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Pg-1

PH 2202 ~~Ass-1~~ H/W-6

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Q.7) T.P $C_p - C_v \cong R\left(1 + \frac{2a}{RTv}\right)$

Ans For ~~ideal~~ a VNW gas.

$n=1$

$$\left(P + \frac{a}{V^2}\right)(V-b) = RT$$

Now,

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P \; ; \; C_v = T\left(\frac{\partial S}{\partial T}\right)_v$$

Let, $S = S(T,V)$

$$\therefore dS = \left(\frac{\partial S}{\partial T}\right)_v dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\therefore T\left(\frac{\partial S}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_v + T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

Putting values,

$$\Rightarrow C_p - C_v = T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

using Maxwell's Relations

$$C_p - C_v = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P .$$

Now we know that

~~$\left(\frac{\partial P}{\partial T}\right)_V \cdot \left(\frac{\partial V}{\partial P}\right)_T \cdot$~~

$$\left(\frac{\partial V}{\partial T}\right)_P \cdot \left(\frac{\partial T}{\partial P}\right)_V \cdot \left(\frac{\partial P}{\partial V}\right)_T = -1$$

$$\therefore C_p - C_v = \frac{-T\left(\frac{\partial P}{\partial T}\right)_V^2}{\left(\frac{\partial P}{\partial V}\right)_T}$$

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{-RT}{(V-b)^2} + \frac{2a}{V^3}$$

$$\therefore \quad C_p - C_v = \frac{\cancel{T}\,\frac{R\cancel{T}}{(V-b)^2}}{\cancel{RT}\left(\frac{1}{(V-b)^2} - \frac{2a}{RTV^3}\right)}$$

$$= \frac{R/\cancel{(V-b)}}{\cancel{(V-b)}\left(1 - \frac{2a(V-b)^2}{RTV^3}\right)} = \frac{R}{\left(1 - \frac{2a(V-b)^2}{RTV^3}\right)}$$

Now, we approximate

$$V - b \simeq V \quad (\because V \gg b).$$

$$C_p - C_v \simeq R\left(1 - \frac{2a}{RTV}\right)^{-1}$$

Also, since, $\frac{2a}{RTV} \ll 1$

Under Binomial approximation.

$$C_p - C_v \simeq R\left(1 + \frac{2a}{RTV}\right) \text{ D}$$

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⑥ Show $\mu = \mu_0(T) + RT \ln(P/P_0)$ for ideal gas.

We have,

$$dG = VdP - SdT + \mu dN \quad \cdots (1)$$

$$\therefore \mu \equiv \left(\frac{\partial G}{\partial N}\right)_{P,T}$$

If, $G \to G(T, P, N)$,

for it to be extensive (as N is also extensive)

It must be of the form.

$$G(T, P, N) = N f(T, P)$$

↳ intensive variables

$$\therefore \mu = f(T, P) = \frac{G}{N}$$

$$\therefore G = N\mu$$

$$dG = N d\mu + \mu dN = VdP - SdT + \mu dN$$

$$\Rightarrow d\mu = \left(\frac{V}{N}\right) dP - \frac{S}{N} dT$$

$$\therefore \left(\frac{\partial \mu}{\partial P}\right)_T = \frac{V}{N}$$

From ideal gas eqn, $PV = N K_B T$ (N = No. of particles)

$$\therefore \frac{V}{N} = \frac{K_B T}{P}$$

So, $$\left(\frac{\partial \mu}{\partial P}\right)_T = \frac{K_B T}{P}$$

$$\Rightarrow \mu(P, T) = K_B T \ln P + f(T)$$

& $$\mu^0(T) \equiv \mu(P_0, T) = K_B T \ln P_0 + f(T)$$

Subtract.

$$\mu(P, T) = \mu^0(T) + K_B T \ln(P/P_0)$$

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$R = N_A K_B$

$$\therefore \boxed{\mu'(P,T) = \mu'_0(T) + RT \ln(P/P_0)} \quad \square$$

where

$\mu'(P,T) = N_A \cdot \mu(P,T)$

↓ is Total chemical potential of system, (of i.e 1 Mole).

↑ each particle

(5) $L = 540\ cal/g = 540 \times 4.184 \times 10^7\ erg/g$

$v_{vap} = 1674\ cc/g$

$\therefore v_{liq} = \frac{1}{\rho_{liq}} = 1\ cc/g$; $r = 2mm$; $m = 140g$

~~$P_i = P_0$~~

Now, $P_i = P_0$ $\quad T_i = 100°C = 373K$

$P_f = P_0 + \frac{mg}{A}$ $\quad T_f = ?$ (New boiling Point of Water)

$\therefore \Delta P = mg/A$

From clausius clayperon equation

$$\frac{L}{T\Delta v} = \frac{dP}{dT}$$

$$\Rightarrow \int_i^f dP = \frac{L}{\Delta v} \int_i^f \frac{dT}{T}$$

$$\Delta P = \frac{L}{\Delta v} \ln\left(\frac{T_f}{T_i}\right)$$

$$\rightarrow \ln\left(\frac{T_f}{T_i}\right) = \frac{\Delta P \cdot \Delta v}{L} = \frac{mg\,\Delta v}{AL}$$

~~$= m$~~

$1\ erg = 1\ dyn\text{-}cm$

$mg = 140\ g \times 9.8\ \frac{m}{s^2} = 140\ g \cdot (980)\ \frac{cm}{s^2} = 140 \times 980$ dyn.

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$$\therefore \ln\left(\frac{T_f}{T_i}\right) = \frac{(140 \times 580)\ \text{dyn} \times (1674-1)\ \frac{\text{cm}^3}{\text{g}}}{\pi (0.2)^2\ \text{cm}^2 \times 540 \times 4.184 \times 10^7\ \frac{\text{dyn-cm}}{\text{g}}}$$

$$= 0.08084$$

$$\Rightarrow T_f = (T_i) \times 1.0842$$

$$T_i = 373.15\ \text{K}$$

$$T_f = 404.57\ \text{K}$$

$$= 131.42^\circ\text{C}$$ New boiling pt of water

(4) $\rho = 3.71\ \text{g/cc}$

$T = 458.3\ \text{K}$

$L = 40.9\ \text{cal/g}$.

$v_{vap} = ?$

$$\frac{\Delta P}{\Delta T} = 17\ \frac{\text{mm Hg}}{\text{K}}$$

Ans

$$v_{liq} = \frac{V}{m} = \frac{m}{\rho m} = \frac{1}{\rho} = 0.2695\ \text{cc/g}$$

$$\therefore \frac{\Delta P}{\Delta T} = 17 \times 133.322 \times 10\ \text{dyn/cm}^2\text{-K}$$

From clausius clayperon eqn,

$$\frac{L}{v_{vap} - v_{liq}} = T\left(\frac{\Delta P}{\Delta T}\right)$$

$$\Rightarrow v_{vap} - v_{liq} = \frac{40.9 \times 4.184 \times 10^7}{458.3 \times 17 \times 133.322 \times 10}$$

$$= 164.7458$$

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∴ specific volume of vapour

$= v_{liq} + 164.74T^8$

$$\boxed{v_{vap} \triangleq 165.02 \text{ cc/gg}}$$

(2) System whose $G = 0$

For any system we have

$$dG = -SdT + VdP + \mu dN.$$

If $G = 0 \Rightarrow dG = 0$

$$SdT = VdP + \mu dN$$

$$\Rightarrow \frac{S}{V} = \left(\frac{\partial P}{\partial T}\right)_V + \frac{\mu}{V}\left(\frac{\partial N}{\partial T}\right)_V$$

Clearly in a closed system (i.e. $V = \text{const}$) No. of particle, N also be constant

$$\therefore \left(\frac{\partial N}{\partial T}\right)_V = 0$$

And from Maxwell's Relation,

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\therefore \frac{S}{V} = \left(\frac{\partial S}{\partial V}\right)_T$$

Integrating we have

$$\ln S = \ln V + f(T)$$

$$\Rightarrow \boxed{S = V f(T)}$$

This is the equation of state of system.

(3) Gibbs free energy for a blackbody (EM) radiation.

Ans From Callen ebook we have for EM radiation,

$$U = bVT^4, \quad P = \frac{U}{3V}$$ (where b is some constant)

Now, $G := H - TS$

$$= U + PV - TS$$

From Fundamental ~~theorem~~ law we have

$$dU = TdS - PdV$$

($dV = 0 \because V$ = constant, closed system / cavity)

$$\therefore dS = \frac{dU}{T}$$

Further. $U \equiv U(T, V)$

$$\therefore dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T \overset{0}{dV}$$

$$= C_V dT$$

$$= 4bVT^3$$

$$\therefore \int_{S=0}^{S} dS = \int_{T=0}^{T} 4bV \frac{T^3}{T} \cdot dT$$

$$S = 4bV \int T^2 \cdot dT = \frac{4bV}{3} T^3$$

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$$\therefore TS = \frac{4}{3} bV T^4 = \frac{4U}{3}$$

So, $G = U + pV - TS$

$$= \frac{U + \not{V}}{3} - \frac{4U}{3} = 0$$

Hence $\boxed{G = 0}$ for EM radiation

$\Rightarrow$ From Q. 2, it's equation state is,

$$S = V f(T)$$

$$\therefore \left(\frac{\partial S}{\partial V}\right)_T = f(T) = \left(\frac{\partial P}{\partial T}\right)_V \quad \text{(Maxwell Rel}^n\text{)}$$

$$\Rightarrow P = \int f(T) \cdot dT + \alpha$$

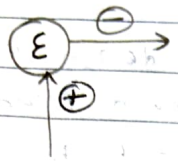
pure function of temperature (at const. volume).

$\alpha \rightarrow$ some constant.

i.e $\left(\frac{\partial P}{\partial V}\right)_T = 0$

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Q.1) ~~Condition~~ Convention:



Claussius Inequality:

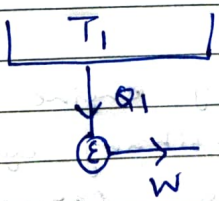
Consider a thermodynamic system P that performs a complete cycle. To do that it interacts with Reservoirs $R_1, R_2, \ldots, R_n$ with temp $T_1, \ldots, T_n$ and exchange heat $Q_1, \ldots, Q_n$

Then $\sum_{i=1}^{N} \frac{Q_i}{T_i} \leq 0$

(a) Kelvin Planck Statement:

It is impossible to design a device that works on a cycle and produces no other effect other than heat transfer from a single body (Reservoir) for the production of work.

consider,



Then $Q_1 > 0$ (as per our convention).

$$\Rightarrow \sum_i \frac{Q_i}{T_i} = \frac{Q_1}{T_1} > 0$$

Which violates claussius Inequality.

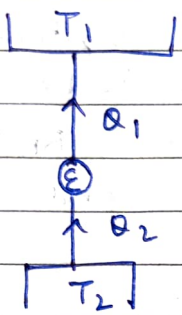
Hence $Q_1 \not\leq 0$ | K.P statement proved □

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(b) Clausius statement:

It is not possible to design a device which works on a cycle and produces no effect other than heat transfer from a cold body to a hot body

Let



$(T_1 > T_2)$

i.e $W = 0$

So, $|Q_1| = |Q_2|$

$\therefore Q_2 = -Q_1 > 0$

So, $\sum_i \frac{Q_i}{T_i} = \frac{Q_1}{T_1} + \frac{Q_2}{T_2}$

$= Q_2 \left(\frac{1}{T_2} - \frac{1}{T_1} \right) > 0$

which is a contradiction.

Hence $W \neq 0$ always.

C. statement proved □

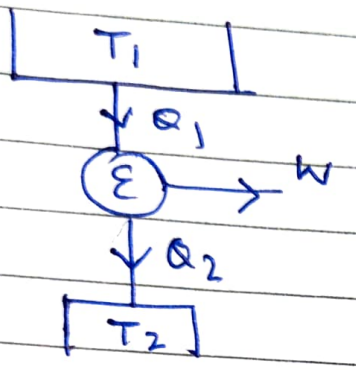
(c) Carnot's Theorem.

The efficiency of any engine (other than Carnot) running in an arbitrary cycle is always less than that of a Carnot Engine running between reservoirs at the maximum and minimum temperatures attained during the cycle.

$$\eta \leq \eta_{carnot} = 1 - \frac{T_{min}}{T_{max}}$$

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Consider any engine,



$(T_1 > T_2)$

From Clausius Ineq. we have,

$$\sum_i \frac{Q_i}{T_i} \leq 0$$

$$\Rightarrow \frac{Q_2}{T_2} \leq -\frac{Q_1}{T_1} \Rightarrow \boxed{\frac{Q_2}{Q_1} \leq -\frac{T_2}{T_1}} \quad \ldots (i)$$

Now, $Q_1 = (-W) + (-Q_2)$

$\therefore -W = Q_1 + Q_2 > 0$

$$\text{Efficiency} = \frac{|W|}{Q_1} = \frac{Q_1 + Q_2}{Q_1}$$

$$= 1 - \frac{Q_2}{Q_1} \leq 1 - \frac{T_2}{T_1}$$

(from eq (i))

Hence proved, Carnot's Theorem

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