1.

$P_1 = 10\,atm$, $T = 300K$, $1\,mol$

(a) isothermal process (10atm → 5atm)

$$P_1V_1 = nRT \Rightarrow V_1 = \frac{nRT}{P_1} = \frac{(1mol)\times(0.08206\,L\cdot atm/K\cdot mol)(300K)}{10atm} = 2.462L$$

isothermal process 이므로 $P_1V_1 = P_2V_2 \Rightarrow V_2 = \frac{P_1V_1}{P_2} = \frac{(10atm)(2.462L)}{(5atm)} = 4.924L$

$$\Delta S = \frac{q_{rev}}{T}, \quad q_{rev} = W_{max} = \int_{V_1}^{V_2} P\,dV = \int_{V_1}^{V_2} \frac{nRT}{V}\,dV = \left[nRT\ln V\right]_{V_1}^{V_2}$$
$$= nRT\ln\frac{V_2}{V_1}$$

$$\therefore \Delta S = \frac{q_{rev}}{T} = \frac{nRT\ln\frac{V_2}{V_1}}{T} = nR\ln\frac{V_2}{V_1} = (1mol)(8.3144\,J/K\cdot mol)\ln\frac{4.924L}{2.462L}$$
$$= 5.76\,J/K$$

(b) reversible adiabatic expansion (10atm → 5atm)

adiabatic process 이므로 $q = 0$ 이다. 또한 reversible 하므로

$\therefore \Delta S = 0$

(c) constant - volume decrease (10atm → 5atm)

$$P_1V_1 = nRT_1 \Rightarrow V_1 = \frac{nRT_1}{P_1} = \frac{(1mol)\times(0.08206\,L\cdot atm/K\cdot mol)(300K)}{10atm} = 2.462L$$
$$P_2V_2 = nRT_2 \Rightarrow T_2 = \frac{P_2V_2}{nR} = \frac{(5atm)(2.462L)}{(1mol)(0.08206\,L\cdot atm/K\cdot mol)} = 150K$$

$$\delta q = PdV + nC_v dT = \frac{nRT}{V} dV + nC_v dT$$

$$\Rightarrow \frac{\delta q}{T} = \frac{nR}{V} dV + \frac{nC_v}{T} dT = \frac{nC_v}{T} dT \quad (dV = 0)$$

$$\Rightarrow \Delta S = \int_{T_1}^{T_2} \frac{nC_v}{T} dT = \left[nC_v \ln T \right]_{T_1}^{T_2} = nC_v \ln \frac{T_2}{T_1}$$

$$\therefore \Delta S = nC_v \ln \frac{T_2}{T_1} = (1\,\mathrm{mol}) \times \left(\frac{3}{2} \times 8.3144\ \mathrm{J/K \cdot mol} \right) \times \ln\left(\frac{150\,K}{300\,K} \right) = -8.65\ \mathrm{J/K}$$

2.

a. $T_1 = 300K$, $P_1 = 10atm$ $V \rightarrow 3V$ ($V_2 = 3V_1$)

$P_1V_1 = nRT_1 \Rightarrow V_1 = \frac{nRT_1}{P_1} = \frac{(1mol)(0.08206\ L \cdot atm/K \cdot mol)(300K)}{10\ atm} = 2.462L$

$T_2 = T_1 = 300K$, $V_2 = 3V_1 = 7.386L$, $P_2 = \frac{nRT_2}{V_2} = \frac{1}{3}P_1 = 3.33atm$

진공 자유 팽창이므로 $q = w = \Delta U = \Delta H = 0$ 이다.

$\Delta S = nR \ln\frac{V_2}{V_1} = (1mol)(8.3144J/K \cdot mol) \ln 3 = 9.134J/K$

$\therefore$ $q = w = \Delta U = \Delta H = 0$, $\Delta S = 9.134J/K$

b. $T_2 = 300K$, $V_2 = 7.386L$, $P_2 = 3.33atm$

$V_3 = V_2 = 7.386L$, $T_3 = 400K$, $P_3 = \frac{nRT_3}{V_3} = \frac{4}{3}P_2 = 4.44atm$

$q = q_V = nC_V\Delta T = C_V(T_3 - T_2) = (1mol) \times (\frac{3}{2} \times 8.3144\ J/K \cdot mol)(400K - 300K)$
$= 1247J$

$w = 0$ ($\because$ costant volume), $\Delta U = q - w = q = 1247J$

$\Delta H = nC_P\Delta T = (1mol)(\frac{5}{3} \times 8.3144J/K \cdot mol)(400K - 300K) = 2079J$
$\Delta S = nC_V \ln\frac{T_3}{T_2} = (1mol)(\frac{3}{2} \times 8.3144J/K \cdot mol) \ln\frac{4}{3} = 3.588J/K$

$\therefore$ $q = 1247J$, $w = 0$, $\Delta U = 1247J$, $\Delta H = 2079J$, $\Delta S = 3.588J/K$

c. $T_3 = 400k$, $V_3 = 7.386L$, $P_3 = 4.44atm$

$T_4 = T_3 = 400k$, $V_4 = 3V_3 = 22.16L$, $P_4 = \frac{1}{3}P_3 = 1.48\,atm$

reversible isothermal process 이므로

$$W_{max} = q_{rev} = nRT \ln\frac{V_4}{V_3} = (1mol)(8.3144J/k\cdot mol)(400k)\ln\frac{22.16L}{7.386L} = 3654J$$

$\Delta U = q - w = 0$, reversible isothermal process 이므로 $\Delta H = 0$

$$\Delta S = \frac{q_{rev}}{T} = \frac{3654J}{400k} = 9.135J/k$$

$\therefore$ $q = 3654J$, $w = 3654J$, $\Delta U = 0$, $\Delta H = 0$, $\Delta S = 9.135J/k$

d. $T_4 = 400k$, $V_4 = 22.16L$, $P_4 = 1.48atm$

$P_5 = P_4 = 1.48atm$, $T_5 = 300k$, $V_5 = \frac{nRT_5}{P_5} = \frac{(1mol)(0.08206\ L\cdot atm/k\cdot mol)(300k)}{1.48\,atm} = 16.6L$

$$q = q_p = nC_p\Delta T = (1mol)(\tfrac{5}{2}\cdot 8.3144J/k\cdot mol)(300k - 400k) = -2079J$$

$$w = P\Delta V = (1.48atm)\cdot(16.6L - 22.16L) = -8.23L\cdot atm = -833J$$

$$\Delta U = q - w = -2079J - (-833J) = -1246J$$

$\Delta H = q_p = -2079 J$

$\Delta S = nC_p \ln \frac{T_5}{T_4} = (1 mol)(\frac{5}{2} \cdot 8.3144 J/K \cdot mol) \ln \frac{300K}{400K} = -59.8 J/K$

$\therefore q = -2079 J, \ w = -833 J, \ \Delta U = -1246 J, \ \Delta H = -2079 J, \ \Delta S = -59.8 J/K$

3.

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

$f_x = \frac{\partial z}{\partial x} = 2(x-2)$, $f_y = \frac{\partial z}{\partial y} = 2(y-2)$

$f_x = f_y = 0$ 에서 critical point 이므로 $(2,2)$가 critical point 이다.

$\therefore$ $(2,2)$에서 minimum value $z=4$를 갖는다.

(b) $x+y=1 \Rightarrow y = 1-x$

$\Rightarrow z = (x-2)^2 + (1-x-2)^2 + 4 = (x-2)^2 + (x+1)^2 + 4$

$= x^2 - 4x + 4 + x^2 + 2x + 1 + 4 = 2x^2 - 2x + 9$

$= 2(x^2 - x + \frac{1}{4}) + 9 - \frac{1}{2}$

$= 2(x - \frac{1}{2})^2 + \frac{17}{2}$

$\Rightarrow x = \frac{1}{2}$, $y = 1 - \frac{1}{2} = \frac{1}{2}$ $\Rightarrow$ $(\frac{1}{2}, \frac{1}{2})$ 에서 minimum value $z = \frac{17}{2}$을 갖는다.

(c) $g(x,y) = x+y-1$ 이라 하면

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

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

$\nabla f = \lambda \nabla g$ 에서 $2(x-2) = \lambda \cdot 1$, $2(y-2) = \lambda \cdot 1$

$$\Rightarrow \begin{cases} x+y-1=0 \\ 2x-4-\lambda=0 \\ 2y-4-\lambda=0 \end{cases} \Rightarrow x=y \Rightarrow x=\frac{1}{2}, y=\frac{1}{2}, \lambda=-3$$

$f(\frac{1}{2},\frac{1}{2}) = (\frac{1}{2}-2)^2 + (\frac{1}{2}-2)^2 + 4 = \frac{17}{2}$

$\Rightarrow$ $(\frac{1}{2},\frac{1}{2})$ 에서 minimum value $z = \frac{17}{2}$ 을 갖는 다.

4.

(a)

A (V, 1mol)	B (V, 1mol)

$\Rightarrow$

A (2V, 1mol), B (2V, 1mol)

$$\Delta S = R \ln \frac{V_2}{V_1} \Rightarrow \Delta S_A = R \ln \frac{2V}{V} = R \ln 2$$

$$\Delta S_B = R \ln \frac{2V}{V} = R \ln 2$$

$$\therefore \Delta S_{tot} = \Delta S_A + \Delta S_B = R \ln 2 + R \ln 2 = R \ln 4$$

(b)

A (V, 2mol)	B (V, 1mol)

$\Rightarrow$

A (2V, 2mol) B (2V, 1mol)

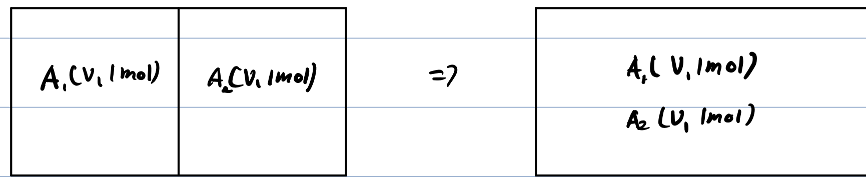
$$\Delta S = R \ln \frac{V_2}{V_1} \Rightarrow \Delta S_A = 2R \ln \frac{2V}{V} = 2R \ln 2$$

$$\Delta S_B = R \ln \frac{2V}{V} = R \ln 2$$

$$\therefore \Delta S_{tot} = \Delta S_A + \Delta S_B = 2R \ln 2 + R \ln 2 = 3R \ln 2 = R \ln 8$$

(c)

i)

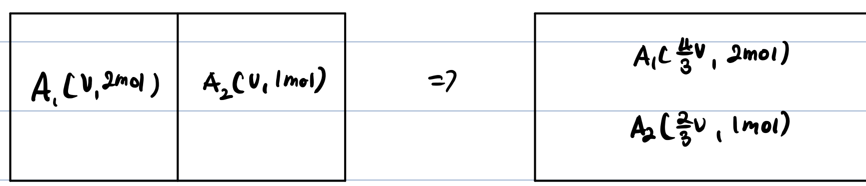


$$\Delta S = R\ln\frac{V_2}{V_1} \Rightarrow \Delta S_{A_1} = R\ln\frac{V}{V} = 0$$

$$\Delta S_{A_2} = R\ln\frac{V}{V} = 0$$

$$\therefore \Delta S_{tot} = \Delta S_{A_1} + \Delta S_{A_2} = 0$$

ii)



$$\Delta S = R\ln\frac{V_2}{V_1} \Rightarrow \Delta S_{A_1} = 2R\ln\frac{\frac{4}{3}V}{V} = 2R\ln\frac{4}{3}$$

$$\Delta S_{A_2} = R\ln\frac{\frac{2}{3}V}{V} = R\ln\frac{2}{3}$$

$$\therefore \Delta S_{tot} = \Delta S_{A_1} + \Delta S_{A_2} = 2R\ln\frac{4}{3} + R\ln\frac{2}{3} = R\ln\frac{32}{27}$$