

Supplementary materials on 2nd laws

Numerical Problems:

- ① An ideal heat engine operates between T_1 and T_2 ($T_1 > T_2$). Per cycle q_2 is -4.5×10^6 cal and ΔS_2 is -15000 cal K^{-1} . T_1 is $300^\circ C$. Calculate η of the engine and w per cycle.

Soln.

1 corresponds to source &
2 corresponds to the sink.

$$\eta = \frac{T_1 - T_2}{T_1} ; \quad T_1 = 300^\circ C = 573 K$$

$$T_2 = ?$$

Heat released at the sink, $q_2 = -4.5 \times 10^6$ cal.

$$\text{And, } \Delta S_2 = \frac{q_2}{T_2} = -15000 \text{ cal } K^{-1}$$

$$\text{Hence, } T_2 = \frac{q_2}{-15000} = \frac{-4.5 \times 10^6}{-15000} K$$

$$= 300 K$$

$$\therefore \eta = \frac{573 - 300}{573} = 0.48, \text{ or } 48\%$$

$$w = (\text{Heat released absorbed from the higher temp source}) \times \eta$$

$$\text{or } q_1 = ?$$

From the Carnot Cycle:

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0.$$

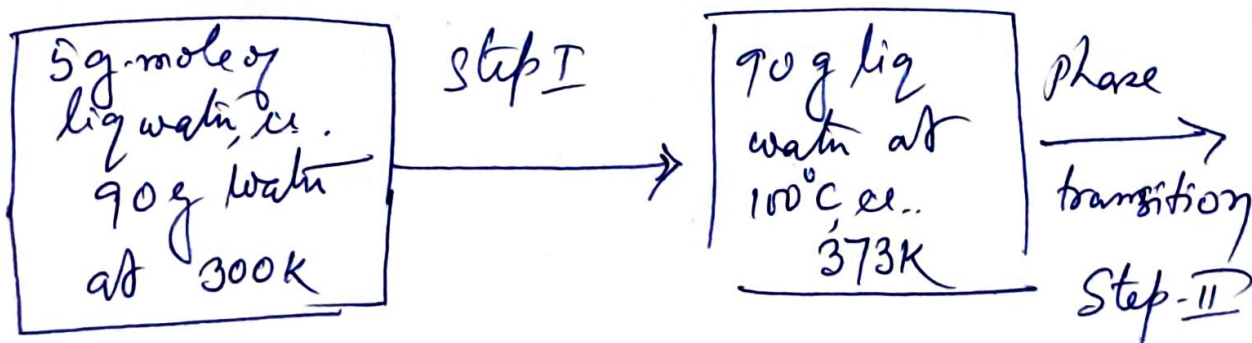
$$\therefore q_1 = - \frac{q_2}{T_2} \times T_1 = \frac{4.5 \times 10^6 \times 573}{300}$$

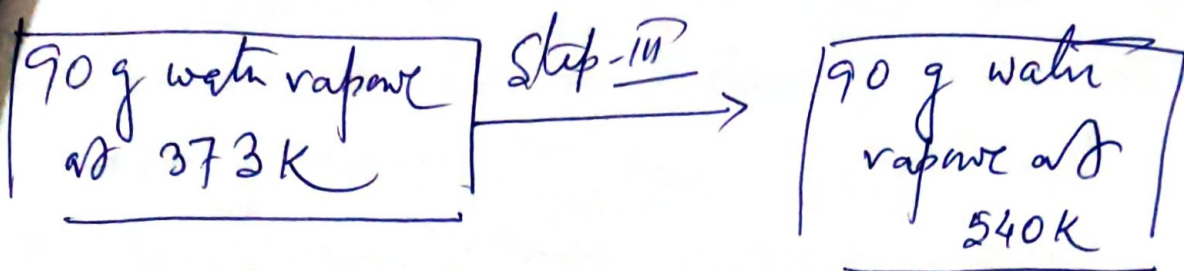
$$\therefore \text{Work done per cycle:} = 8.59 \times 10^6 \text{ cal}$$

$$\Rightarrow W = q_1 \times \eta = 8.59 \times 10^6 \times 0.48 = 4.12 \times 10^6 \text{ cal per cycle.}$$

- (2) 5 g-mole of water initially at 27°C are converted to a final state of water vapour at 227°C , the conversion being effected under 1 atm pressure. Assuming the vapour to behave ideally, compute the total change in entropy.

Given: Heat capacity of water = 1 cal/g
 that of water vapour = 0.40 cal/g
 & Latent heat of vaporization of water = 540 cal/g





(No change in pressure)

For step I: $\Delta S_I = (n \times \bar{C}) \ln \left(\frac{T_2}{T_1} \right)$

Total heat capacity of

this system = $\underbrace{5 \times 18}_{\text{g}} \times 1 \text{ cal/g (cal K}^{-1} \text{ g}^{-1})$

$= 90 \times \ln \left(\frac{373}{300} \right) = 19.6 \text{ Cal K}^{-1}$

For step II: $\Delta S_{II} = \frac{\text{Total latent heat of evaporation}}{\text{Boiling temp}}$

$= \frac{90 \times 540}{373} = 130.29 \text{ Cal K}^{-1}$

For step III: $\Delta S_{III} = 90 \times 0.4 \times \ln \left(\frac{540}{373} \right) = 10.55 \text{ Cal K}^{-1}$

Total change in entropy:

$\Delta S = (\Delta S_I + \Delta S_{II} + \Delta S_{III}) = \underline{160.44 \text{ Cal K}^{-1}}$

Calculate ΔS when 10 g of ice at 0°C are added to 50 g of water at 40°C in an isolated system. The latent heat of fusion of ice is 79.7 Cal g^{-1} . Specific heat of water = $1 \text{ Cal g}^{-1} \text{ K}^{-1}$.

During mixing entire ice will melt, and let the mixture attains temp $t^\circ\text{C}$.

Hence, heat gained by ice during melting and subsequent heating upto $t^\circ\text{C}$:

$$\begin{aligned} & (\text{Total latent heat}) + (m.s.\theta) \\ &= (10 \times 79.7) + [10 \times 1 \times (t - 0)] \text{ Cal} \\ &= (797 + 10t) \text{ Cal.} \end{aligned}$$

And, heat lost by hot water

$$= 50 \times 1 \times (40 - t) = 2000 - 50t$$

Now, heat gain = heat loss.

$$797 + 10t = 2000 - 50t$$

$$\therefore 60t = 2000 - 797 = 1203$$

$$\therefore t = \frac{1203}{60} = 20.05^\circ\text{C} = 293.05 \text{ K.}$$

Now, entropy change during melting of 10 g ice at 0°C :

$$= \frac{10 \times 79.7}{273} \text{ cal K}^{-1} = 2.92 \text{ cal K}^{-1}$$

Entropy change during heating 10 g water
at 273 K to 293.05 K (at const P):

$$= 10 \times 1 \times \ln \left(\frac{293.05}{273} \right) = 0.71 \text{ cal K}^{-1}$$

Entropy change during cooling of 50 g
water from 40°C (313 K) to 293.05 K:

$$= 50 \times 1 \times \ln \left(\frac{293.05}{313} \right)$$

$$= -3.29 \text{ cal K}^{-1}$$

Hence, total entropy change = $(2.92 + 0.71 - 3.29)$
 $= 0.34 \text{ cal K}^{-1}$

Calculate the change in G when 36 g water
initially at 100°C and 10 atm pressure
is converted to vapour at 100°C and 0.01 atm
pressure?

[Given: vol. of 1 g water at 100°C = 1 ml]
 Vapour obeys ideal gas law]

Soln:

$$\boxed{36 \text{ g water}} \\ \boxed{100^\circ\text{C}, 10 \text{ atm}}$$

I →

$$\boxed{36 \text{ g water}} \\ \boxed{100^\circ\text{C}, 1 \text{ atm}}$$

II ↓

$$\boxed{36 \text{ g vapor}} \\ \boxed{\text{at } 100^\circ\text{C}, 1 \text{ atm}}$$

Phase transition
step

III ↓

$$\boxed{36 \text{ g vapor}} \\ \boxed{100^\circ\text{C}, 0.01 \text{ atm}}$$

$$\boxed{dG = -SdT + VdP}$$

Step-I: $\Delta G = V(P_2 - P_1)$

[Considering liq water has low compressibility, i.e. vol. remains almost unchanged due to change in press]

$$36 \text{ g water} \equiv 36 \text{ ml water} \equiv 0.036 \text{ L of water}$$

$$\therefore \Delta G_I = 0.036 (1-10) \text{ lit-atm} = -7.84 \text{ cal}$$

[1 lit-atm = 24.2 cal]

Step-II: Reversible phase transition $\Rightarrow \Delta G_{TP} = 0$

Step-III

$$dG = VdP = \left(\frac{nRT}{P} \right) dP \quad \left\{ PV = nRT \right\}$$

$$\therefore \Delta G = nRT \ln \left(\frac{P_2}{P_1} \right)$$

$$\left| n = \frac{36}{18} = 2 \text{ mol} \right.$$

$$= 2 \times 1.987 \times 373 \ln \left(\frac{0.01}{1} \right)$$

$$= -6826.25 \text{ cal}$$

$$= -6834.09 \text{ cal}$$

$$\therefore \Delta G_{\text{total}} = \Delta G_I + \Delta G_{II}$$

The Carnot theorem:

Two important deductions derived from the 2nd law:

a) A reversible engine is more efficient than an irreversible engine.

b) All reversible engines are equally efficient working between the same temperature limits.

- H.W
- i) A stretched spring or a rubber band, when released, comes back to its original state spontaneously - explain.
 - ii) Compressed air has more efficiency to do work than expanded air.

Four fundamental relations in thermodynamics:

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dG = -SdT + VdP$$

$$dA = -SdT - PdV$$

A \Rightarrow Helmholtz work function

$$\boxed{A = U - TS} \Rightarrow \boxed{-\Delta A_T = W_{rev}}$$

$$\begin{aligned} & \parallel \begin{aligned} dU &= dq + dw \\ \therefore dU &= dq - PdV \quad \left[\begin{array}{l} P-V \\ \text{work} \\ \text{done by} \\ \text{the system} \end{array} \right] \\ dU &= TdS - PdV \end{aligned} \\ & H = U + PV \\ & dH = dU + P.dV + VdP \quad \left| \begin{array}{l} ds = \frac{dq_{rev}}{T} \end{array} \right. \\ \therefore dH &= TdS - PdV + PdV + VdP \\ \therefore dH &= TdS + VdP \end{aligned}$$