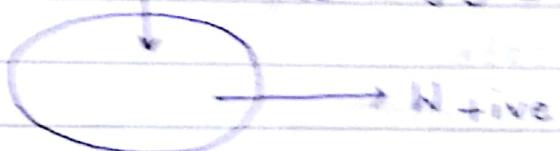


CHEMICAL ENGG. THERMO.

Classical Thermodynamics - Deals with macroscopic system comprising of a large number of particles.

$$\delta Q + \delta W = \delta U$$



System has to be enclosed by well-defined - boundary.

System : Any part of the universe we chose to study or analyse is a system.

Thermodynamic Properties :-

Properties which undergo change with change in energy. The change in any property value, depends only on the initial and final states.

$$\int_1^2 dP = P_2 - P_1$$

$$dP = M dx + N dy$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 P}{\partial x \partial y} = \frac{\partial^2 P}{\partial y \partial x}$$

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- Should have a definite value when the system is in a particular state.
- Should be determinable irrespective of how system brought to that state.

Properties are relevant only when the system is in equilibrium.

Equality of Thermal Equilibrium implies temperature is same.

Equality of Mechanical Equilibrium implies pressure is same.

Equality of Chemical Equilibrium implies chemical potential is same.

Thermodynamic equilibrium :
Thermal, mechanical and chemical equilibrium.

No tendency for change in the system, stable thermodynamic equilibrium.

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Unstable thermodynamic equilibrium state - boiling water { phase transitions }.

All systems in equilibrium state are in steady state and not vice-versa.

Steady state : Only time-dependent
Equilibrium state : Depends on time as well as space.

Characterised by a definite set of properties.

The Gibb's Phase Rule :-

It gives the number of intensive properties that must be specified in order to completely determine the system.

$$F = C - P + 2$$

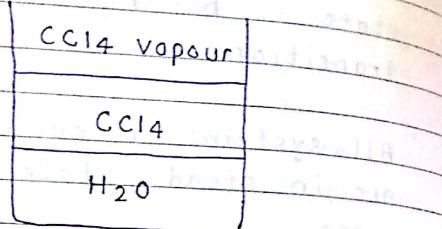
P = No. of phases in the system
(phases are mechanically separable components)

C = Minimum number of components
2 : refers to the temperature and pressure conditions.

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Example: Mixture of water and CCl_4

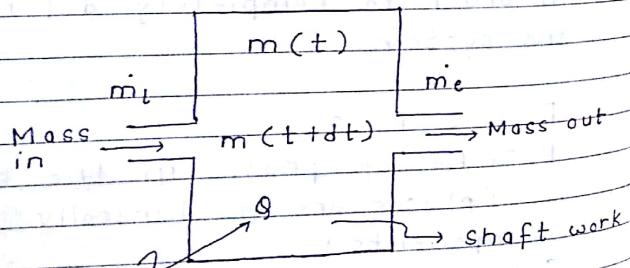


$$C = 2, P = 3$$

$$F = 2 - 3 + 2 = 1$$

- A phase needs to be homogeneous but not continuous.
- Independent of size or composition of the system.

Control mass approach :-



$$m(t) + m_i dt = m(t+dt) + m_e$$

A phase is that portion of a thermodynamic system which has the same physical properties and the same chemical composition.

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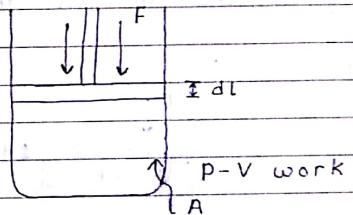
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System is defined in such a way that mass remains constant (control mass).

What is energy?

Energy is the capacity to induce a change in that which inherently resists a change.



$$\delta W = F dl$$

$$= P A dl$$

$$\delta W = P dV$$

Thermodynamic displacement : extensive
Thermodynamic driving force : intensive

→ Redlich - Kwong Eqn :-

$$P = \frac{RT}{v - B} - \frac{A}{T^{0.5} v(v+B)}$$

→ Peng - Robinson Eqn :-

$$P = \frac{RT}{v - \beta} - \frac{\alpha}{v(v+\beta)+\beta(v-\beta)}$$

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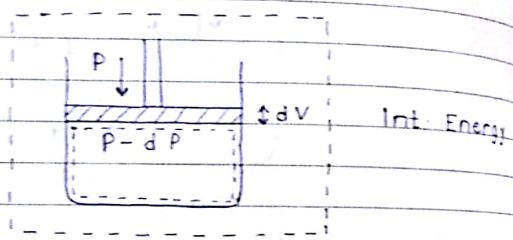
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Energy = Thermodynamic driving force
x Thermodynamic displacement

Thermodynamic Force - Scalar, intensive
Displacement - Scalar, extensive

There has to be one driving force
and one disp. which when mult
gives the amount of energy



Pressure acting externally at the boundary.
Vol. change occurs within the system

Work is a path f^n (energy in transit), it is neither of the system nor of the surrounding

If the temp. diff. is the driving force, the energy in transit is heat.

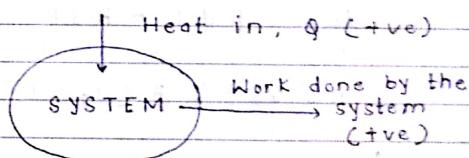
Any driving force other than temp. diff., the energy in transit is work.

Work and heat are path functions
and their differentials are inexact differentials.

$$\int_1^2 dP = P_2 - P_1 \quad \text{State } f^n$$
$$\int_1^2 dq \neq q_2 - q_1 \quad \text{Path } f^n$$

There is no heat content of the system.

Heat and work have the same effect
in closed system, type of interaction
depends on the choice of the system



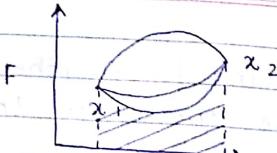
PdV work in various quasi-static
Process:-

Reversible Process - Driving force is
changed infinitesimally.

On reversing the process, both system
and surrounding comes back in its
original state.

Irreversible Process :-

The system might come back to initial state but the surroundings ~~to its~~ comes on reversing the process.



$$\int_1^2 dW = \int_1^2 F dr$$

For calculation of work done, entire path from 1 to 2 is to be known.

Equation of State :-

$$f(P, V, T) = 0$$

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

$$dV = \beta V dT - kV dP$$

$$dV = \beta dT - k dP$$

V

$$\ln\left(\frac{V_2}{V_1}\right) = \beta(T_2 - T_1) - k(P_2 - P_1)$$

For solids and liquids.

Eqⁿ of State

Cubic Compressibility factor chart Virial (RK, PR)

Not only gases but also for liquids and saturated vapor.

Near the critical point, it is necessary to use at least three virial coefficient.

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(Saathi)

Virial Equation of State :-

$$Z = 1 + B_2 P(T) + B_3 P(T) P^2 + \dots$$

$$Z = 1 + \frac{B_2 V(T)}{V} + \frac{B_3 V(T)}{V^2} + \dots$$

$$B = \lim_{P \rightarrow 0} \left(\frac{\partial Z}{\partial P}\right)_T = 0$$

$$\frac{PV}{RT} = Z$$

$$Z = 1$$

for ideal gas

At Boyle's temp, $B=0$

for low to moderate pressure

$$\frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \dots$$

$$\frac{PV}{RT} = 1 + B' P + C' P^2 + \dots$$

RT

$$B' = \frac{B}{RT} ; C' = \frac{C - B^2}{(CRT)^2}$$

$$D' = \frac{D - 3BC + 2B^3}{(CRT)^3}$$

At critical point :-

$$\left(\frac{\partial P}{\partial V}\right)_{T=T_c} = 0 ; \left(\frac{\partial^2 P}{\partial V^2}\right)_{T=T_c} = 0$$

$$\left(\frac{\partial T}{\partial V}\right)_{P=P_c} = 0 ; \left(\frac{\partial^2 T}{\partial V^2}\right)_{P=P_c} = 0$$

Point of inflection.

$$\frac{PV}{RT} = 1 + \frac{B}{V}$$

$$\frac{P}{RT} + \frac{V}{RT} \frac{\partial P}{\partial V} = - \frac{B}{V^2}$$

$$\frac{P}{RT} + \frac{V}{RT} \frac{\partial P}{\partial V} = - \frac{B}{V^2}$$

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$$V \frac{\partial P}{\partial V} = -B - P$$

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

$$\frac{\partial P}{\partial V} = -BRT - \frac{P}{V}$$

$$\frac{\partial P}{\partial V} \Big|_{T=T_c} = -RT_c - \frac{2RT_c B}{V_c^2} = 0$$

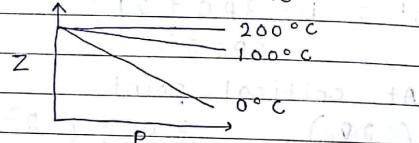
$$\frac{\partial^2 P}{\partial V^2} \Big|_{T=T_c} = \frac{2RT_c}{V_c^3} + \frac{6BR T_c}{V_c^4} = 0$$

$$\begin{aligned} B &= -V_c & \text{Two diff. values of } B \text{ are not possible.} \\ &2 & \text{B are not possible.} \\ &3 & \therefore \text{Near critical point, truncate at 3rd term.} \end{aligned}$$

$$PV = 1 + \frac{B}{V} P$$

$$C = \frac{V_c^2}{3}$$

$$RT = \frac{PV}{C} = \frac{PV}{\frac{V_c^2}{3}} = \frac{3PV}{V_c^2}$$



$B = 0$ at Boyle's temp. where gas appears to be ideal.

$$V = \frac{RT}{P} + B$$

$$B(T) = V - V^* \text{ at that } T$$

$$= \Delta V^*$$

Residual property / Departure Functions (ΔP^*)

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(Saathi)

Q. Molar vol. of ethane at 300 K and 200 atm using :-

i) Ideal gas eqⁿ

ii) van der Waals eqⁿ $a = 5.5088 \text{ dm}^6 \text{ atm/mol}^2$, $b = 0.065144 \text{ dm}^3/\text{mol}$

iii) Redlich Kwong eqⁿ (better for high P) $A = 97.539 \text{ dm}^6 \text{ atm mol}^{-1} \text{ K}^{-0.5}$

$$B = 0.045153 \text{ dm}^3/\text{mol}$$

Q. At 142.69 atm, argon exists as two phases with $P_{L,sat} = 22.491 \text{ mol/l}$ and $P_{V,sat} = 5.291 \text{ mol/l}$. Verify using.

i) van der waals $a = 1.3307$ $b = 0.03183$

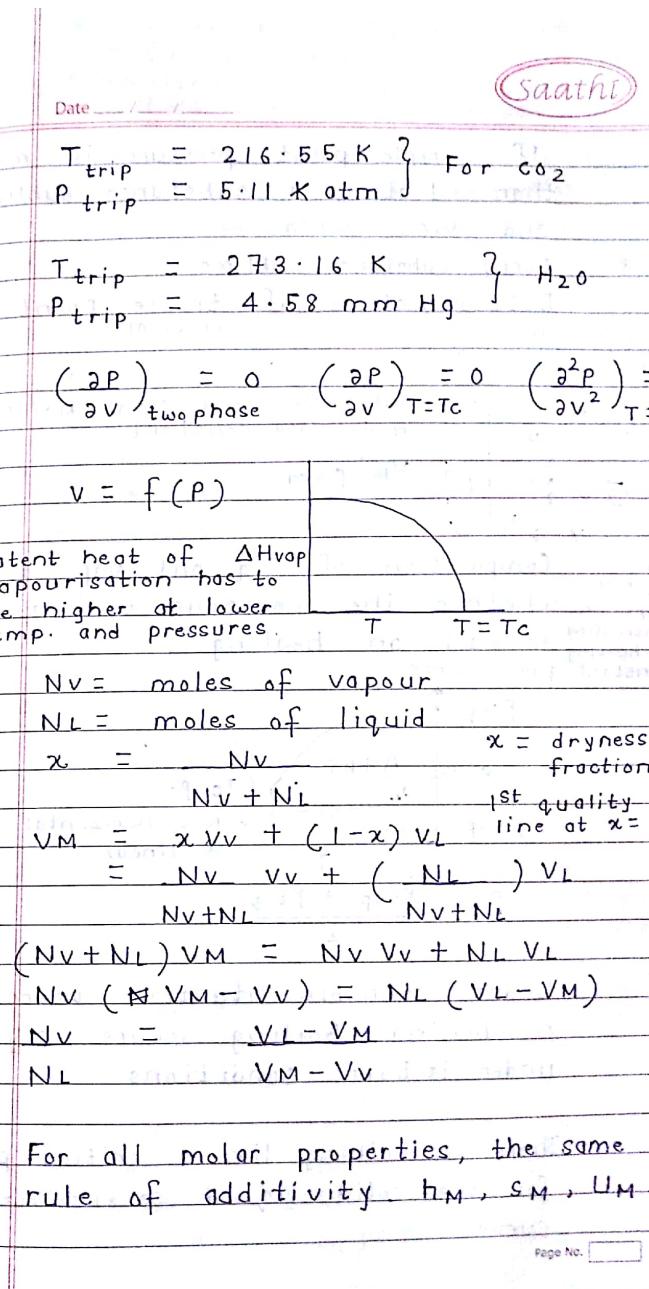
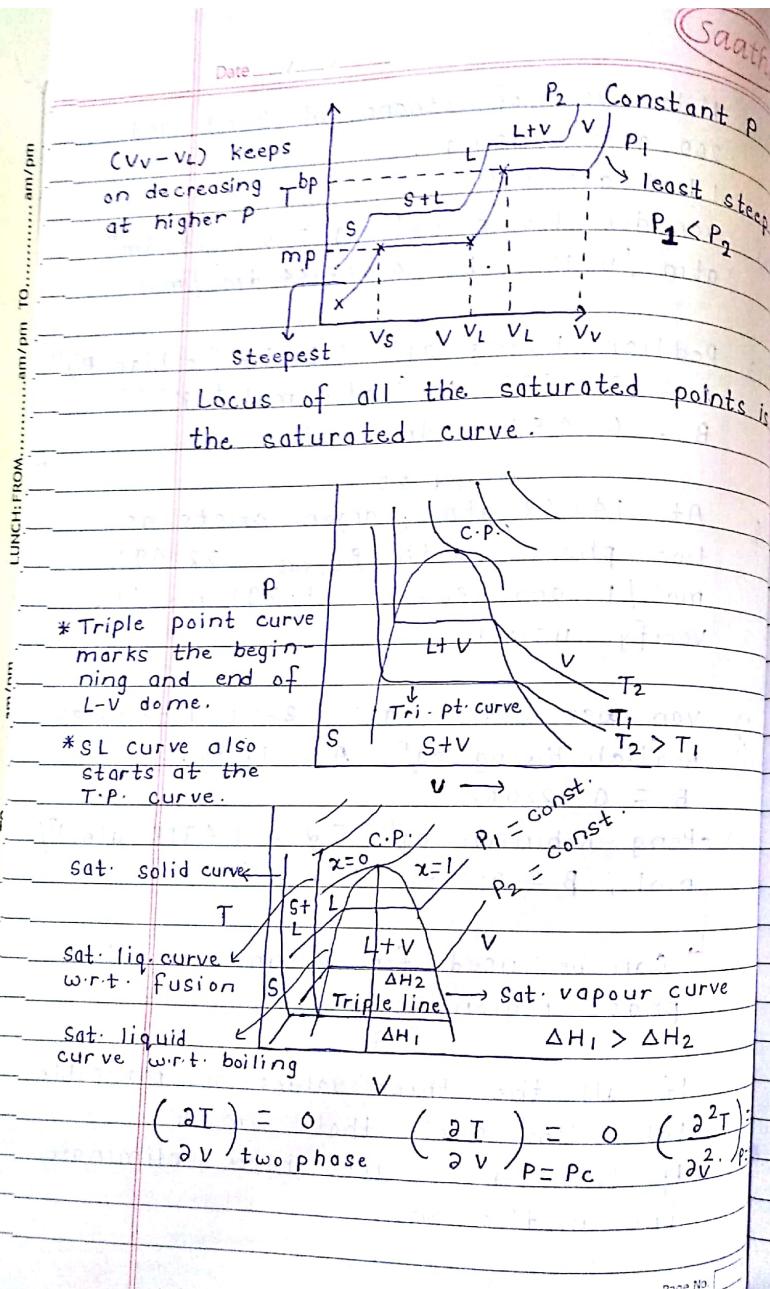
ii) Redlich Kwong eqⁿ $A = 16.566$, $B = 0.022062$

iii) Peng Robinson eqⁿ $[a = 1.4915 \text{ atm}^2/\text{mol}$, $b = 0.01981 \text{ l/mol}]$

Can be used for volumes in two phase region.

If all the three values are realisable, take V_m such that $V_m > b$.

If there are 3 real roots, eliminate the middle one.



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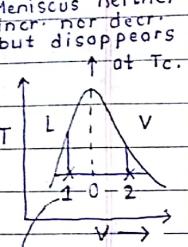
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If Triple point pressure is more than 1 atm, a substance sublimates and vice-versa.

* Every substance sublimes.

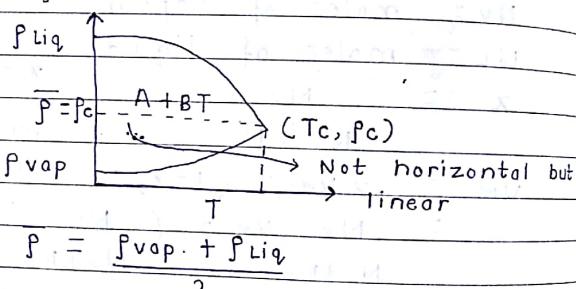
Determination of triple point critical

Meniscus neither incr. nor decr. but disappears at T_c .



Total Vol. and Total no. of moles are constant.
VM fixed

Composition of liq. and vap. determined by whether the meniscus will rise or fall on heating.

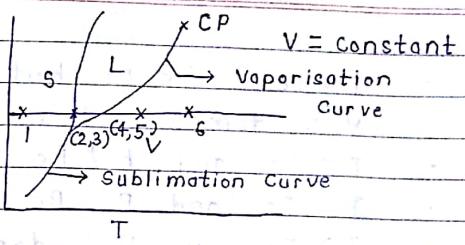


Under isochoric situation, there is no boiling. Boiling occurs only under isobaric conditions.

There is nothing like a critical point for the solid liquid coexistence curve.

At critical point liquid and gas becomes a single phase and are indistinguishable thermodynamically. For liquid-solid transitions this equivalency of phase doesn't hold true.

Hence solid-liquid transition doesn't have an indis. P phase like the gas-liquid transition.
Hence no critical point.



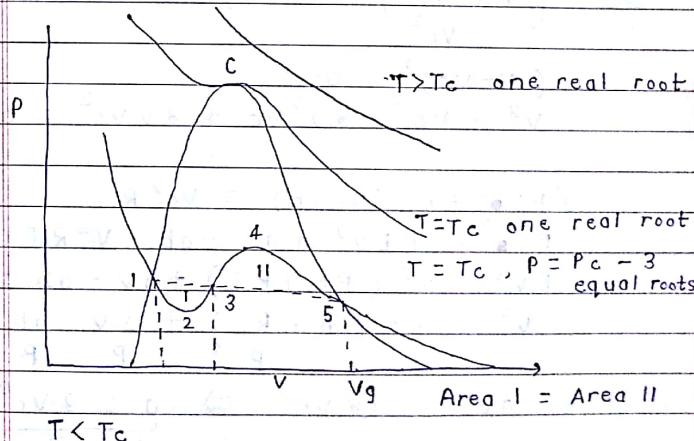
Solid - Liquid Curve goes indefinitely.
Sublimation Curve goes till triple point.

Liquid - Vapour Curve starts at triple point and goes till critical point.

* Critical opalescence

Supercritical fluid: low viscosity

↳ Food industry



$T < T_c$

Physically realisable roots :-
v should be real, positive and $v > b$.

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- $T > T_c$, $T < T_c$ but away from V-L dome, 1 real root
- $T = T_c$ and $P \neq P_c$, 1 real root
- $T = T_c$ and $P = P_c$, 3 real roots
- $T > T_c$ in V-L dome $P = P_{sat}$
- 3 physically realisable roots
- higher $v = v_V$
- lower $v = v_L$
- $T_c < T_c$, $P \neq P_{sat}$
- smaller root: Liq. like volume
- larger root: vap. like volume

Express 'a, b' in terms of critical constants :-

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

$$(V - V_c)^3 = 0$$

$$V^3 - V_c^3 - 3V^2V_c + 3VvV_c^2 = 0$$

$$(PV^2 + a)(V_c - b) = V_c^2 RT$$

$$PV^3 - PbV^2 + aV - ab - V^2 RT = 0$$

$$PV^3 - V^2(Pb + RT) + aV - ab = 0$$

$$V^3 - V^2(b + RT) + aV - ab = 0$$

$$\frac{aV}{P} = \frac{3V^2V_c^2}{P} \Rightarrow a = \frac{3V_c^2P_c}{P}$$

At critical pt

$$\frac{-ab}{P} = -\frac{V_c^3}{P}$$

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$$3V_c^2Pb = V_c^3 \Rightarrow b = \frac{V_c}{3}$$

Put value of 'a' and 'b' in
Wander Waals eqn
then, $P_cV_c = \frac{3RT_c}{8}$

$$a = \frac{27R^2T_c^2}{64P_c}, b = \frac{RT_c}{8P_c}, z_c = \frac{3}{8}$$

$$\left(\frac{P + a}{V^2} \right) (V - b) = RT \quad \left. \begin{array}{l} \{ \\ \times \\ \end{array} \right. \frac{1}{P_cV_c}$$

$$\left(\frac{P_r + \frac{3}{V_r^2}}{V_r^2} \right) (V_r - 1) = \frac{8}{3} T_r$$

$$V_r = f(T_r, P_r)$$

$$z = \frac{V_r}{V_r - \frac{9}{8} V_r T_r}$$

$$z_c = 0.375$$

Two parameter form for wander waals

Law of corresponding states fail
under critical conditions and
saturated conditions.

→ Why all gases (non-polar / slightly polar)
follow law of corresponding states?

*** All gases behave identically at critical
conditions. Therefore, when equally
removed from the c.c. they again
behave identically.

$$z = f_n(T_r, P_r) = f_n(T_r, V_r)$$

Law of corresponding states.

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Law of corresponding states:
fails near saturation curve and
critical point.
Works well for non-polar and Saathi
polar gases ($\pm 5\%$). Deviation slight
highly polar gases.

$0.23 \leq z_c \leq 0.3$ All gases do not have the same z_c
(Experimentally observed).

$$z = z(T_r, P_r, z_c)$$

For perfectly spherical mol. $w = 1$

$$1/T_r \quad w = -\log P_r \quad T_r = 0.7$$

where $P_r^z = P^z = \text{reduced vap. pres.}$
 P_c at $T_r = 0.7$
 $z = z(T_r, P_r, w)$
 $= z^0(T_r, P_r) + w z'(T_r, P_r)$
 $w = \text{Accentric factor}$

H.W. Write reduced formula for
virial eqⁿ.

Q. Estimate the pressure developed
in a tank of 1 m^3 filled with
100 kg CH_4 at $T = 40^\circ\text{C}$

$$T_c = 190.7$$

$$P_c = 46.41$$

$$w = 0.011$$

Q. $V = 0.1 \text{ m}^3 \quad P = 8.25 \text{ MPa} \quad T = 25^\circ\text{C}$

Determine mass of ethylene using

a) Van der Waals

b) two and three parameter com. fact. correlation

$$T_c = 283.1 \text{ K} \quad P_c = 51.17 \text{ bar}$$

$$w = 0.089 \quad a = 453.046 \text{ Pa} \cdot (\text{m}^3/\text{mol})^2$$

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$$b = 0.057 \times 10^{-3} \text{ m}^3/\text{mol}$$

Q. Methyl Chloride at 100°C $B_{1V} = -242.5$
 cm^3/mol and $B_{2V} = 25200.0 \text{ cm}^6/\text{mol}^2$.
Calculate the work for rev. isothermal
compression of 1 mol of methyl chloride
from 1 bar to 55 bar at 100°C
using the Berlin and Leiden form
of eqⁿ truncated after three terms.

$$B_{1P} = B_{1V} / RT \quad B_{2P} = (B_{2V} - B_{1V}^2)z / (RT)^2$$

$$1. \quad z = P V_m = K P$$

$$RT$$

$$N = 100 \times 10^3 / 16 = 6.25 \times 10^3 \text{ mol}$$

$$V_m = 1 / 6250 = 1.6 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$$

$$P = z_0 RT; \quad P = P_r P_c$$

$$\therefore P_r = z_0 RT \Rightarrow z_0 = V_m P_c / P$$

$$z_0 = 0.28534 P$$

$$T_r = T / T_c = 313.15 / 190.7 = 1.642$$

$$z_0 = 0.87 \text{ (approx)}$$

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$$P = Z_0 RT / \hat{V}$$

$$P = 0.87 \times (0.082) (313) \times 100$$

$$P = 139.55 \text{ atm}$$

By 3 parameter compressibility

$$Z = Z_0 + \omega Z_1$$

Initially $Z = Z_0$

$$Z_0 = 0.87$$

$$P_r = \left(\frac{Z}{0.284} \right) = \frac{0.87}{0.284} = 3.063$$

From, $P_r = 3.063$ and $T_r = 1.6413$

$$Z' = 0.24$$

$$\therefore Z = Z_0 + \omega Z'$$

$$Z = 0.87 + 0.011 \times 0.24$$

$$Z = 0.872$$

$$\therefore P = Z R T$$

$$= 0.872 \times 0.082 \times 313 \times 100$$

$$P = 139.88 \text{ atm}$$

2. a) C_2H_4 : $M \cdot W = 28$

$$(P + an^2) (V - nb) = nRT$$

$$PV - Pnb + \frac{an^2}{V} - \frac{an^3b}{V^2} - nRT = 0$$

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$$PV^3 - PnbV^2 + an^2V - an^3b - nRTV^2 = 0$$

$$n^3ab - aVn^2 + PbV^2n + (nRTV^2 - PV^3) = 0$$

Putting all values,

$$n = 1754$$

$$M = 1754$$

28

$$M = 1754 \times 28 = 49.1 \text{ kg}$$

$$b) P = 8.25 \times 10^6 \text{ Pa} \quad P_c = 51.17 \times 10^5$$

$$P_r = \frac{P}{P_c} = 1.49$$

Pc

$$T = 298.15 \text{ K}, \quad T_c = 283.1 \text{ K}$$

$$T_r = 1.053$$

Z = 0.325 from graph

$$n = PV$$

$$Z RT$$

$$n = \frac{8.25 \times 10^6 \times 0.1}{0.325 \times 8.314 \times 298.15}$$

$$n = 1024$$

$$M = 1024$$

28

$$M = 1024 \times 28 = 28.67 \text{ kg}$$

$$c) Z = Z_0 + \omega Z_1$$

$$Z_1 = 0.025$$

$$\omega = 0.089$$

$$Z = 0.325 + 0.089 \times 0.025 = 0.327$$

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$$n = \frac{PV}{ZRT}$$

$$n = \frac{8.25 \times 10^6 \times 0.1}{0.827 \times 8.314 \times 298.35}$$

$$n = 1017.12$$

$$M = 1017.12$$

28

$$M = 1017.12 \times 28 = 28479.36$$

$$M = 28.48 \text{ kg}$$

Mass of ethylene = 28.48 kg

$$3. a) \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} \quad \{ \text{Leidenz} \}$$

$$PV^3 = V^2 + BV + C$$

RT

$$V^3 \times 0.98 - V^2 + 0.2425V - 0.0252 = 0.082 \times 373$$

$$V_1 = 30.97 \text{ L}$$

$$V_2 = 0.24 \text{ L}$$

$$W = \int_{V_1}^{V_2} P dV$$

$$W = \int_{30.97}^{0.24} \left(\frac{RT}{V} + \frac{BRT}{V^2} + \frac{CRT}{V^3} \right) dV$$

$$W = -124.7 \text{ L atm}$$

(Saathi)

practise book get width of 10 cm
and depth and width will be 10 cm
Total width of book will be 20 cm

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$$b) \frac{PV}{RT} = 1 + \frac{B}{P} + \frac{C}{P^2}$$

$$V = RT \left(\frac{1}{P} + \frac{B}{P} + \frac{C}{P^2} \right)$$

$$dV = RT \left(-\frac{1}{P^2} + \frac{C}{P^3} \right) dP$$

$$W = \int_{P_1}^{P_2} P dV$$

$$W = \int_{P_1}^{P_2} RT P \left(-\frac{1}{P^2} + \frac{C}{P^3} \right) dP$$

$$W = RT \int_{P_1}^{P_2} \left(-\frac{1}{P} + \frac{C}{P^2} \right) dP$$

$$W = RT \left[-\ln P_1 + \frac{C}{P_1} \right]_{P_1}^{P_2}$$

$$W = RT \left[\ln \frac{P_1}{P_2} + \frac{C}{2} \left(\frac{P_2^2 - P_1^2}{P_1 P_2} \right) \right]$$

$$C' = \left(\frac{C - B^2}{(RT)^2} \right)$$

$$C' = -3.5 \times 10^{-6}$$

$$W = -124.187 \text{ L atm}$$

Heating can be done by performing work. But the mass couldn't be lowered just by using the heat. *Heat is a lower grade of energy.*

* Cyclic changes can be reversible or irreversible. Basis for the laws of thermodynamics.

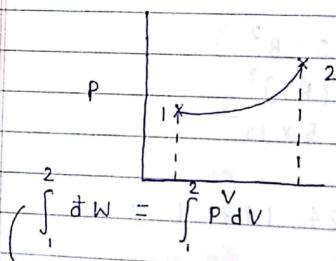
$\oint dq - \oint dW = 0$ {cyclic process}
Amount of work in each case, temp. changed from T_1 to T_2 .

1. We cannot have a cyclic adiabatic process.
2. We can go from 1 \rightarrow 2 but not from 2 \rightarrow 1, just by doing work.
3. For every case, total work done is total amount of heat lost.

$$\oint dq \propto \oint dW \\ = T \oint dW$$

In S.I. units

$$\oint dq = \oint dW \quad \{ \text{For cyclic processes} \}$$



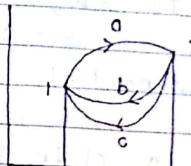
depends on path and thus work is a path function.

→ 1st law doesn't give law of conservation of energy, rather its a consequence of the first law.

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$$\oint dq - \oint dW = 0 \\ 1a2b1 \quad 1a2b1$$

$$\oint_{1a2} dq = \oint_{1a2} dW$$

$$\oint_{1a2} dq + \oint_{2b1} dq = \oint_{1a2} dW + \oint_{2b1} dW$$

$$\oint_{1a2c1} dq = \oint_{1a2c1} dW$$

$$\oint_{1a2} dq + \oint_{2c1} dq = \oint_{1a2} dW + \oint_{2c1} dW$$

(i) - (ii)

$$\oint_{2b1} dq - \oint_{2c1} dq = \oint_{2b1} dW - \oint_{2c1} dW$$

$$\text{But } \oint_{2b1} dW \neq \oint_{2c1} dW$$

$$\therefore \oint_{2b1} dq - \oint_{2c1} dq \neq 0$$

Initial and final states are same but q differs.

If W is a path f^n , q is also path f^n .

$$\oint_{2b1} dq - \oint_{2b1} dW = \oint_{2c1} dq - \oint_{2c1} dW$$

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$$f(\delta q - \delta w) = f(\delta q - \delta w) = dE$$

2b1

Not path dependent. Depends only on state.

Energy is a state function.

$$\Delta E = \Delta E_{KE} + \Delta E_{PE} + \Delta U$$

For an isolated system:

$$\delta q = \delta w = 0$$

$$dE_{\text{isolated}} = 0$$

$$E_2 - E_1 = 0 \Rightarrow E_2 - E_1$$

→ Energy remains conserved in an isolated system. $\{\delta q = \delta w = 0\}$

$\delta q - \delta w = dU$ $\{\text{Valid for any process, be it reversible or irreversible}\}$. System has to be a closed system.

Isochoric Process $\{\text{Irreversible}\}$:-

$$\delta q = 0 \quad \{\text{insulated}\}$$

$$dU = -\delta w_{\text{shaft}}$$

$$\therefore dV = 0, \quad PdV = 0$$

Reversible Isochoric process:-

$$PdV = 0$$

$$\delta w = 0$$

$$\delta q = dU$$

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Saath:

For an ideal gas,

$$dU = Cv dT$$

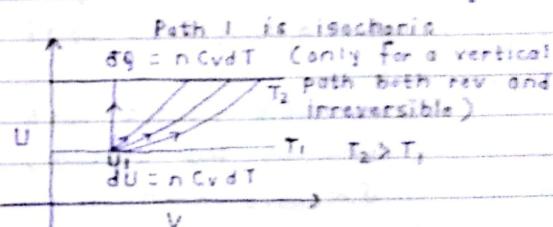
For an isochoric process,

$$\delta q = nCv dT$$

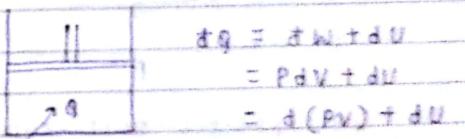
$$dU = nCv dT \quad \{\text{always}\}$$

$\delta q \neq nCv dT \quad \{\text{not an isochoric process}\}$

For solids and liquids also, $dU = Cv dT$ because vol. doesn't much change.



Isochoric Process



$$dU^{\circ} = Cv dT$$

$$dH^{\circ} = Cp dT$$

Isobaric Process with work done
the system :- (No heat)

$$\delta Q = 0$$

$$-\delta W_{\text{shaft}} - PdV = dU$$

$$dU + PdV = -\delta W_{\text{shaft}}$$

$$dU + d(PV) = -\delta W_{\text{shaft}}$$

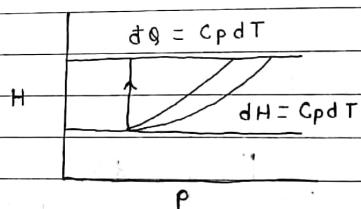
$$\therefore -\delta W_{\text{shaft}} = dH$$

∴ Reversible isobaric process :

$$dQ = dH \quad \{ dH = CpdT \text{ for ideal gas}$$

Irreversible (shaft work has to be done in the system) :

$$-\delta W_{\text{shaft}} = dH$$



C → Specific heat capacity

Specific heat is a state function, once the path is defined.

$$C_{\text{path}} = \left(\frac{\partial Q}{\partial T} \right)_{\text{path}}$$

→ C is infinite during phase changes

→ Measurement of C must always refer to a closed system.

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1. Work done during an isothermal reversible process :

$$W = \int_{V_1}^{V_2} PdV \quad \{ P = P_{\text{ext}} \}$$

For reversible process,

$$P_{\text{ext}} = P_{\text{in}} + dP$$

$$\therefore PdV = (P_{\text{in}} + dP)dV$$

$$= P_{\text{in}}dV + dPdV$$

$dPdV$ being so small can be neglected.

$$\therefore PdV = P_{\text{in}}dV$$

For an ideal gas,

$$P_{\text{in}}V = nRT$$

$$P_{\text{in}} = nRT, \therefore PdV = nRTdV$$

$$W = \int_{V_1}^{V_2} nRT dV = nRT \int_{V_1}^{V_2} dV$$

$$W = nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{V_2}{V_1}$$

∴ For an isothermal reversible process on an ideal gas,

$$W = nRT \ln \frac{V_2}{V_1}$$

2. For an adiabatic process,
 $dQ = 0 \Rightarrow dU + dW = 0$ - *
 $dW = PdV$ {any process} - 1

For an ideal gas,
 $dU = nC_V dT$, $PV = nRT$
Also $d(PV) = n dT \cdot R$
 $\therefore PdV + VdP = dT$

$$\therefore dU = C_V (PdV + VdP) - 2.$$

Using 1. and 2. in eqⁿ *
 $C_V (PdV + VdP) + PdV = 0$

$$PdV (C_V + 1) + C_V V dP = 0$$

$$PdV C_p + C_V V dP = 0 \quad \{ C_p = C_V + R \}$$

Rearranging the eqⁿ gives,

$$dP/P = - (C_p/C_V) (dV/V)$$

Integrating both sides,

$$\ln P = -r \ln V + c \quad \{ r = C_p/C_V \}$$

$$\ln P = -\ln V^r + c$$

$$\ln(PV^r) = c \Rightarrow PV^r = c$$

∴ For an adiabatic process,
 $PV^r = c$. {for an ideal gas}
Only for reversible adiabatic process, and irreversible also.

For an adiabatic reversible process :-

We know, 1.

$$W = \int_{V_1}^{V_2} P_{ext} dV$$

For a reversible process,

$$P_{ext} \approx P_{in} \quad \{ \text{for any process} \}$$

For reversible adiabatic process

$$PV^r = K \Rightarrow P = K/V^r$$

Using P in eqⁿ 1.

$$W = \int_{V_1}^{V_2} K dV$$

$$W = K \int_{V_1}^{V_2} V^{-r} dV = KV^{-r+1} \Big|_{V_1}^{V_2}$$

$$W = K \left[V_1^{-r+1} - V_2^{-r+1} \right]$$

$$W = KV_1^{-r+1} - KV_2^{-r+1}$$

$$W = P_1 V_1^r V^{-r+1} - P_2 V_2^r V^{-r+1}$$

$$\therefore W = P_1 V_1 - P_2 V_2$$

In an irreversible process, $P_{ext} \neq P_{in}$.

$$W = \int_{V_1}^{V_2} P_{ext} dV \quad \{ PV^r \text{ can't be used} \}$$

Assuming P_{ext} to be constant,

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$$W = p_{ext} \int_{V_1}^{V_2} dV = p_{ext} (V_2 - V_1)$$

$$W = p_{ext} \Delta V \quad \{ \text{Irreversible process} \}$$

* For irreversible adiabatic process

$$T_2^{\text{irr}} = \left(\frac{nR}{P_1} \frac{P_2}{P_1} + C_v \right) T_1$$

C_p

$$PV^n = K$$

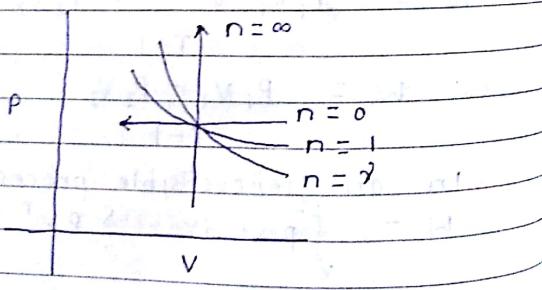
Isobaric, $n = 0$

Isochoric, $n = \infty$

Isothermal, $n = 1$

Adiabatic, $n = \gamma$

When an ideal gas performs P-V work along a polytropic process, the specific heat remains constant:



$$C_{\text{path}} = \left(\frac{\partial Q}{\partial T} \right)_{\text{path}}$$

$$PV^n = K$$

From first law,

$$Q = U + W$$

$$\delta Q = dU + PdV$$

$$dU = C_v dT$$

$$PdV = RT dV \quad [\text{Ideal gas}]$$

$$\delta Q = C_v dT + RT dV$$

$$\text{As } C_{\text{path}} = \left(\frac{\partial Q}{\partial T} \right)_{\text{path}}$$

$$\text{So, } dQ = C_{\text{path}} dT$$

$$(C_{\text{path}} - C_v) dT = RT (dV)$$

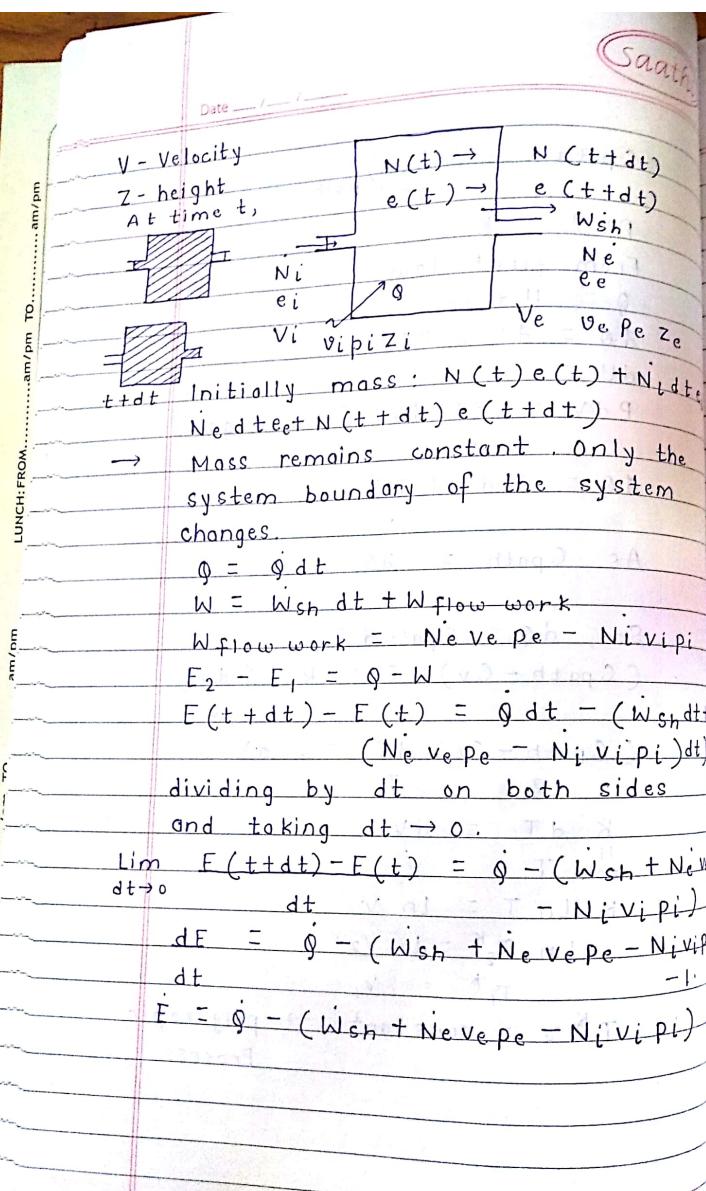
$$(C_{\text{path}} - C_v) \frac{dT}{T} = \frac{dV}{V}$$

$$K \frac{dT}{T} = \frac{dV}{V}$$

$$K \ln T = \ln V$$

$$\ln \frac{T_2}{T_1} = \ln \frac{V_2}{V_1}$$

$$T^K V = \text{constant} \rightarrow \text{polytropic Process}$$



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 $E(t+dt) - E(t) = N(t+dt)e(t+dt) - N(t)e(t) - N_i dt e_i$
 $E(t+dt) - E(t) = \{N(t+dt)e(t+dt) - N(t)e(t)\} + N e e dt - N_i dt e_i$
 Dividing by dt on both sides and taking $dt \rightarrow 0$
 $\frac{dE}{dt} = \frac{d(Ne)}{dt} + Ne e - N_i e_i - 2$
 Using 2. in 1. and simplifying
 $\frac{dE}{dt} = -\{Ne [h_e + v_e^2 + gz_e] + W_{sh}\}$
 $+ \{N_i [h_i + v_i^2 + gz_i]\}$
 where $h_e = u_e + P_e v_e$
 $\frac{dE}{dt} =$ Rate of energy in - Rate of energy out
 first law of thermodynamics for open systems.
 At steady state, $\frac{dE}{dt} = 0$
 $N = N_i = N_e \quad \dot{q} = \text{const.} \quad W = \text{const.}$
 $\sum N [(h_e - h_i) + \frac{v_e^2 - v_i^2}{2} + g (z_e - z_i)]$
 $= \dot{q} - W_{sh}$
 For more than one stream.

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$$(h_e - h_i) + \frac{v_e^2 - v_i^2}{2} + g(z_e - z_i) = dQ - dW_{sh}$$

1st Law for open system, under Steady state, for one stream:

To derive Bernoulli's eqn:-

→ There is no heat exchange and work done.

$$h_e + \frac{v_e^2}{2} + g z_e = h_i + \frac{v_i^2}{2} + g z_i$$

$$dQ = dU - pdV$$

$$\cancel{dQ}^0 = d(pdV) + v dp = dU$$

$$dH = v dp$$

$$\Delta P + \Delta v^2 + g \Delta z = 0$$

$$p = ?$$

For a reacting system,

$$\sum N (h_e - h_i) = 0$$

$$H_e - H_i = 0$$

$$\Delta H = 0$$

Heat of reaction

$$\Delta h_p^0$$

Enthalpy is not energy as it does not obey law of cons. of energy.

Suppose a rigid system enclosed by an adiabatic wall. $\therefore dV = 0, \cancel{dQ} = 0$
 $p dV = 0 \Rightarrow \cancel{dW} = 0, dU = 0$. There is no energy change, enthalpy increases because pressure increases. A fluid whose

$$dH = \cancel{\frac{\partial U}{\partial T} + P \cancel{\frac{\partial V}{\partial P}}}^0 + V \cancel{\frac{\partial P}{\partial T}}^0 \quad \text{Vol doesn't change even if pressure is changed.}$$

$$dH = V dP$$

Enthalpy can be included in energy balance for -

i) Reversible flow processes

ii) Non-flow processes at constant P (only for expansion work / vol. change)

Q. Valve opened till mechanical equilibrium.

| | |
|--------------------------|--------------------------|
| $V_A = 1 \text{ m}^3$ | $V_B = 9 \text{ m}^3$ |
| 10 MPa | Evacuated |
| $T_{Ai} = 300 \text{ K}$ | $T_{Bi} = 300 \text{ K}$ |

$$P_f = P_f$$

$$T_{Af} = ? \quad T_{Bf} = ?$$

$$\gamma = 1.4$$

Adiabatic Expansion.

No. of moles will remain constant
For 1st tank,

$$P_A V_A = n R T_A \quad \{ \text{Assuming ideal gas} \}$$

$$10 \times 10^6 \times 1 = n$$

$$8.314 \times 300$$

$$n = 4009 \text{ moles}$$

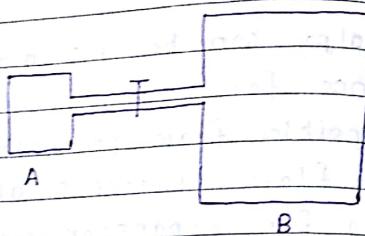
$$P_1 V_1^\gamma = P_2 V_2^\gamma$$

$$V_1 = 1, V_2 = 10$$

$$P_2 = 10 \times 10^6 \left(\frac{1}{10}\right)^{1.4} = 0.4 \text{ MPa}$$

$$P_{f,A} = P_{f,B} = 0.4 \text{ MPa}$$

Soln:



$$\Delta U_{\text{sys}} = 0$$

$$N_0 = N_{Af} + N_{Bf}$$

$$P_0 V_A = P_{Af} V_A + P_{Bf} V_B$$

$$R T_0 \quad R T_{Af} \quad R T_{Bf}$$

$$U_i = N_0 C_v T_0$$

$$U_f = N_{Af} C_v T_{Af} + N_{Bf} C_v T_{Bf}$$

$$\Delta U = N_{Af} C_v (T_{Af} - T_0) + N_{Bf} C_v (T_{Bf} - T_0)$$

$$\Delta U = 0 = \frac{P_f V_A C_v}{R} (1 - \frac{T_0}{T_{Af}}) + \frac{P_f V_B C_v}{R} (1 - \frac{T_0}{T_{Bf}})$$

$$0 = \frac{P_f V_A C_v}{R} + \frac{P_f V_B C_v}{R} - \frac{P_f T_A C_v}{R} (V_A + V_B)$$

$$R \quad R \quad R \quad T_{Af} T_{Bf}$$

$$P_f = \frac{V_A P_0}{V_A + V_B} = \frac{10}{10} = 1 \text{ MPa}$$

Adiabatic expansion: $P_0 = 10 \text{ MPa}$ $T_0 = 30^\circ\text{C}$

$$T_{Af} = \left(\frac{P_0}{P_{Af}} \right)^{1-\frac{1}{\gamma}} T_0 = 155.38 \text{ K}$$

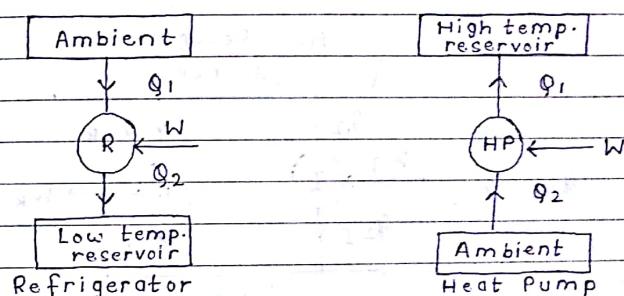
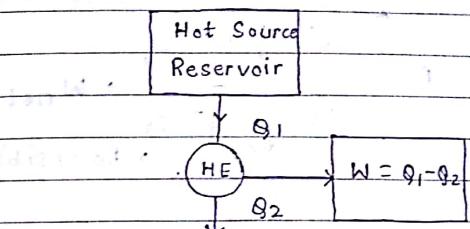
$$T_{Bf} = 334.6 \text{ K}$$

Date 24/01/2018

Saathi

SECOND LAW OF THERMODYNAMICS :-

All the devices are based on heat engines and heat pumps.



Effectiveness = $\frac{\text{Energy effect sought}}{\text{Energy expended}}$

$$\eta_{HE} = \frac{W}{Q_1}$$

$$(COP)_R = \frac{Q_2}{W} ; (COP) = \frac{Q_1}{W}$$

Coefficient of performance.

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