ln\left[\left(\frac{T}{T_0}\right)\cdot\left(\frac{V}{V_0}\right)^{2/3}\cdot\left(\frac{N_0}{N}\right)^{2/3}\right]$$

again, $PV = NRT$

$$P_0V_0 = N_0RT_0$$

$$\Rightarrow \frac{V}{V_0} = \frac{P_0}{P}\cdot\frac{N}{N_0}\cdot\frac{T}{T_0}$$

$$\Rightarrow \left(\frac{V}{V_0}\right)^{2/3} = \left(\frac{P_0}{P}\right)^{2/3}\cdot\left(\frac{N}{N_0}\right)^{2/3}\cdot\left(\frac{T}{T_0}\right)^{2/3}$$

$$G = \left(\frac{5}{2} NR - NS_0\right) T - \frac{3}{2} NRT \ln\left[\left(\frac{T}{T_0}\right)\cdot\left(\frac{P_0}{P}\right)^{2/3}\cdot\left(\frac{N}{N_0}\right)^{2/3}\left(\frac{T}{T_0}\right)^{2/3}\cdot\left(\frac{N_0}{N}\right)^{2/3}\right]$$

$$= \left(\frac{5}{2} NR - NS_0\right) T - \frac{3}{2} NRT \ln\left[\left(\frac{T}{T_0}\right)^{5/3}\cdot\left(\frac{P_0}{P}\right)^{2/3}\right]$$

$$\boxed{G = \left(\frac{5}{2} NR - NS_0\right) T - NRT \ln\left[\left(\frac{T}{T_0}\right)^{5/2}\cdot\left(\frac{P_0}{P}\right)\right]} \quad ✓ 2$$

$$-S = \left(\frac{\partial G}{\partial T}\right)\Big|_{P,N}$$

$$G = \left(\frac{5}{2}NR - NS_0\right)T - \frac{5}{2}NRT \ln\left(\frac{T}{T_0}\right) + NRT \ln\left(\frac{P}{P_0}\right)$$

$$-S = \left(\frac{\partial G}{\partial T}\right)\Big|_{P,N} = \left(\frac{5}{2}NR - NS_0\right) - \frac{5}{2}NRT \cdot \frac{1}{T} - \frac{5}{2}NR \ln\left(\frac{T}{T_0}\right) + NR \ln\left(\frac{P}{P_0}\right)$$

$$= -NS_0 - NR \ln\left[\left(\frac{T}{T_0}\right)^{5/2} \cdot \left(\frac{P_0}{P}\right)\right]$$

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$$\boxed{S = NS_0 + NR \ln\left[\left(\frac{T}{T_0}\right)^{5/2} \cdot \left(\frac{P_0}{P}\right)\right]}$$ ✓ 2

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,N} = \frac{NRT}{P} \Rightarrow \boxed{V = \frac{NRT}{P}}$$ ✓ 1

$$\mu = \left(\frac{\partial G}{\partial N}\right)\Big|_{T,P} = \frac{5}{2}RT - S_0T - \frac{5}{2}RT \ln\left(\frac{T}{T_0}\right) + NR \ln\left(\frac{P}{P_0}\right)$$

$$\boxed{\mu = \frac{G}{N}}$$ ✓ 1