

Problem #1: Huang MTA F08

Given:  $l_m = 5.6 \times 10^{-8} \text{ m}$  at STP

Find:  $d_{co}$

Solution: Use  $l_m = \frac{1}{4\pi r^2 N/V}$

[One common mistake: using the formula  $l_m = \frac{1}{4\pi r^2 (N/V)}$ ]

Note:  $V$  = volume, not velocity

Solve for  $r$ :

$$\left( l_m = \frac{1}{4\pi r^2 (N/V)} \right) \frac{r^2}{l_m}$$

$$r^2 = \frac{1}{4\pi r^2 l_m (N/V)}$$

$$r = \sqrt{\frac{1}{4\pi r^2 l_m (N/V)}}$$

$$\Rightarrow d = 2r = 2\sqrt{\frac{1}{4\pi r^2 l_m (N/V)}}$$

$$= \sqrt{\frac{1}{4\pi r^2 l_m (N/V)}}$$

Give diameter,  
not radius  
as answer

Now, need to find  $N/V$ :  
Method 1: 1 mol occupies 22.4 L at STP and  $1 \text{ mol} = 6.02 \times 10^{23} \text{ mol}$ .

However,  $V$  has to be in units of  $\text{m}^3$  not L,  $V = 0.0224 \text{ m}^3$

$$\frac{N}{V} = \frac{6.02 \times 10^{23} \text{ mol}}{0.0224 \text{ m}^3} = 2.68 \times 10^{25} \text{ mol/m}^3$$

Method 2:  $PV = NkT \Rightarrow \frac{N}{V} = \frac{P}{kT}$

At STP,  $P = 1 \text{ atm}$  but we need to convert this to  $\text{N/m}^2$ ,  $P \approx 10^5 \text{ N/m}^2 (\text{Pa})$

$$\frac{N}{V} = \frac{10^5 \text{ N/m}^2}{1.38 \cdot 10^{-23} \text{ J/K} \cdot 273 \text{ K}} = 7.65 \times 10^{25} \text{ mol/m}^3$$

Note: Both  $T = 273 \text{ K}$  &  $T = 293 \text{ K}$  were accepted

$$d = \sqrt{\frac{1}{\pi \cdot 5.6 \cdot 10^{-8} \cdot 2.68 \times 10^{25}}} = 3.87 \cdot 10^{-10} \text{ m} \quad (1 \text{ atm}, 273 \text{ K})$$

Also acceptable

$$d = 4.0 \cdot 10^{-10} \text{ m} \quad (1 \text{ atm}, 293 \text{ K})$$

Problem # 2: Huang MT1 F08

i) D:  $P = \epsilon \sigma A T^4$

ii) A : From class

iii) D :  $P(\text{all heads}) = \frac{1}{2^{1000}}$  so

need to throw it many times  
to achieve this microstate

iv) C : Carnot cycles & isothermal  
expansions are always reversible  
a) is reversible because any chemical  
equation has some non-zero probability  
of reversing.

v) C :  $\ln = \ln(1 + \alpha \Delta T)$

$$A = \ln^2 = \ln^2(1 + \alpha \Delta T)^2$$

$$= \ln^2(1 + 2\alpha \Delta T + \cancel{\alpha^2 \Delta T^2})$$

neglect

$$= \ln^2(1 + 2\alpha \Delta T)$$

$$3) Q = 0$$

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

$$P_1 V_1^\gamma = P_2 V_2^\gamma$$

$$V_2 = \left(\frac{P_1}{P_2}\right)^{\frac{1}{\gamma}} V_1 = \left(\frac{P_1}{P_2}\right)^{\frac{3}{5}} V_1$$

$$T_1 = \frac{P_1 V_1}{nR}$$

$$T_2 = \frac{P_2 V_2}{nR} = \frac{P_2 \left(\frac{P_1}{P_2}\right)^{\frac{3}{5}} V_1}{nR}$$

$$\Delta E = \frac{3}{2} n R \Delta T = \frac{3}{2} n R \left( \frac{P_2 \left(\frac{P_1}{P_2}\right)^{\frac{3}{5}} V_1}{nR} - \frac{P_1 V_1}{nR} \right)$$

$$\Delta E = \frac{3}{2} \left( P_2 \left(\frac{P_1}{P_2}\right)^{\frac{3}{5}} V_1 - P_1 V_1 \right)$$

$$\Delta E = Q - W \Rightarrow W = -\Delta E$$

$$W = \frac{3}{2} \left( P_1 V_1 - P_2 \left(\frac{P_1}{P_2}\right)^{\frac{3}{5}} V_1 \right)$$

$$b) \Delta T = 0$$

$$\Delta E = \frac{3}{2}nR\Delta T = 0$$

$$\Delta E = Q - W = 0 \Rightarrow Q = W$$

$$W = \int_{V_2}^{V_3} P dV = nRT_2 \int_{V_2}^{V_3} \frac{dV}{V} = nRT_2 \ln\left(\frac{V_3}{V_2}\right)$$

$$PV = nRT \quad T \text{ is constant}$$

$$\frac{PV}{nR} = \text{constant} \Rightarrow P_2 V_2 = P_3 V_3$$

$$\frac{P_2}{P_3} = \frac{V_3}{V_2}$$

$$W = nRT_2 \ln\left(\frac{P_2}{P_3}\right)$$

$$P_3 = P_1$$

$$T_2 = \frac{P_2 \left(\frac{P_1}{P_2}\right)^{\frac{3}{5}} V_1}{nR} \quad \text{from part a}$$

$$W = P_2 \left(\frac{P_1}{P_2}\right)^{\frac{3}{5}} V_1 \ln\left(\frac{P_2}{P_1}\right)$$

$$Q = W$$

$$G) \quad \Delta E = \frac{3}{2} n R (T_1 - T_2) = \frac{3}{2} n R (T_1 - T_2)$$

$$\Delta E = \frac{3}{2} n R \left( \frac{P_1 V_1}{n R} - \frac{P_2 \left( \frac{P_1}{P_2} \right)^{\frac{3}{5}} V_1}{n R} \right)$$

$$\Delta E = \frac{3}{2} \left( P_1 V_1 - P_2 \left( \frac{P_1}{P_2} \right)^{\frac{3}{5}} V_1 \right)$$

$$Q = n C_p \Delta T = \frac{5}{2} n R (T_1 - T_2)$$

$$\boxed{Q = \frac{5}{2} \left( P_1 V_1 - P_2 \left( \frac{P_1}{P_2} \right)^{\frac{3}{5}} V_1 \right)}$$

$$\Delta E = Q - W \Rightarrow W = Q - \Delta E$$

$$W = \left( \frac{5}{2} - \frac{3}{2} \right) \left( P_1 V_1 - P_2 \left( \frac{P_1}{P_2} \right)^{\frac{3}{5}} V_1 \right)$$

$$\boxed{W = P_1 V_1 - P_2 \left( \frac{P_1}{P_2} \right)^{\frac{3}{5}} V_1}$$

d)

$$PV = nRT$$

$$V = \frac{nRT}{P} \Rightarrow \frac{1}{V} = \frac{P}{nRT}$$

$$\frac{dV}{dT} = \frac{nR}{P}$$

$$\beta = \frac{1}{V} \frac{dV}{dT}$$

$$\beta = \left( \frac{P}{nRT} \right) \left( \frac{nR}{P} \right)$$

$$\boxed{\beta = \frac{1}{T}}$$

4) (35 pts.) One mole of water is cooled from  $T_1=25\text{ }^{\circ}\text{C}$  to  $T_2=0\text{ }^{\circ}\text{C}$  and frozen in a refrigerator. You can treat the heat being taken out of the water as the low-temperature heat input for the refrigerator. The refrigerator operates at maximum theoretical efficiency (no entropy created) and exhausts heat into a second mole of water at (again)  $T_1=25\text{ }^{\circ}\text{C}$ , heating it to  $T_3=100\text{ }^{\circ}\text{C}$  and converting a fraction ( $n'$  mole) into vapor.

Note: For parts *a*) through *d*), express your answer for each part in terms of any or all of the quantities given in the problem,  $T_1$ ,  $T_2$ ,  $T_3$  and  $n'$ , and relevant physical constants. You can use  $m$  as the mass of one mole of water. Also remember that there are two thermodynamic processes for each of these parts: the cooling and the freezing, or, the warming and the vaporization.

*a)* Find the total amount of heat,  $|Q_1|$ , that flows out of the first mole of water.

*'Assume all the water gets frozen'*

$$Q_{1, 25^{\circ}\text{C} \rightarrow 0^{\circ}\text{C}} = mC(T_2 - T_1)$$

$$Q_{1, \text{liquid} \rightarrow \text{solid}} = mL_f$$

$$|Q_1| = |Q_{1, 25^{\circ}\text{C} \rightarrow 0^{\circ}\text{C}} + Q_{1, \text{liquid} \rightarrow \text{solid}}|$$

Answer:

$$\boxed{|mC(T_2 - T_1) - mL_f|}$$

b) Find the total amount of entropy,  $|\Delta S_f|$ , that flows out of the first mole of water.

$$\begin{aligned}\Delta S_e_{25^\circ \rightarrow 0^\circ C} &= \int_{25^\circ C}^{0^\circ C} \frac{1}{T} dQ \\ &= \int_{25^\circ C}^{0^\circ C} \frac{1}{T} mc dT \\ &= mc \ln\left(\frac{T_1}{T_2}\right) \quad \begin{matrix} \text{numerically convert to Kelvin!} \\ T = 273 + T_n \end{matrix}\end{aligned}$$

$$\begin{aligned}\Delta S_e_{\text{Liquid} \rightarrow \text{Solid}} &= \frac{\Delta Q_{\text{Liquid} \rightarrow \text{Solid}}}{T_2} \\ &= \frac{m L_f}{T_2}\end{aligned}$$

Answer:

$$\boxed{|\ln\left(\frac{T_1}{T_2}\right) - \frac{L_f}{T_2}|}$$

c) Find the total amount of heat,  $|Q_2|$ , that flows into the second mole of water.

$$Q_2 \underset{25^\circ\text{C} \rightarrow 100^\circ\text{C}}{=} mc(T_3 - T_2)$$

$$Q_{2 \text{ vaporize}} = n'm L_v$$

Answer:

$$|mc(T_3 - T_2) + n'm L_v|$$

d) Find the total amount of entropy,  $|\Delta S_2|$ , that flows into the second mole of water.

$$\begin{aligned}\Delta S_{25^\circ \rightarrow 100^\circ} &= \int_{25^\circ}^{100^\circ} \frac{1}{T} dQ \\ &= mc \int_{T_1}^{T_3} \frac{1}{T} dT \\ &= mc \ln\left(\frac{T_3}{T_1}\right)\end{aligned}$$

$$\begin{aligned}\Delta S_{\text{liquid} \rightarrow \text{gas}} &= \frac{\Delta Q}{T_3} \\ &= \frac{n'mL_v}{T_3}\end{aligned}$$

Answer:

$$\boxed{\left| mc \ln\left(\frac{T_3}{T_1}\right) + \frac{n'mL_v}{T_3} \right|}$$

e) What is  $\Delta S_1 + \Delta S_2$ ? Note that there are no absolute value signs around the entropy changes here. (Hint: Can this process be reversed?)

$$\begin{aligned} & mc \ln\left(\frac{T_2}{T_1}\right) - m \frac{\Delta f}{T_2} + mc \ln\left(\frac{T_3}{T_1}\right) + \frac{n' m L_v}{T_3} \\ & = mc \ln\left(\frac{T_2 T_3}{T_1^2}\right) - m\left(\frac{\Delta f}{T_2} - \frac{n' L_v}{T_3}\right) \end{aligned}$$

Answer:

0 reversible

f) Find  $n'$ .

$$m c \ln\left(\frac{T_3 T_2}{T_1^2}\right) - m \left(\frac{L_f}{T_2} - n' L_v\right) = 0$$

$$c \ln\left(\frac{T_3 T_2}{T_1^2}\right) = \frac{L_f}{T_2} - n' L_v$$

$$n' = \frac{T_2}{L_v} \left[ \frac{L_f}{T_2} - c \ln\left(\frac{T_3 T_2}{T_1^2}\right) \right]$$

Formulaic Answer:

$$\frac{T_2}{L_v} \left[ \frac{L_f}{T_2} - c \ln\left(\frac{T_3 T_2}{T_1^2}\right) \right]$$

$$T_1 = 298K \quad T_2 = 273K \quad T_3 = 373K$$

$$L_f = 3.33 \times 10^5 \frac{\text{J}}{\text{kg}} \quad \Rightarrow L_v = 22.6 \times 10^5 \frac{\text{J}}{\text{kg}}$$

$$c = 4.19 \times 10^3 \frac{\text{J}}{\text{kg}\cdot\text{K}}$$

Numerical Answer:

$$n' = 0.107$$

f) How much work,  $|W|$ , must be done by the refrigerator?

$$|Q_2| = |W| + |Q_1|$$

$$\begin{aligned}|W| &= |mc(T_3 - T_2) + n^2 m L_v| - |n c(T_2 - T_1) - m L_f| \\&= |mc(T_3 - T_2) + n^2 m L_v - m c(T_2 - T_1) - m L_f|\end{aligned}$$

Formulaic Answer:

$$|mc(T_3 - T_2) + n^2 m L_v - m(T_2 - T_1) - m L_f|$$

Numerical Answer:

$$W = 2116 \text{ J}$$