

# CHM225- PS#3 SOLUTIONS.

1. Calculate  $\Delta U_{i \rightarrow i'}$ ,  $q_{i \rightarrow i'}$ ,  $w_{i \rightarrow i'}$  for the isothermal process  $(T_i, V_i) \rightarrow (T_i, V_{i'})$

$$dw = -pdV$$

$$\Rightarrow w_{i \rightarrow i'} = - \int_i^{i'} \frac{RT}{V-b} dV = -RT_i \int \frac{dV}{V-b}$$

$$\boxed{w_{i \rightarrow i'} = -RT_i \ln \left( \frac{V_{i'} - b}{V_i - b} \right)}$$

$$\Delta U_{i \rightarrow i'} = \int_i^{i'} du$$

$$du = \left( \frac{\partial u}{\partial T} \right)_V dT + \left( \frac{\partial u}{\partial V} \right)_T dV$$

$$= C_v dT + \left( \frac{\partial u}{\partial V} \right)_T dV$$

isothermal process

need to express  $\left( \frac{\partial u}{\partial V} \right)_T$  in terms of  $P, V$  &  $T$

$$u \equiv u(S, V)$$

$$du = Tds - pdV$$

$$\Rightarrow du_T = Tds_T - pdV_T \quad (\text{keeping } T \text{ constant})$$

$$\Rightarrow \left( \frac{du_T}{dV_T} \right) = T \frac{ds_T}{dV_T} - p \frac{dV_T}{dV_T}$$

$$\Rightarrow \left( \frac{\partial u}{\partial V} \right)_T = T \left( \frac{\partial s}{\partial V} \right)_T - p$$

Need to express  $\left(\frac{\partial S}{\partial V}\right)_T$  in terms of  $P, V$  &  $T$   
Use Maxwell's Relations:

$$dU = TdS - PdV$$

$$dA = -SdT - PdV$$

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

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

$$P = \frac{RT}{V-b} \Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$$

$$\Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{R}{V-b}\right) - P = 0$$

$$\Rightarrow dU = 0 \quad (\text{for an isothermal process})$$

$$\Rightarrow \boxed{\Delta U_{1 \rightarrow 1'} = 0}$$

$$\Rightarrow \Delta U_{1 \rightarrow 1'} = q_{1 \rightarrow 1'} + w_{1 \rightarrow 1'}$$

$$\Rightarrow \boxed{\begin{aligned} q_{1 \rightarrow 1'} &= -w_{1 \rightarrow 1'} \\ &= RT_1 \ln\left(\frac{V_1 - b}{V_1' - b}\right) \end{aligned}}$$

1(ii) Compute  $\Delta U_{\text{cycle}}$ ,  $q_{\text{cycle}}$ ,  $w_{\text{cycle}}$ .

$$\boxed{\Delta U = \Delta U_{1 \rightarrow 1} = U_1 - U_1 = 0} \quad (U \text{ is a state variable})$$

$$q = q_{1 \rightarrow 1'} + \overset{\text{adiabatic}}{q_{1' \rightarrow 2}} + q_{2 \rightarrow 2'} + \overset{\text{adiabatic}}{q_{2' \rightarrow 1}}$$

$$q_{2 \rightarrow 2'} = -RT_2 \ln\left(\frac{V_{2'} - b}{V_2 - b}\right)$$

$$\Rightarrow \boxed{q = -RT_1 \ln\left(\frac{V_{1'} - b}{V_1 - b}\right) - RT_2 \ln\left(\frac{V_{2'} - b}{V_2 - b}\right)}$$

$$\Delta U = q + w$$

$$\Rightarrow \boxed{w = -q = RT_1 \ln\left(\frac{V_{1'} - b}{V_1 - b}\right) + RT_2 \ln\left(\frac{V_{2'} - b}{V_2 - b}\right)}$$

1(iii) Compute the efficiency of the Carnot Cycle engine.

$$\varepsilon = -\frac{w}{q_H} = \frac{q}{q_{1 \rightarrow 1'}}$$

$$= \frac{-RT_1 \ln\left(\frac{V_{1'} - b}{V_1 - b}\right) - RT_2 \ln\left(\frac{V_{2'} - b}{V_2 - b}\right)}{-RT_1 \ln\left(\frac{V_{1'} - b}{V_1 - b}\right)}$$

$$= 1 + \frac{T_2}{T_1} \frac{\ln\left(\frac{V_{1'} - b}{V_1 - b}\right)}{\ln\left(\frac{V_{2'} - b}{V_2 - b}\right)}$$

To simplify further we need to relate the ratio of volumes. Since  $1' \rightarrow 2$  &  $2' \rightarrow 1$  are adiabatic processes we have:

$$dq_{\text{rev}} = 0$$

$$dU = dw_{\text{rev}}$$

$$\Rightarrow \int_{1'}^2 dU = \int_{1'}^2 C_v$$

$$\Rightarrow C_v dT = -pdV$$

$$\Rightarrow C_v dT = -\frac{RT}{V-b} dV$$

$$\Rightarrow -\frac{C_v}{R} \int_{1'}^2 \frac{dT}{T} = \int_{1'}^2 \frac{dV}{V-b}$$

$$\Rightarrow -\frac{C_v}{R} \ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{V_2-b}{V_1'-b}\right)$$

Similarly consider the adiabatic process  $2' \rightarrow 1$

$$\Rightarrow -\frac{C_v}{R} \ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{V_2'-b}{V_1-b}\right)$$

$$\Rightarrow \ln\left(\frac{V_2-b}{V_1'-b}\right) = \ln\left(\frac{V_2'-b}{V_1-b}\right)$$

$$\Rightarrow \ln(V_2-b) - \ln(V_1'-b) = \ln(V_2'-b) - \ln(V_1-b)$$

$$\Rightarrow \ln(V_2-b) - \ln(V_2'-b) = -(\ln(V_1'-b) - \ln(V_1-b))$$

$$\Rightarrow \ln \left( \frac{V_2' - b}{V_2 - b} \right) = - \ln \left( \frac{V_1' - b}{V_1 - b} \right)$$

$$\Rightarrow \varepsilon = 1 + \frac{T_2}{T_1} \frac{-\left(\ln \left( \frac{V_1' - b}{V_1 - b} \right)\right)}{\ln \left( \frac{V_1' - b}{V_1 - b} \right)}$$

$$\boxed{\varepsilon = 1 - \frac{T_2}{T_1}}$$

The efficiency of the Carnot cycle engine is identical to the efficiency of Carnot cycle engine that uses an ideal gas as the working substance. It can be proved, in fact, that the efficiency of any Carnot Cycle engine is identical to this expression irrespective of the working substance!

Q2. (i)  $S = S(T, V)$

calculate  $\Delta S_{1 \rightarrow 2}^{(a)}$  (path (a) is reversible).

for a reversible process

$$\Delta S_{1 \rightarrow 2}^{(a)} = \int_1^2 dS \quad (\text{irrespective of path since } S \text{ is a state variable})$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$dU_V = T dS_V - P dV_V$$

$$\Rightarrow \frac{dU_V}{dT_V} = T \frac{dS_V}{dT_V}$$

$$\Rightarrow \left(\frac{\partial U}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V$$

$$\Rightarrow \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

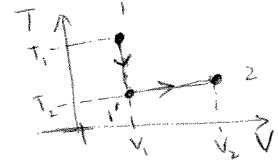
Use Maxwell's Relation to express  $\left(\frac{\partial S}{\partial V}\right)_T$  in  $P, V$  &  $T$  terms.

$$dA = -S dT - P dV$$

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

$$\Rightarrow P = \frac{RT}{V-b} \Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$$

$$\Rightarrow dS = C_v \frac{dT}{T} + \frac{R}{V-b} dV$$



$$\begin{aligned} \Rightarrow \Delta S_{1 \rightarrow 2} &= \int_1^2 C_v \frac{dT}{T} + \int_{V_1}^{V_2} \frac{R}{V-b} dV \\ &= C_v \ln \left( \frac{T_2}{T_1} \right) + R \ln \left( \frac{V_2 - b}{V_1 - b} \right) \end{aligned}$$

(ii) Let  $S = S(T, P)$

$$dS = \left( \frac{\partial S}{\partial T} \right)_P dT + \left( \frac{\partial S}{\partial P} \right)_T dP$$

~~$$dG = SdT + VdP$$~~

$$dH = TdS + VdP$$

$$\Rightarrow \frac{dH}_P = T \frac{dS}_P$$

$$\Rightarrow \left( \frac{\partial H}{\partial T} \right)_P = T \left( \frac{\partial S}{\partial T} \right)_P$$

$$\Rightarrow \left( \frac{\partial S}{\partial T} \right)_P = \frac{C_P}{T}$$

Using Maxwell's Relation:

$$dG = -SdT + VdP$$

$$\Rightarrow \left( \frac{\partial S}{\partial P} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_P$$

$$dS = \frac{C_p}{T} dT - \left( \frac{\partial V}{\partial T} \right)_P dP$$

$$P(V-b) = RT$$

$$\Rightarrow V = \frac{RT}{P} + b$$

$$\Rightarrow \left( \frac{\partial V}{\partial T} \right)_P = \frac{R}{P}$$

$$\Rightarrow dS = \frac{C_p}{T} dT - \frac{R}{P} dP$$

$$\begin{aligned} \Delta S_{1 \rightarrow 2}^{(a)} &= \int_1^2 \frac{C_p}{T} dT - \int_1^2 \frac{R}{P} dP \\ &= C_p \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{P_2}{P_1}\right) \\ &= C_p \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{P_1}{P_2}\right) \end{aligned}$$

Substitute  $P = \frac{RT}{V-b}$

$$\Delta S_{1 \rightarrow 2}^{(a)} = C_p \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{\frac{RT_1}{V_1-b}}{\frac{RT_2}{V_2-b}}\right)$$

$$= C_p \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{T_1}{T_2} \cdot \frac{V_2-b}{V_1-b}\right)$$

$$= C_p \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{V_2-b}{V_1-b}\right)$$

$$\Delta S_{1 \rightarrow 2}^{(a)} = (C_p - R) \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{V_2-b}{V_1-b}\right)$$

Comparing Results (i) & (ii) we conclude that  $C_v = C_p - R$ . The change in  $S$  does not depend on which variable we choose to treat as independent.

(iii) Compute  $\Delta S_{1 \rightarrow 2}^{(b)}$

where (b) is a spontaneous irreversible path.

$$\boxed{\Delta S_{1 \rightarrow 2}^{(b)} = \Delta S_{1 \rightarrow 2}^{(a)}}$$

since  $S$  is a state variable and it does not depend on the path.

(iv) cyclic process  $(T_1, V_1) \xrightarrow{(a)} (T_2, V_2) \xrightarrow{(c)} (T_1, V_1)$ .

where path (a) is reversible and path (c) is spontaneous (irreversible).

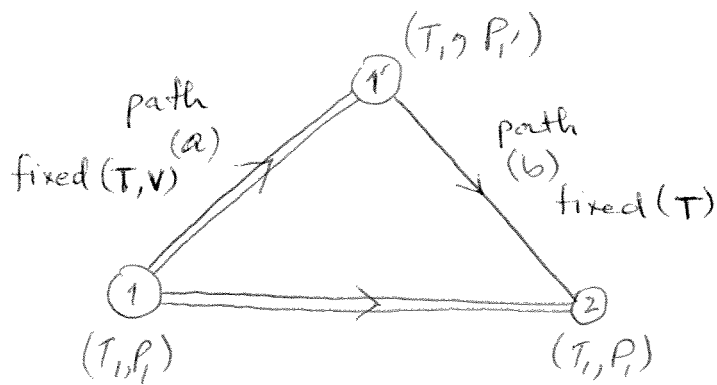
$$\Delta S_{\text{cycle}} = \Delta S_{1 \rightarrow 2}^{(a)} + \Delta S_{2 \rightarrow 1}^{(c)}$$

$$\text{but } \Delta S_{1 \rightarrow 2}^{(a)} = -\Delta S_{2 \rightarrow 1}^{(a)} \quad (\text{reversible})$$

$$\text{and } \Delta S_{2 \rightarrow 1}^{(a)} = \Delta S_{2 \rightarrow 1}^{(c)} \quad (S \text{ is a state fn})$$

$$\Rightarrow \boxed{\Delta S_{\text{cycle}} = \Delta S_{1 \rightarrow 2}^{(a)} - \Delta S_{1 \rightarrow 2}^{(a)} = 0}$$

3). Show that condition for spontaneity for a process with fixed  $(T, P)$  is  $\Delta G < 0$ .



path (a): irreversible process at fixed  $(T, V)$

$\Rightarrow \Delta A_{1 \rightarrow 1'} < 0$ . Pressure changes.

Suppose  $P_1' > P_1 \Rightarrow V_1' > V_2$  (since (b) is an isothermal process)

path (b): isothermal reversible compression to restore pressure to its initial value.

$$\begin{aligned} \Delta A_{1 \rightarrow 2} &= \Delta U_{1 \rightarrow 2} - T_1 \Delta S_{1 \rightarrow 2} \\ &= \omega_{1 \rightarrow 2} + q_{1 \rightarrow 2} - T_1 \frac{q_{1 \rightarrow 2}}{T_1} = \omega_{1 \rightarrow 2} \end{aligned}$$

$$\Rightarrow \Delta A_{1 \rightarrow 2} = - \int_{V_1'}^{V_2} p dV \leq -P_1 (V_2 - V_1) = -P_1 \Delta V_{1 \rightarrow 2}$$

$$\Delta G_{1 \rightarrow 2} = \Delta A_{1 \rightarrow 2} + P_1 \Delta V_{1 \rightarrow 2} = \underbrace{\Delta A_{1 \rightarrow 1'}}_{< 0} + \underbrace{\Delta A_{1 \rightarrow 2} + P_1 \Delta V_{1 \rightarrow 2}}_{< 0} < 0$$

since  $\Delta A_{1 \rightarrow 2} + P_1 \Delta V_{1 \rightarrow 2} = - \int_{V_1'}^{V_2} (P - P_1) dV < 0$

4.

$$\text{VdW gas: } \left(p + \frac{a}{V^2}\right)(V-b) = RT.$$

Reversible isothermal expansion  $(T, V_1) \rightarrow (T, V_2)$

Calculate  $\Delta S_{1 \rightarrow 2}$ .

$$\text{let } S \equiv S(T, V).$$

$$\text{Then from Q2: } \Delta S_{1 \rightarrow 2} = \int_{T_1}^{T_2} \frac{C_v}{T} dT$$

$$dS = \frac{C_v}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV.$$

↑  
isothermal

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}.$$

$$\Rightarrow dS = \frac{R}{V-b} dV$$

$$\boxed{\Delta S_{1 \rightarrow 2}^{\text{vdw}} = R \ln\left(\frac{V_2 - b}{V_1 - b}\right)} \quad \text{for VdW gas}$$

$$\text{for an ideal gas } P = \frac{RT}{V} \Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}.$$

$$\Delta S_{1 \rightarrow 2}^{\text{id}} = R \ln\left(\frac{V_2}{V_1}\right)$$

$$\text{since } \frac{V_2 - b}{V_1 - b} > \frac{V_2}{V_1} \quad (\text{when } V_2 > V_1 \text{ \& } b > 0)$$

$$\therefore \Delta S_{1 \rightarrow 2}^{\text{vdw}} > \Delta S_{1 \rightarrow 2}^{\text{id}}$$

The entropy change for a VdW gas is greater than the entropy change for ideal gas for isothermal expansion.