

Assignment 7

1a) For one mole $RT = \left(P + \frac{a}{V^2} \right) (V - b)$

$$RT = \left(100 \text{ atm} + \frac{5.5 \text{ l}^2 \text{ atm/mol}^2}{(0.3 \text{ l/mol})^2} \right) (0.3 - 0.03) \text{ l/mol}$$

$$= 43.5 \frac{\text{atm l}}{\text{mol}} \times 10^5 \frac{\text{Pa}}{\text{atm}} \times \frac{1}{10^3} \frac{\text{m}^3}{\text{l}}$$

$$= 4.35 \times 10^3 \text{ J/mol}$$

$$T = \frac{4.35 \times 10^3}{8.314}$$

$$\therefore T = 523 \text{ K}$$

b) Isobaric $\Rightarrow P$ is constant

$$V_2 = 2V_1$$

$$\therefore RT_2 = \left(100 + \frac{5.5}{(0.6)^2} \right) (0.6 - 0.03) \frac{\text{atm l}}{\text{mol}}$$

$$= 65.7 \frac{\text{atm l}}{\text{mol}}$$

$$= 6.57 \times 10^3 \text{ J/mol}$$

$$T = 790 \text{ K}$$

c) Isothermal $\Rightarrow T$ is constant

$$100 \left(P_2 + \frac{5.5}{0.6^2} \right) (0.6 - 0.07) = 8.314 \times 523$$

$$P_2 = 66.8 \text{ atm}$$

$$2) \quad \Delta T = \frac{0.25 \text{ l/mol}}{81 \frac{\text{J}}{\text{mol K}}} \left(1 - 2 \times 10^{-3} \times 273 \right) \text{ atm}$$

$$= 1.4 \times 10^{-3} \frac{\text{atm l}}{\text{J/K}}$$

$$\therefore \Delta T = 1.4 \times 10^{-1} \text{ K using } 1 \text{ atm l} = 100 \text{ J}$$

$$3a) \quad W = \int_{V_i}^{V_f} P dV$$

$$= \int_{V_i}^{V_f} \frac{nRT}{V} dV$$

$$= nRT \ln\left(\frac{V_f}{V_i}\right)$$

$$W = P_i V_i \ln\left(\frac{V_f}{V_i}\right)$$

$$b) \quad P_i V_i = P_f V_f \Rightarrow P_f = \frac{P_i V_i}{V_f}$$

$$c) i. \quad W = \int_{V_i}^{V_f} P dV \quad \text{where } PV^\gamma = K \text{ constant } + \gamma = \frac{7}{5}$$

$$= K \int_{V_i}^{V_f} V^{-\gamma} dV$$

$$= \frac{K}{-\gamma+1} (V_f^{-\gamma+1} - V_i^{-\gamma+1})$$

$$\therefore W = (P_f V_f - P_i V_i) \frac{1}{-\gamma+1}$$

$$ii) \quad P_i V_i^\gamma = P_f V_f^\gamma$$

$$P_f = P_i \left(\frac{V_i}{V_f}\right)^\gamma$$

4a) Helmholtz Free Energy $F \equiv E - TS$

$$dF = dE - TdS - SdT$$

$$= TdS - PdV + \mu dN - TdS - SdT \text{ using 1st Law of T.O.}$$

$$dF = -SdT - PdV + \mu dN$$

$$b) \left(\frac{\partial F}{\partial T} \right)_{V,N} = -S \quad \left(\frac{\partial F}{\partial V} \right)_{T,N} = -P$$

$$\frac{\partial^2 F}{\partial T \partial V} = \frac{\partial^2 F}{\partial V \partial T} \Rightarrow \left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$$

$$c) \Delta Q = T \Delta S$$

$$= T \left[\left(\frac{\partial S}{\partial T} \right)_V \Delta T + \left(\frac{\partial S}{\partial V} \right)_T \Delta V \right]$$

$$= T \left(\frac{\partial P}{\partial T} \right)_V \Delta V \text{ for isothermal process \& using Maxwell relation}$$

$$d) PV^{10} T^{-5} = K,$$

$$\left(\frac{\partial P}{\partial T} \right)_V V^{10} T^{-5} + PV^{10} (-5) T^{-6} = 0.$$

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{5P}{T}.$$

$$\therefore \Delta Q = T \frac{5P}{T} \Delta V$$

$$= 5P \Delta V$$

$$= 5 \times 10^5 \text{ Pa} \times (-0.01 \times 0.5 \text{ l}) \times 10^{-3} \frac{\text{m}^3}{\text{l}}$$

$$\Delta Q = -2.5 \text{ J}$$

Note $\Delta Q < 0 \Rightarrow$ heat is produced.

$$\begin{aligned} 5a) \text{ Heat Produced} &= 57 \frac{\text{eV}}{\text{molecule}} \times \frac{0.7 \text{ kg}}{114 \frac{\text{amu}}{\text{molecule}} \times 1.67 \times 10^{-27} \frac{\text{kg}}{\text{amu}}} \\ &= 2.1 \times 10^{26} \text{ eV} \\ &= 3.4 \times 10^7 \text{ J} \end{aligned}$$

$$\begin{aligned} b) \text{ Engine Efficiency } \eta &= \frac{6 \text{ kW} \times 20 \text{ min} \times 60 \frac{\text{sec}}{\text{min}}}{3.4 \times 10^7 \text{ J}} \\ &= \frac{7.2 \times 10^6 \text{ J}}{3.4 \times 10^7 \text{ J}} \end{aligned}$$

$$\eta = 21\%$$