/ 1st Sem students

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 °C. Calculate η of the engine and w per cycle.

Soln. 1 corresponds to source &
2 corresponds to the sink.

$$\eta = \frac{T_1 - T_2}{T_1} \quad ; \quad T_1 = 300°C = 573 K$$
$$T_2 \Rightarrow ?$$

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

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

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

$= 300$ K.

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

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

$$\text{i.e. } q_1 = ?$$

From the Carnot Cycle:

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

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

$$= 8.59 \times 10^6 \text{ cal}$$

$\therefore$ Work done per cycle:

$$\Rightarrow W = q_1 \times \eta = 8.59 \times 10^6 \times 0.48$$

$$= 4.12 \times 10^6 \text{ cal per cycle.}$$

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(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.

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5 g-mole of liq water, i.e. 90 g water at 300K	$\xrightarrow{\text{step I}}$	90 g liq water at 100°C i.e. 373K	$\xrightarrow[\text{Step-II}]{\text{Phase transition}}$

$$\boxed{\text{90 g water vapour at 373 K}} \xrightarrow{\text{Step - III}} \boxed{\text{90 g water vapour at 540K}}$$

(No change in pressure)

For step I: $\Delta S_I = \underbrace{(n \times \bar{C})}_{\text{Total heat capacity of the system}} \ln\left(\frac{T_2}{T_1}\right)$

Total heat capacity of the system $= \underbrace{5 \times 18}_{g} \times 1 \; \cancel{cal/g} \; (cal K^{-1} g^{-1})$

$= 90$ cal.

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

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:

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

Calculate ΔS when 10g of ice at 0°C are added to 50g 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 Cal $g^{-1}K^{-1}$.

During mixing entire ice will melt, and let the mixture attains temp t°C.

Hence, heat gained by ice during melting and subsequent heating upto t°C:

$$(\text{Total latent heat}) + (m.s.\theta)$$

$$= (10 \times 79.7) + [10 \times 1 \times (t-0)] \text{ Cal}$$

$$= (797 + 10t) \text{ Cal.}$$

And, heat lost by hot water

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

Now, heat gain = heat loss.

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

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

$$\therefore t = \frac{1203}{60} = 20.05°C = 293.05 K.$$

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 273K 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 (313K) to 293.05 K:

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

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

Hence, total entropy change $= (2.92 + 0.71 - 3.27)$

$$= 0.34 \text{ cal K}^{-1}.$$

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.:

$\boxed{\begin{matrix}36\text{ g water}\\100^\circ C, 10\text{ atm}\end{matrix}} \xrightarrow{\text{I}} \boxed{\begin{matrix}36\text{ g water}\\100^\circ C, 1\text{ atm}\end{matrix}} \xrightarrow{\text{II}} \boxed{\begin{matrix}36\text{ g vapour}\\\text{at }100^\circ C, 1\text{ atm}\end{matrix}}$

Phase transition step.

III

$\boxed{\begin{matrix}36\text{ g vapour}\\100^\circ C, 0.01\text{ atm}\end{matrix}}$

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

step-I: $\Delta G_I = V(P_2 - P_1)$

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

36 g water ≡ 36 ml water ≡ 0.036 L of water

$\therefore \Delta G_I = 0.036(1-10)$ lit-atm $= -7.84$ Cal

[1 lit-atm = 24.2 Cal]

step-II: Reversible phase transition ⇒ $\Delta G_{T,P} = 0$.

step-III $dG = VdP = \left(\frac{nRT}{P}\right)dP$ [$PV = nRT$]

$\therefore \Delta G = nRT \ln\left(\frac{P_2}{P_1}\right)$ | $n = \frac{36}{18} = 2$ mol

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

$= -6826.25$ cal.

$\therefore \Delta G_{total} = \Delta G_I + \Delta G_{III} = -6834.09$ Cal

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.

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[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:

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dG = -SdT + VdP$$

$$dA = -SdT - P.dV$$

$dU = dq + dw$

or, $dU = dq - P.dV$ [P-V work done by the system

$dU = T.dS - PdV$

$H = U + PV$

$dH = dU + P.dV + VdP$ | $dS = \frac{dq_{rev}}{T}$

or, $dH = TdS - PdV + PdV + VdP$

or, $dH = TdS + VdP$

A ⇒ Helmholtz work function

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