

1. $P_1 = 1 \text{ atm}$, $V_1 = 1 \text{ l}$, $T_1 = 313 \text{ K}$.

$P_2 = P_2$, $V_2 = 2 \text{ l}$, $T_2 = 313 \text{ K}$.

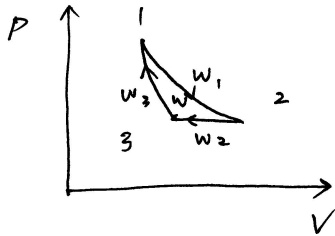
$P_3 = P_2$, $V_3 = V$, $T_3 = T_3$.

$P_1 = 1 \text{ atm}$, $V_1 = 1 \text{ l}$, $T_1 = 313 \text{ K}$.

↓ reversible isothermal expansion, w_1 .

↓ reversible isobaric compression, w_2 .

↓ reversible adiabatic compression, w_3 .



① reversible isothermal expansion.

$$dU = \delta q - \delta w = 0 \quad \therefore \delta w = \delta q = PdV.$$

$$w_1 = \int PdV = \int \frac{nRT}{V} dV = nRT \ln \frac{V_f}{V_i} = nRT \ln 2.$$

from the ideal gas law, $n = \frac{P_1 V_1}{RT} = 0.0327 \text{ mol}$.

$$\therefore w_1 = 0.0327 \cdot 8.3144 \cdot 313 \cdot \ln 2 = 70.29 \text{ J}.$$

② reversible isobaric compression.

$$w_2 = \int PdV = P_2(V_3 - V_2).$$

since, $P_2 = P_3 = \frac{nRT_2}{V_2} = 0.5 \text{ atm}$. and $P_3 V_3^\gamma = P_1 V_1^\gamma \therefore V_3 = \left(\frac{P_1}{P_2}\right)^{\frac{1}{\gamma}} \cdot V_1 = 2^{\frac{5}{2}} = 1.516 \text{ l}$.

($\gamma = \frac{5}{2}$ for monoatomic gas.)

$$\therefore w_2 = 0.5(1.516 - 2) \cdot 101.3 = -24.51 \text{ J}.$$

③ reversible adiabatic compression.

$$dU = -\delta w = nC_v dT. \quad (C_v = \frac{3}{2}R \text{ for monoatomic gas}).$$

$$\therefore w_3 = -\int nC_v dT = -\frac{3}{2}nR(T_1 - T_3) = -\frac{3}{2} \times 0.0327 \times 8.3144 \times (313 - T_3).$$

since $T_3 = \frac{P_3 V_3}{nR} = 282.5 \text{ K}$.

$$\therefore w_3 = -\frac{3}{2} \times 0.0327 \times 8.3144 \times (313 - 282.5) = -36.91 \text{ J}.$$

$$w = w_1 + w_2 + w_3 = 70.29 - 24.51 - 36.91 = 8.87 \text{ J}.$$

2. (a). First law.

$$dU = \delta q - \delta w. = \delta q - PdV. \quad (1)$$

Second law.

$$dS = \frac{\delta q_{rev}}{T}. \rightarrow \delta q_{rev} = TdS. \quad (2)$$

combining (1) and (2) gives, $dU = TdS - PdV$.

(b). $\cdot H = U + PV.$

$$\begin{aligned} dH &= dU + PdV + VdP. \\ &= TdS - PdV + PdV + VdP. \\ &= TdS + VdP. \end{aligned}$$

$\cdot A = U - TS$

$$\begin{aligned} dA &= dU - TdS - SdT. \\ &= TdS - PdV - TdS - SdT. \\ &= -PdV - SdT. \end{aligned}$$

$\cdot G = H - TS.$

$$\begin{aligned} dG &= dH - TdS - SdT \\ &= TdS + VdP - TdS - SdT. \\ &= VdP - SdT. \end{aligned}$$

(c). $G = H - TS.$

$$dG = VdP - SdT. \rightarrow \left(\frac{\partial G}{\partial T}\right)_P = -S. \quad \text{at constant pressure.}$$

$$G = H + T\left(\frac{dG}{dT}\right) \quad \text{or} \quad GdT = HdT + TdG.$$

dividing throughout by T^2 gives.

$$\frac{TdG - GdT}{T^2} = -\frac{HdT}{T^2} \quad \text{or} \quad \frac{T\left(\frac{dG}{dT}\right) - G}{T^2} = -\frac{H}{T^2}$$

$$\therefore \frac{d(G/T)}{dT} = -\frac{H}{T^2}.$$

this equation allows ΔH to be obtained from a measurement of the ΔG , vice versa.

$$(d). \quad dG = -SdT + VdP + \sum_{i=1}^k \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j, \dots} dn_i$$

The term $\left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j, \dots}$ is called the chemical potential of species i , μ_i

$$\therefore dG = -SdT + VdP + \sum_i \mu_i dn_i.$$

Similarly,

$$dU = TdS - PdV + \sum_{i=1}^k \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_j, \dots} dn_i$$

$$= TdS - PdV + \sum_i \mu_i dn_i.$$

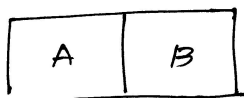
$$dH = TdS - VdP + \sum_{i=1}^k \left(\frac{\partial H}{\partial n_i} \right)_{S, P, n_j, \dots} dn_i$$

$$= TdS - VdP + \sum_i \mu_i dn_i.$$

$$dA = -SdT + PdV + \sum_{i=1}^k \left(\frac{\partial A}{\partial n_i} \right)_{T, V, n_j, \dots} dn_i$$

$$= -SdT + PdV + \sum_i \mu_i dn_i.$$

3. (a).



1 mole 1 mole
1 atm 1 atm.

$$dS = \frac{\delta q}{T} = \frac{PdV}{T} = nR \frac{dV}{V}.$$

$$\Delta S = nR \ln \frac{V_2}{V_1}.$$

when the partition is removed,

the volume occupied by 1 mole of A doubles, $\therefore \Delta S_A = nR \ln 2 = R \ln 2$ ($n=1$).

the volume occupied by 1 mole of B doubles, $\therefore \Delta S_B = R \ln 2$.

$$\therefore \Delta S_{\text{total}} = \Delta S_A + \Delta S_B = R \ln 4 = 11.53 \text{ J/K}.$$

(b). number of atoms of Au, $n_{\text{Au}} = \frac{10}{197} \times 6.023 \times 10^{23}$.

number of atoms of Ag, $n_{\text{Ag}} = \frac{20}{107.9} \times 6.023 \times 10^{23}$.

$$\Delta S_{\text{conf.}} = k \ln \frac{(n_{\text{Au}} + n_{\text{Ag}})!}{n_{\text{Au}}! n_{\text{Ag}}!}$$

$$= k [(n_{\text{Au}} + n_{\text{Ag}}) \ln (n_{\text{Au}} + n_{\text{Ag}}) - n_{\text{Au}} \ln n_{\text{Au}} - n_{\text{Ag}} \ln n_{\text{Ag}}].$$

$$= 1.3805 \times 10^{-23} [7.574 - 1.575 - 5.925] \times 10^{24}$$

$$= 1.02 \text{ J/K}.$$

4. An adiabatic process, $dS = \frac{\delta q}{T} = 0$, isentropic process.

$$\therefore \left(\frac{\partial T}{\partial P}\right)_S$$

from the upstairs - downstairs - inside - out formula,

$$\left(\frac{\partial T}{\partial P}\right)_S \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_P = -1, \quad \text{--- (1)}$$

and, since

$$C_p = T \left(\frac{\partial S}{\partial T}\right)_P \text{ gives}$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T} \quad \text{--- (2)}$$

From the Maxwell's relation,

$$\left(\frac{\partial P}{\partial S}\right)_T = -\left(\frac{\partial T}{\partial V}\right)_P \quad \text{--- (3)}$$

and the isobaric thermal expansivity is defined as

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \text{ or } \left(\frac{\partial V}{\partial T}\right)_P = \alpha V. \quad \text{--- (4)}$$

(2), (3), (4) into (1) gives

$$\left(\frac{\partial T}{\partial P}\right)_S \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{C_p}{T}\right) = -1$$

$$\left(\frac{\partial T}{\partial P}\right)_S \left(-\frac{1}{V\alpha}\right) \left(\frac{C_p}{T}\right) = -1$$

$$\therefore \left(\frac{\partial T}{\partial P}\right)_S = \frac{TV\alpha}{C_p}$$

$$\Delta T = \frac{298 \text{ K} \cdot 2.56 \times 10^{-5} \text{ m}^3/\text{mole} \cdot 2.2 \times 10^{-5} / \text{K} \cdot 500 \text{ MPa}}{80 \text{ J/mole} \cdot \text{K}}$$

$$= 1.049 \text{ K}$$

5. (a). At constant pressure, $dH = c_p dT$.

Integration between (T_2, P) and (T_1, P) gives.

$$\Delta H = H(T_2, P) - H(T_1, P) = \int_{T_1}^{T_2} c_p dT. \quad -\textcircled{1}$$

At constant pre temperature

$dH = \left(\frac{\partial H}{\partial P}\right)_T dP$, since $dH = TdS + VdP$, and thus

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V.$$

From Maxwell's equation, $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$, in which case,

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

$$= -T\alpha V + V = V(1 - \alpha T).$$

Integration between (P_2, T) and (P_1, T) gives

$$\Delta H = H(P_2, T) - H(P_1, T) = \int_{P_1}^{P_2} V(1 - \alpha T) dP. \quad -\textcircled{2}$$

$\textcircled{1} + \textcircled{2}$ gives.

$$\Delta H = H(P_2, T_2) - H(P_1, T_1) = \int_{T_1}^{T_2} c_p dT + \int_{P_1}^{P_2} V(1 - \alpha T) dP,$$

$$5. (b) \quad dS = \frac{\delta q}{T}$$

at constant pressure,

$$dS = \left(\frac{\delta q}{T} \right)_P = \left(\frac{dH}{T} \right)_P = C_p \frac{dT}{T}$$

$$\therefore \Delta S = S(T_2, P) - S(T_1, P) = \int_{T_1}^{T_2} \frac{C_p}{T} dT \quad - (1)$$

At constant temperature,

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

From Maxwell's equation, $\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P = -\alpha V$

$$\therefore \Delta S = S(P_2, T) - S(P_1, T) = - \int_{P_1}^{P_2} \alpha V dP \quad - (2)$$

(1) + (2) gives.

$$\Delta S = S(P_2, T_2) - S(P_1, T_1) = \int_{T_1}^{T_2} \frac{C_p}{T} dT - \int_{P_1}^{P_2} \alpha V dP$$

5. (c). An isothermal expansion of ideal gas from V_1 to $2V_1$.

constant T .

$$\Delta S = - \int_{P_1}^{P_2} \alpha V dP$$

$$= - \int_{P_1}^{P_2} \alpha \cdot \frac{nRT}{P} dP$$

$$= - \alpha nRT \ln \frac{P_2}{P_1}$$

$$= \alpha nRT \ln \frac{V_2}{V_1}$$

$$= \alpha nRT \ln 2$$

which is positive value

\therefore spontaneous process.