1.

$P_i = 10\,atm,\quad T_i = 300K \quad P_f = 5\,atm \quad n=1$

$P_iV_i = nRT_i \quad V_i = 2.462L$

(a) isothermal

$P_iV_i = P_fV_f \quad \therefore V_f = \frac{P_i}{P_f}V_i = 4.924L$

$\Delta T = 0 \Rightarrow \Delta U = 0 \quad \Rightarrow \quad q = W$

$W = \int_{2.462}^{4.924} \frac{nRT}{V} dV = nRT \ln 2 = 1.728\,kJ = q$

$\Delta S = \frac{q}{T} = 5.763\,J/K$

(b) reversible adiabatic

monoatomic $\Rightarrow C_v = \frac{3}{2}R,\ C_p = \frac{5}{2}R,\ \gamma = \frac{5}{3}$

$P_iV_i^{\gamma} = P_fV_f^{\gamma} \quad V_f = V_i \cdot \left(\frac{P_i}{P_f}\right)^{1/\gamma} = 3.732L$ …… 아…

$q = 0$ 이므로 $\Delta S = \frac{q}{T} = 0$

(c) Constant-volume

$\Delta U = q \quad (\because W = 0)$

$P_fV_f = nRT_f \Rightarrow \quad T_f = \frac{P_fV_f}{nR} = 150K$

$\Delta S = \frac{q}{T} = \frac{\Delta U}{T} = \int_{300}^{150} \frac{n \cdot C_v}{T} dT = C_v \cdot \ln\frac{1}{2} = -8.645\,J/K$

2.

$n=1$, monoatomic ideal gas

a. $T_0 = 300K$, $P_0 = 10\,atm$ $\Rightarrow V_0 = 2.462\,L$

expands freely $C_V = \frac{3}{2}R$, $C_p = \frac{5}{2}R$, $\gamma = \frac{5}{3}$, $V_a = 3V_0$

$$P_0 V_0^{\gamma} = P_a V_a^{\gamma} \qquad P_a = P_0 \left(\frac{V_0}{V_a}\right)^{\gamma} = 10 \cdot \left(\frac{1}{3}\right)^{\frac{5}{3}} = 1.602\ atm$$

$$T_a = \frac{P_a V_a}{nR} = 144.24\,K$$

$$\Delta U_a = \int_{300}^{144.24} C_V\, dT = -1.942\,kJ, \quad \Delta H_a = \int_{300}^{144.24} C_p\, dT = -3.238\,kJ$$

$\Delta S_a = 0$ ($\because$ adiabatic process $\Rightarrow q = 0$)

$q_a = 0$, $W_a = -\Delta U_a = 1.942\,kJ$

b. $V_a = V_b$, $T_b = 400$ constant volume

$$P_b = \frac{nRT_b}{V_b} = 4.444\,atm$$

$$\Delta U_b = \int_{144.24}^{400} C_V\, dT = 3.190\,kJ, \qquad \Delta H_b = \int_{144.24}^{400} C_p\, dT = 5.316\,kJ$$

$$\Delta S_b = \int_{144.24}^{400} \frac{C_V}{T}\, dT = C_V \ln\frac{400}{144.24} = 12.72\ J/K$$

$W_b = 0$ ($\because \Delta V = 0$) $q_b = \Delta U_b = 3.190\,kJ$

c. isothermal $\quad V_c = V_b \times 3 = 7.386 \times 3 = 22.16\,L$

$$P_b V_b = P_c V_c \quad \Rightarrow P_c = \frac{P_b V_b}{V_c} = 1.481\ atm$$

$$\Delta U_c = \Delta H_c = 0 \quad (\because dT = 0)$$

$$\Delta S_c = \frac{q}{T} = \frac{w}{T} = \frac{1}{T} \cdot \int_{7.358}^{22.16} \frac{RT}{V} dV = R \ln 3 = 9.134\ J/K$$

$$q_c = W_c = 3.654\ kJ$$

d. constant pressure. $\quad T_d = 300$

$$V_d = \frac{nRT_d}{P_d} = 16.62\,L$$

$$\Delta U_d = \int_{400}^{300} C_v dT = -1.247\ kJ \qquad \Delta H_d = \int_{400}^{300} C_p dT = -2.079\ kJ$$

$$\Delta S_d = \int_{400}^{300} \frac{C_p}{T} dT = C_p \ln \frac{3}{4} = -5.980\ J/K$$

$$W_d = P \Delta V = 5.99\,L \times 1.481\ atm \times 101.325\ J/L\cdot atm = -0.899\ kJ$$

$$q_d = \Delta U_d + W_d = -2.146\ kJ$$

$$q = q_a + q_d + q_c + q_d = (0 + 3.190 + 3.654 - 2.146)\,kJ = 4.698\ kJ$$

$$W = W_a + W_b + W_c + W_d = (1.942 + 0 + 3.654 - 0.899)\,kJ = 4.697\ kJ$$

$$\Delta U = \Delta U_a + \Delta U_b + \Delta U_c + \Delta U_d = (-1.942 + 3.190 + 0 - 1.247)\,kJ = 0.001\ kJ$$

$$\Delta H = \Delta H_a + \Delta H_b + \Delta H_c + \Delta H_d = (-3.238 + 5.316 + 0 - 2.079)\,kJ = -0.001\ kJ$$

$$\Delta S = \Delta S_a + \Delta S_b + \Delta S_c + \Delta S_d = (0 + 12.72 + 9.134 - 5.980)\,J/K = 15.874\ J/K$$

3.

$z = (x-2)^2 + (y-2)^2 + 4 =: f(x,y)$

$g(x,y) := x+y-1 = 0$

$\nabla f = (2x-4,\ 2y-4)$

$\nabla g = (1,\ 1)$

extreme point 를 (a,b)라 하면

$$\begin{cases} a+b-1=0 \\ (2a-4,\ 2b-4) = \lambda(1,1) \end{cases}$$

$$\begin{cases} a+b=1 \\ 2a=\lambda+4 \\ 2b=\lambda+4 \end{cases} \rightarrow \lambda=-3,\quad a=b=\frac{1}{2}$$

$\therefore$ extreme value $= f(\frac{1}{2}, \frac{1}{2}) = \frac{17}{2}$

4.

$\Delta S_{total} = \Delta S_{configuration}$ (No chemical reaction)

(a) $\Omega_{divided} = \frac{N_A!}{0!\,N_A!} \cdot \frac{N_A!}{0!\,N_A!} = 1$

partition이 제거된 후 most probable한 state는 반반씩 섞이는 것이다.

N_A는 매우 크므로 $\Omega_{mixed} \approx \Omega$(A, B 반반 섞임) 이다.

$\Rightarrow \Omega_{mixed} = \frac{(2N_A)!}{N_A!\,N_A!}$, $\ln(x!) \approx x\ln x - x$

$$\Delta S_{conf} = k_B \ln \frac{\Omega_{mixed}}{\Omega_{divided}} = k_B\left(2N_A \ln(2N_A) - 2N_A \ln N_A\right) = 11.53\,J/K$$

(b) $\Omega_{divided} = \dfrac{(2N_A)!}{0!\,(2N_A)!} \cdot \dfrac{N_A!}{0!\,N_A!} = 1$

(a) 에서와 마찬가지로 반씩 있을 때가 most probable하며, N_A가 크므로

$\Omega_{mixed} \approx \Omega$ (A, B 반반) 이 성립한다.

$$\Rightarrow \Omega_{mixed} = \frac{(2N_A)!}{N_A!\,N_A!} \cdot \frac{N_A!}{\left(\frac{N_A}{2}\right)!\left(\frac{N_A}{2}\right)!}$$

$$\therefore \Delta S_{tot} = k_B \ln \frac{\Omega_{mixed}}{\Omega_{divided}} = k_B \ln \Omega_{mixed}$$

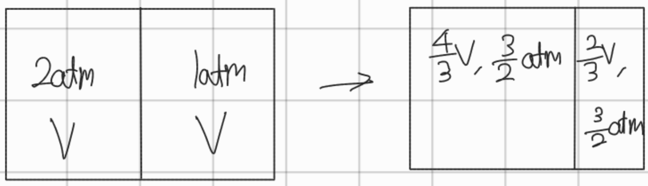
$$= k_B \left(2N_A \ln(2N_A) \cancel{- 2N_A} - 2N_A \ln N_A \cancel{+ 2N_A} + N_A \ln N_A - N_A \ln \frac{N_A}{2} \right)$$

$$= 17.29\ \mathrm{J/K}$$

(c) 두 part 모두 ideal gas A를 가지므로 indistinguishable

$$\Rightarrow \Delta S = \Delta S_{conf} = 0$$

(d) S는 state function 이므로 left part 와 right part 의 압력을 맞춘 후 partition 을 제거해도 같을 것이다.



$$\Delta S = \frac{PdV}{T} = \frac{1}{T}\left(\int_{V}^{\frac{4}{3}V} \frac{2RT}{V} dV + \int_{V}^{\frac{2}{3}V} \frac{RT}{V} dV \right)$$

$$= 2R \ln\frac{4}{3} + R \ln\frac{2}{3} = 1.413 \text{ J/K}$$

partition 이동 후 양 part 의 Pressure는 같으므로 (c)에 의해 partition 제거의 $\Delta S = 0$

$$\Rightarrow \Delta S_{tot} = 1.413 \text{ J/K}$$