2.1 An monatomic ideal gas at 300 K has a volume of 15 liters at a pressure of 15 atm. Calculate

a. The final volume of the system
b. The work done by the system
c. The heat entering or leaving the system
d. The change in the internal energy
e. The change in the enthalpy when the gas undergoes
   i. A reversible isothermal expansion to a pressure of 10 atm
   ii. A reversible adiabatic expansion to a pressure of 10 atm

The constant-volume molar heat capacity of the gas, c_v, has the value 1.5 R.

Sol) $C_V = \frac{3}{2}R$ $T_1 = 300K$ $V_1 = 15L$ $P_1 = 15atm$.

i) Reversible isothermal expansion ($P_2 = 10\,atm$)

a) $P_1V_1 = P_2V_2$ (isothermal $PV = nRT$)

$15atm \cdot 15L = 10atm \cdot V_2$

$V_2 = \frac{15atm}{10atm} 15L = \frac{3}{2} \times 15L = 22.5L$

b) $W = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT \ln\left(\frac{V_2}{V_1}\right)$

$P_1V_1 = nRT_1 \rightarrow n = \frac{P_1V_1}{RT_1} = \frac{15 \times 15}{0.0820 \times 300} = 9.14mol$

$W = 9.14mol \times 0.0820\ atm \cdot L/mol \cdot K \times 300K \times \ln\left(\frac{22.5L}{15L}\right)$

$= 91.2\ atm \cdot L = 91.2 \times 101.325\ J = 9240\ J$

c) $\Delta U = q - W \rightarrow$ isothermal: $\Delta U = 0$

$q = W = 9240J$

d) $\Delta U = 0$ ($\because \Delta T = 0$) ($nC_V\Delta T = 0$)

e) $\Delta H = nC_p\Delta T$

$= 0$

ii) Reversible adiabatic expansion ($P_2 = 10atm$)

a) $P_1V_1^{\gamma} = P_2V_2^{\gamma}$

$C_p = \frac{3}{2}R + R = \frac{5}{2}R$ $C_V = \frac{3}{2}R$ $\gamma = \frac{5}{3} = \frac{C_p}{C_V}$

$15atm \cdot 15L^{5/3} = 10atm \cdot V_2^{5/3}$

$V_2^{5/3} = \frac{3}{2} \cdot 15^{5/3}$ $V_2 = \left(\frac{3}{2}15^{5/3}\right)^{3/5} = \left(\frac{3}{2}\right)^{3/5} 15 = 19.1\,L$

b) $q=0 \therefore \Delta U = \cancel{q}^{0} - W = -W$

$W = -\Delta U = -nC_v\Delta T = -9.14\text{mol} \times \frac{3}{2}R \times (T_2 - T_1)$

$T_2 = \frac{P_2V_2}{nR} = \frac{10\text{atm} \cdot 19.1\text{L}}{9.14 \times 0.082} = 255\text{K}$

$\therefore W = -9.14 \times \frac{3}{2} \times 0.082 \times (255 - 300)$

$= 50.6\ \text{atm} \cdot \text{L} = 50.6 \times 101.325\ \text{J}$

$= 5127\text{J}$

c) 단열과정 이므로 $q=0$

d) $\Delta U = -W = -5127\text{J}$

e) $\Delta H = nC_p\Delta T = 9.14\text{mol} \times \frac{5}{2} \times 0.082\ \text{atm-L/mol-K} \times (255-300)\text{K}$

$= -84.3\ \text{atm} \cdot \text{L}$

$= -84.3 \times 101.325\text{J} = -8543\text{J}$

2.3 The initial state of a quantity of monatomic ideal gas is $P = 1$ atm, $V = 1$ liter, and $T = 373$ K. The gas is isothermally expanded to a volume of 2 liters and is then cooled at constant pressure to the volume V. This volume is such that a reversible adiabatic compression to a pressure of 1 atm returns the system to its initial state. All of the changes of state are conducted reversibly. Calculate the value of V and the total work done on or by the gas.

Sol) $P_1 = 1\text{atm}$ $V_1 = 1\text{L}$ $T_1 = 373\text{K}$

등온팽창 ($V_2 = 2\text{L}$) → 등압냉각 (constant P_3, V)

$n = \frac{P_1V_1}{RT_1} = \frac{1 \times 1}{0.08206 \times 373} = 0.0327\ \text{mol}$

등온팽창 : $P_1V_1 = P_2V_2 \rightarrow P_2 = \frac{P_1V_1}{V_2} = \frac{1\text{atm} \cdot 1\text{L}}{2\text{L}} = \frac{1}{2}\text{atm}$

$P_3 = P_2 = 0.5\text{atm}$, $T_2 = 373\text{K}$

Adiabatic compression : $P_1V_1^{\gamma} = P_3V^{\gamma}$

$\Rightarrow 1\text{atm} \times 1\text{L}^{5/3} = 0.5\text{atm}\ V^{5/3}$

$V^{5/3} = 2 \rightarrow \boxed{V = 2^{3/5} = 1.52\text{L}}$

$T_3 = \frac{P_3V}{nR}$

$= \frac{0.5 \times 1.52}{0.0327 \times 0.082}$

$= 283\text{K}$

$W = W_1 + W_2 + W_3$

W_1 (등온팽창) $= -nRT\ln\frac{V_2}{V_1} = -0.0327\,mol \times 8.314\,J/mol\cdot K \times 373\,K \times \ln\left(\frac{2}{1}\right)$

$= -70.3J$

W_2 (등압 냉각) $= -P_2\Delta V = -P_2(V - V_2) = -0.5atm\,(1.52L - 2L)$

$= +0.24\,atm\cdot L$

$= +24.3\,J$

W_3' (단열압축) $= -\Delta U + \cancel{q}^{\,0} = -\Delta U$

$= -nC_V(T_1 - T_3) = -0.0327 \times \frac{3}{2} \times 8.314\,(373 - 282)$

$= -37.1\,J$

↳ 계에서 한일

$W_3 = -W_3' = 37.1J$

↓ 계에서 받은일

한일은 $+8.9J$

$W = W_1 + W_2 + W_3 = -70.3 + 24.3 + 37.1 = \underline{-8.9J}$ ✱

2.5 One mole of N_2 gas is contained at 273 K and a pressure of 1 atm. The addition of 3000 J of heat to the gas at constant pressure causes 832 J of work to be done during the expansion. Calculate

a. The final state of the gas
b. The values of ΔU and ΔH for the change of state
c. The values of c_v and c_p for N_2

Assume that nitrogen behaves as an ideal gas, and that the change of state is conducted reversibly.

sol) $n = 1mol$ N_2 $T_1 = 273K$ $P_1 = 1atm$

$q = 3000\,J$, constant pressure → $W = 832J$ expansion.

∥ q_p (∵ P일정) ↳ $P_2 = 1atm$

a) $V_1 = \frac{nRT_1}{P_1} = \frac{0.082 \times 273}{1atm} = 22.4L$

$832J = W = P_2\Delta V = P_2(V_2 - V_1) = 1 \times (V_2 - 22.4)\,atm\cdot L \times \frac{101.325J}{1atm\cdot L}$

$= (V_2 - 22.4) \times 101.325J$

$V_2 - 22.4 = \frac{832}{101.325}$ → $V_2 = 22.4 + \frac{832}{101.325} = 30.6L$

$T_2 = \frac{P_2 V_2}{nR} = \frac{1\text{atm} \cdot 30.6\text{L}}{1 \times 0.082} = 373\text{K}$

$\therefore V_2 = 30.6\text{L} \quad T_2 = 373\text{K} \quad P_2 = 1\text{atm}$

b)&c) $\Delta U = q - W = 3000\text{J} - 832\text{J} = 2168\text{J}$

$\Delta U = nC_V\Delta T = C_V(T_2 - T_1) = C_V(373 - 273) = 100\,C_V$

$C_V = 21.7\text{J/mol·K}$

$\Delta H = nC_p\Delta T = q_p = 3000\text{J}$

$C_p = 3000\text{J}/n\Delta T = \frac{3000}{1 \cdot 100} = 30\text{J/mol·K}$

3.1 The initial state of 1 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

Sol) $P_1 = 10\text{atm} \quad T_1 = 300\text{K} \quad n = 1\text{mol} \quad V_1 = \frac{nRT_1}{P_1} = 2.46\text{L}$

a) $P_2 = 5\text{atm} \quad T_2 = 300\text{K} \quad V_2 = \frac{nRT_2}{P_2} = \frac{1 \times 0.082 \times 300}{5} = 4.92\text{L}$

$\Delta U \overset{0}{=} q - W \Rightarrow q = W = nRT\ln\left(\frac{V_2}{V_1}\right)$

$\Delta S = \frac{q}{T} = \frac{nRT\ln\left(\frac{V_2}{V_1}\right)}{T} = nR\ln\left(\frac{V_2}{V_1}\right) = 8.314\text{J/mol·K} \times 1\text{mol} \times \ln\left(\frac{4.92\text{L}}{2.46\text{L}}\right)$

$= 5.76\text{J/K}$

b) Adiabatic expansion $(q = 0)$, $P_2 = 5\text{atm}$.

$\Delta S = \int \frac{dq_{rev}}{T} = 0 \quad \because q = 0 \rightarrow dq = 0$

c) $V_2 = 2.46\text{L} = V_1 \quad P_2 = 5\text{atm}$

$\Delta U = q - W \overset{0\ (\because \text{등적과정})}{=} q_V = nC_V\Delta T \qquad dq_V = nC_V dT$

$$T_2 = \frac{P_2 V_2}{nR} = \frac{5 \times 2.46}{0.082} = 150\,K$$

$$\Delta S = \int_{T_1}^{T_2} \frac{\delta q_{rev}}{T} = \int_{T_1}^{T_2} \frac{1}{T} nC_v dT = nC_v \ln \frac{T_2}{T_1}$$

$$= n \underbrace{\frac{3}{2}R}_{J} \ln \frac{T_2}{T_1} = \frac{3}{2} \times 8.314\,J/mol\cdot K \times 1mol \times \ln\left(\frac{150}{300}\right)$$

※ 단원자 이상기체

$$= -8.64\,J/K$$

3.2 One mole of a 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.

Sol) $T_1 = 300K$ $P_1 = 10atm$ $n = 1mol$ $V_1 = \frac{nRT_1}{P_1} = 2.46L$

a) 자유팽창 온도변화 X

$T_2 = 300K$, $V_2 = 3V_1 = 7.38L$, $P_2 = \frac{nRT_2}{V_2} = 3.33atm$

$\Delta U_1 = 0$, $\Delta H_1 = 0$, $\Delta U_1 = q_1 - W_1 = 0$

$q_1 = W_1 = 0$

$\Delta S_1 = \frac{nRT\ln(\frac{V_2}{V_1})}{T} = nR\ln\left(\frac{V_2}{V_1}\right)$ (ΔS는 상태함수이므로 등T 가역팽창 가정하고 solve)

$= 1mol \cdot 8.314\,J/mol\cdot K \ln 3 = 9.134\,J/K$

b) $T_3 = 400K$, $V_3 = 7.38L$, $P_3 = \frac{nRT_3}{V_3} = 4.44atm$

$W_2 = P\Delta V = P \cdot 0 = 0$

$\Delta U_2 = q - W = q_V = nC_v\Delta T = C_v\Delta T = C_v(400-300) = 100C_v$

$= 100 \frac{3}{2} 8.314 = 1247J = q_2$

$\Delta H_2 = nC_p\Delta T = C_p\Delta T$

$= \frac{5}{2} 8.314\, 100 = 2078\,J$

$\Delta S_2 = \int_{T_2}^{T_3} \frac{\delta q_{rev}}{T} = \int_{T_2}^{T_3} \frac{1}{T} nC_v dT = nC_v \ln\left(\frac{T_3}{T_2}\right)$

$= \frac{3}{2} 8.314 \times \ln\left(\frac{400}{300}\right) = 3.588\ J/K$

c) $T_4 = 400K$, $V_4 = 3V_3 = 22.1\ L$, $P_4 = \frac{nRT_4}{V_4} = \frac{0.082 \times 400}{22.1} = 1.48\ atm$

$\Delta T = 0 \rightarrow \therefore \Delta U_3 = \Delta H_3 = 0$

$\Delta U_3 = q_3 - W_3 \Rightarrow q_3 = W_3 = \int_{V_3}^{V_4} P_4 dV = \int_{V_3}^{V_4} \frac{nRT_4}{V} dV$

$= nRT_4 \ln\left(\frac{V_4}{V_3}\right) = RT_4 \ln\left(\frac{V_4}{V_3}\right)$

$= 8.314 \times 400 \times \ln 3$

$= 3654\ J$

$\Delta S_3 = \frac{q_3}{T_4} = \frac{3654}{400} = 9.13\ J$

d) $P_5 = 1.48\ atm \quad T_5 = 300K \quad V_5 = \frac{nRT_5}{P_5} = 16.6\ L$

$\Delta U_4 = nC_v \Delta T = C_v \Delta T = C_v(300 - 400)$

$= -100 C_v = -100\ 3/2\ 8.314 = -1247\ J$

$\Delta H_4 = nC_p \Delta T = 5/2 \cdot 8.314 \cdot -100 = -2078\ J = q_p = q_4$

$W_4 = q_p - \Delta U = -2078 + 1247 = -831\ J$

$\Delta S_4 = \int_{T_1}^{T_2} \frac{\delta q_p}{T} = \int_{T_H}^{T_5} \frac{1}{T} nC_p dT = nC_p \ln\left(\frac{T_5}{T_4}\right)$

$= 2.5 \times 8.314 \ln \frac{300}{400} = -5.979\ J/K$

$\therefore \Delta U = \Delta U_1 + \Delta U_2 + \Delta U_3 + \Delta U_4 = 0 + 1247 + 0 - 1247 = 0\ J$

$\Delta H = \sum_{i=1}^{4} \Delta H_i = 0 + 2078 + 0 - 2078 = 0\ J$

$W = W_1 + W_2 + W_3 + W_4 = 0 + 0 + 3654 - 831 = 2823\ J$

$\Delta S = \sum_{j=1}^{4} \Delta S_j = 9.13 + 3.588 + 9.13 - 5.979$

$= 15.87\ J$

$$q = q_1 + q_2 + q_3 + q_4 = 0 + 2417 + 3654 - 2078$$
$$= 2823\,J$$

①

3.3 One mole of a monatomic ideal gas undergoes a reversible expansion at constant pressure, during which the entropy of the gas increases by 14.41 J/K and the gas absorbs 6236 J of thermal energy. Calculate the initial and final temperatures of the gas. ②One mole of a second monatomic ideal gas undergoes a reversible isothermal expansion, during which it doubles its volume, performs 1729 J of work, and increases its entropy by 5.763 J/K. Calculate the temperature at which the expansion was conducted.

Sol) ① $n=1$ p constant $\Delta S = 14.41\,J/k$ $q = 6236\,J$

$$\Delta S = \int_{T_1}^{T_2} \frac{\delta q_p}{T} = \int_{T_1}^{T_2} \frac{1}{T} nC_p dT = nC_p \ln\left(\frac{T_2}{T_1}\right)$$

$$= 1 \times \tfrac{5}{2} \times 8.314 \ln\left(\frac{T_2}{T_1}\right) = 14.41$$

$$\ln\left(\frac{T_2}{T_1}\right) = 0.693 \qquad \frac{T_2}{T_1} = e^{0.693} = 2$$

$$q_p = \Delta H = nC_p \Delta T = \frac{5}{2} 8.314 (T_2 - T_1) = 6236$$

$$T_2 - T_1 = 300$$

$\therefore$ $T_1 = 300K$ $T_2 = 600K$

② $T_1 \to T_2$ $(T_1 = T_2)$, $V_2 = 2V_1$, $W = 1729\,J$

$\Delta S = 5.763\,J/k$

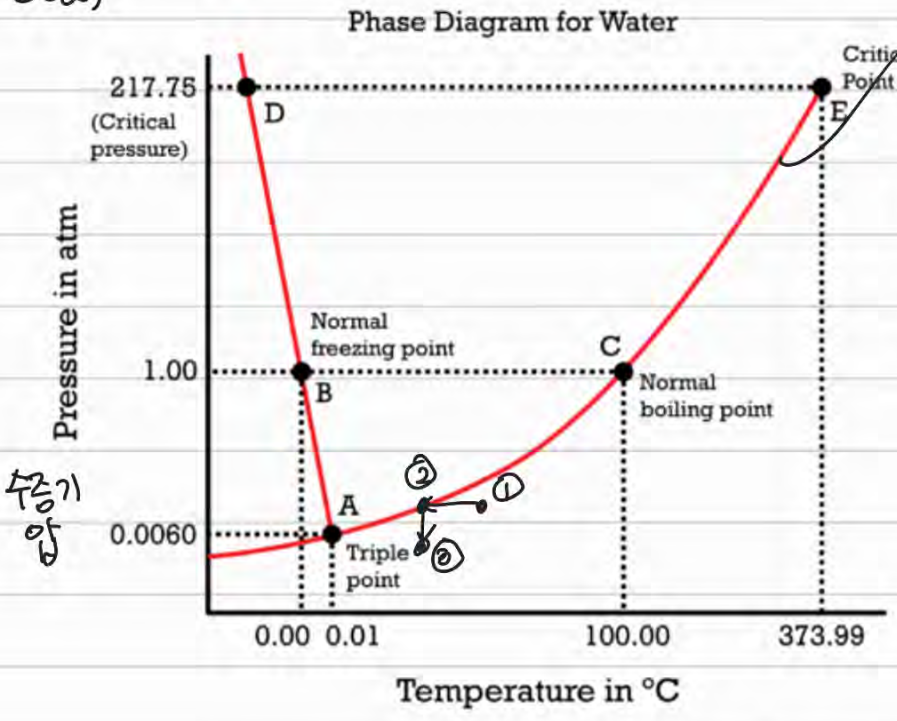
$\Delta U = q - W = 0$ $\quad q = W = 1729\,J$

$(\because \Delta T = 0)$

$$\Delta S = \frac{q}{T_2} = \frac{1729}{T_2} = 5.763 \qquad T_2 = 300K = T_1$$

7. 늦가을 자동차를 운전하면 유리창에 김 서림이 문제가 된다. 자동차 유리창에 김이 서리는 이유를 H_2O의 PT diagram을 이용하여 과학적으로 설명하시오. 이를 제거하기 위해 냉난방 장치를 이용할 경우 창 쪽으로 더운 공기가 나오게 하는 것이 현명한 가, 아니면 에어컨 바람이 나오게 하는 것이 현명한 가? 근거를 대고 설명하시오.

Sol)



포화 수증기압 곡선

늦가을은 외부온도가 차내부의 온도보다 낮으므로 안과 밖의 온도차로 인해 김이 서린다.

차안의 온도에서 수증기압은 ① 인 상태로 기체상태로 존재하고 있다가 창문에서의 낮은 온도로 인해 온도가 내려가면 ② 인 상태가 되어 액화현상이 일어난다.

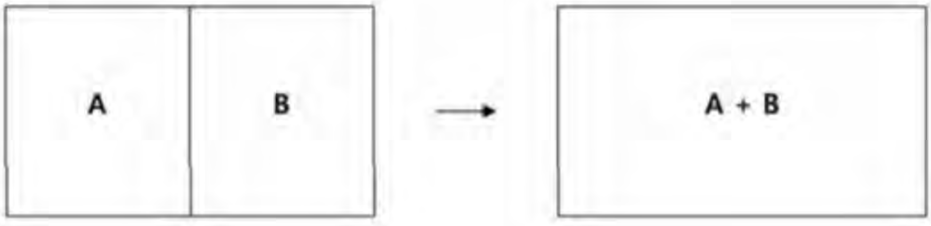
수증기압

여기서 김서림을 방지하기 위해서는 안과밖의 온도차를 낮추어야하며 ② → ③ 으로 vapor가 안정한 상이 되게끔 해주어야 하므로 차 안에 에어컨을 틀어야 합니다.(+에어컨의 제습 효과가 수증기의 분압↓)

에어컨 주변에서 vapor → liquid 액화 ⇒ 수증기압 감소 ⇒ 창문에서의 액화방지

(창문자체의 온도를 높여 ② → ① 로 가게 하는 방법도 있으나 더 효율적인 김서림 방지 방법은 에어컨이라 생각합니다)

8. 그림 왼쪽과 같이 분리되어 있던 두 종류의 gas 입자들은 칸막이를 제거할 경우 서로 섞여 균일한 혼합체를 이룬다. 각 gas 입자들은 자신들이 섞여 있어야 할 운명이라는 것을 미리 알고 있었을까? (서로 섞여야 한다는 어떤 force 같은 것을 느끼게 되는 걸까?) 이 문제에 대한 견해를 밝히시오.



SOL) 칸막이를 제거하면 기체 A 와 B는 균일하게 섞이게 되는 결과를 얻게 되는데, 이는 확률적으로 가장 높은 situation의 결과라 볼 수 있다. 칸막이를 제거하면 각 종류의 입자가 배열될 수 있는 공간이 증가하게 되고 확률적인 경우의 수를 고려해 보았을때, 균일하게 퍼져있는 것이 제일 높다.
(다른 경우의 수도 존재할 수 있으나, 아보가드로 수 만큼의, 많은 수의 기체가 있을때에는 균일하게 퍼져있는 경우가 극단적으로 높은 확률을 가지게 되므로 다른 확률의 situation의 배열가능성은 거의 없다고 볼 수 있다.)
즉, 기체들은 안정해지고 가장 확률이 높은 엔트로피가 증가하는 방향으로 자연스럽게 (자발적) 이동할 것이고 균일하게 섞여 퍼질 것이다.
이러한 자발적인 움직임은 가장 높은 확률의 경우의 수를 가질 수 밖에 없는 쪽으로 향할 것이고 이는 섞여야한다는 force 와 equivalent 하다.