1. The initial state of one mole of a monatomic ideal gas is P = 10 atm and T = 300 K. Calculate the change in the entropy of the gas for (a) an isothermal decrease in the pressure to 5 atm, (b) a reversible adiabatic expansion to a pressure of 5 atm, (c) a constant-volume decrease in the pressure to 5 atm.

Initial : $P_i = 10$ atm , $T_i = 300K$, 1 mol

$$V_i = \frac{nRT}{P} = \frac{(1mol)(0.082\,L\cdot atm/K\cdot mol)(300K)}{(10\,atm)} = 2.46L$$

(a) isothermal → PV = constant

$$P_f = 5\,atm,\ T = 300K,\ V_f = \frac{P_iV_i}{P_f} = \frac{(10atm)(2.46L)}{(5\,atm)} = 4.92\,L\ (= 2V_i)$$

$$\Delta U = 0 = q - w$$

$$\Rightarrow q = w = \int P\,dV = nRT\ln\frac{V_f}{V_i} = (1mol)(8.314\,J/K\cdot mol)(300K)\ln\left(\frac{4.92}{2.46}\right) = 1729J$$

$$\Delta S = \frac{q}{T} = \frac{1729J}{300K} = 5.763\,J/K$$

(b) adiabatic → q=0

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

(c) $V_f = V_i = 2.46\,L$, $P_f = 5atm = \frac{1}{2}P_f$

$$\longrightarrow T = \frac{\overset{P \to \frac{1}{2}P}{PV}}{nR} \Rightarrow T_f = \frac{1}{2}T_i = 150K$$

$$dV = 0 \rightarrow w = 0$$

$$\Rightarrow q = \Delta U = \frac{3}{2}nR\Delta T$$

$$dS = \frac{dQ}{T} \rightarrow S = \int_{T_i}^{T_f}\frac{3nR}{2T}\,dT$$

$$= \frac{3}{2}nR\ln\frac{T_f}{T_i}$$

$$= \frac{3}{2}(1mol)(8.314J/mol\cdot K)\ln\left(\frac{150k}{300k}\right) = -8.644J/k$$

2. One mole of monatomic ideal gas is subjected to the following sequence of steps:
   a. Starting at 300 K and 10 atm, the gas expands freely into a vacuum to triple its volume.
   b. The gas is next heated reversibly to 400 K at constant volume.
   c. The gas is reversibly expanded at constant temperature until its volume is again tripled.
   d. The gas is finally reversibly cooled to 300 K at constant pressure.

   Calculate the values of q and w and the changes in U, H and S.

(a) initial : 1 mol, $T_i = 300\text{K}$, $P_i = 10\text{ atm}$ $\rightarrow V_i = \dfrac{nRT}{P} = \dfrac{(1\text{ mol})(0.082\text{ L}\cdot\text{atm}/\text{K}\cdot\text{mol})(300\text{K})}{(10\text{ atm})} = 2.462\text{ L}$

final : " " $P_a = \frac{1}{3}P_i = 3.333\text{ atm}$, $V_a = 3V_i = 7.38\text{ L}$

free expansion $\longrightarrow W=0,\ q=0,\ \Delta T = 0 \rightarrow \Delta U = 0,\ \Delta H = 0$

$$\Delta S = \int_i^f dS = \int_{V_i}^{V_a} \frac{P}{T}\,dV = \int_{V_i}^{V_a} \frac{nR}{V}\,dV = nR\frac{V_a}{V_i}$$

$$= (1\text{mol})(8.314\text{J/mol}\cdot\text{K})(\ln\frac{3V_i}{V_i}) = 9.134\text{J/K}$$

$\therefore$ $q=0$
$W=0$
$\Delta U=0$
$\Delta H=0$
$\Delta S = 9.134\text{J/K}$

(b) $V_b = 7.38\text{ L}$, $T_b = 400\text{K}$ $\rightarrow P_b = \dfrac{nRT}{V} = \dfrac{(1\text{ mol})(0.082\text{ L}\cdot\text{atm}/\text{K}\cdot\text{mol})(400\text{K})}{(7.38\text{L})} = 4.444\text{ atm}$

$dV = 0 \longrightarrow W = 0$

$\rightarrow \Delta U = q = \frac{3}{2}nR\Delta T = \frac{3}{2}(1\text{mol})(8.314\text{J/mol}\cdot\text{K})(400\text{K} - 300\text{K}) = 1247\text{J}$

$\Delta H = \frac{5}{2}nR\Delta T = \frac{5}{2}(1\text{mol})(8.314\text{J/mol}\cdot\text{K})(400\text{K} - 300\text{K}) = 2079\text{J}$

$\Delta S = \int \frac{dQ}{T} = \int_{T_a}^{T_b} \frac{3}{2}nR\frac{1}{T}dT = \frac{3}{2}nR\ln\frac{T_b}{T_a} = \frac{3}{2}(1\text{mol})(8.314\text{J/K}\cdot\text{mol})\ln\left(\frac{400\text{K}}{300\text{K}}\right) = 3.588\text{ J/K}$

$\therefore$ $q = 1247\text{J}$
$W = 0$
$\Delta U = 1247\text{J}$
$\Delta H = 2079\text{J}$
$\Delta S = 3.588\text{ J/K}$

(c) $T_c = 400\text{K}$. $V_c = 3V_b = 22.14\text{L}$, $P_c = \frac{1}{3}P_b = 1.481\text{ atm}$

$\Delta T = 0 \rightarrow \Delta H, \Delta U = 0$

$\rightarrow q = W = \int P\,dV - \int_{V_b}^{V_c} \frac{nRT}{V}\,dV = nRT\ln\frac{V_c}{V_b} = (1\text{mol})(8.314\text{J/K}\cdot\text{mol})\ln\left(\frac{3V_b}{V_b}\right) = 3654\text{J}$

$\Delta S = \dfrac{q}{T} = \dfrac{3654\text{J}}{400\text{K}} = 9.135\text{ J/K}$

$\therefore$ $q = 3654\text{J}$
$W = 3654\text{J}$
$\Delta U = 0$
$\Delta H = 0$
$\Delta S = 9.135\text{J/K}$

(d) $P_d = P_c = 1.481\text{ atm}$, $T_d = 300\text{K}$, $V_d = \dfrac{nRT}{P} = \dfrac{(1\text{ mol})(0.082\text{ L}\cdot\text{atm}/\text{K}\cdot\text{mol})(300\text{K})}{(1.481\text{ atm})} = 16.61\text{ L}$

$\Delta U = nC_v\Delta T = (1\text{mol})\frac{3}{2}(8.314\text{ J/mol}\cdot\text{K})(300\text{K} - 400\text{K}) = -1247\text{J}$

$\Delta H = nC_p\Delta T = (1\text{mol})\frac{5}{2}(8.314\text{ J/mol}\cdot\text{K})(300\text{K} - 400\text{K}) = -2079\text{J}$

$W = P\Delta V = (1.481\text{ atm})(16.61\text{L} - 22.14\text{L})(101.325\text{J/atm}\cdot\text{L}) = -829.8\text{J}$

$q = \Delta U + W = -1247\text{J} - 829.8\text{J} = -2077\text{J}$

$\Delta S = nC_p\ln\frac{T_2}{T_1} = (1\text{mol})\frac{5}{2}(8.314\text{ J/mol}\cdot\text{K})\ln\left(\frac{300\text{K}}{400\text{K}}\right) = -5.979\text{ J/K}$

$\therefore$ $q = -2077\text{J}$
$W = -829.8\text{J}$
$\Delta U = -1247\text{J}$
$\Delta H = -2079\text{J}$
$\Delta S = -5.979\text{J/K}$

Total : $\Delta U = 0$, $\Delta H = 0$, $W = 2824\text{J}$, $q = 2824\text{J}$, $\Delta S = 15.88\text{J/K}$

3.(a) Find the extreme value of the function,

$$z = (x - 2)^2 + (y - 2)^2 + 4.$$

Find the constrained maximum of this function corresponding to the condition

$$x + y = 1$$

(b) by eliminating one variable and (c) by using a Lagrange undetermined multiplier method.

(a) $\frac{dz}{dx} = 2x - 4 = 0 \quad \rightarrow x = 2$

$\frac{dz}{dy} = 2y - 4 = 0 \quad \rightarrow y = 2 \qquad \therefore f(2,2) = 4$

(b) $x+y = 1 \quad \rightarrow y = 1 - x$

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

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

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

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

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

$x = \frac{1}{2} \longrightarrow y = 1 - \frac{1}{2} = \frac{1}{2} \qquad \therefore f(\frac{1}{2}, \frac{1}{2}) = \frac{17}{2}$

(c) Condition $\longrightarrow x+y-1 = 0$

$L = F(\hat{x}, \hat{y}, \hat{z}) = (x-2)^2 + (y-2)^2 + 4 + \lambda(x+y-1) = 0$

$\frac{dF}{dx} = 2x - 4 + \lambda = 0 \quad \cdots ①$

$\frac{dF}{dy} = 2y - 4 + \lambda = 0 \quad \cdots ②$

$\frac{dF}{d\lambda} = x + y - 1 = 0 \quad \cdots ③$

③ $\Rightarrow x+y = 1 \quad \cdots ④$

①+② $= 2\underbrace{(x+y)}_{=1} + 2\lambda - 8 = 0$

$\Rightarrow 2\lambda = 8 - 2 = 6 \qquad \therefore \lambda = 3$

①−② $= 2x - 2y = 0$

$\rightarrow x - y = 0$

$+)\ x + y = 1 \quad \cdots ④$

$2x = 1$

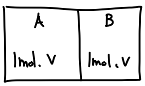
$\therefore x = \frac{1}{2}$

$\rightarrow y = 1 - x = \frac{1}{2}$

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

4. A rigid container is divided into two compartments of equal volume by a partition. One compartment contains 1 mole of ideal gas A at 1 atm, and the other compartment contains 1 mole of ideal gas B at 1 atm.
   (a) Calculate the entropy increase in the container if the partition between the two compartments is removed.
   (b) If the first compartment had contained 2 moles of ideal gas A, what would have been the entropy increase due to gas mixing when the partition was removed?
   (c) Calculate the corresponding entropy changes in each of the above two situations if both compartments had contained ideal gas A.

(a)



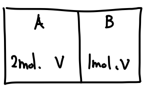
$$\Delta S = \int_{V_i}^{V_f} \frac{nR}{V}\, dV = nR\ln\frac{V_f}{V_i}$$

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

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

$$\Delta S = \Delta S_A + \Delta S_B = 2R\ln 2 = R\ln 4$$

(b)

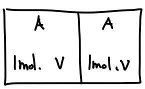


$$\Delta S_A = 2R\ln\frac{2V}{V} = 2R\ln 2 = R\ln 4$$

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

$$\Delta S = \Delta S_A + \Delta S_B = R\ln 4 + R\ln 2 = R\ln 8$$

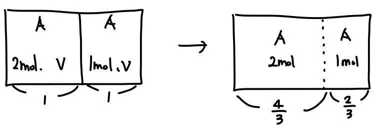
(c)-a



→ 변화없음

→ $\Delta S = 0$

(c)-b



$$\Rightarrow \Delta S_A = 2R\ln\frac{\frac{4}{3}V}{V} = R\ln\frac{16}{9}$$

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

$$\Delta S = \Delta S_A + \Delta S_B = R\left(\ln\frac{16}{9} + \ln\frac{2}{3}\right)$$

$$= R\ln\frac{32}{27}$$