THERMODYNAMICS.

Thermodynamics :-

The study of the effect of work, heat and energy.

Types of system.

open system :-

The system in which mass and heat both are flow.

closed system :-

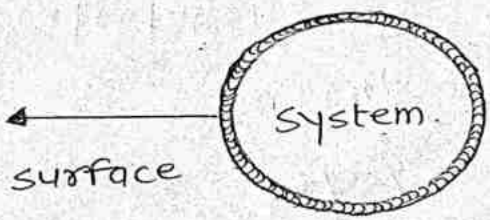
The system in which only heat transfer and no moss transfer.

Isolated system :-

No mass and no heat transfer.

system :-

The object| machine in which work done.



Boundary.

The outer surface of system.

separate the surrounding and system.

surrounding

The outer enviornment from system.

Prepared By:-
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First law of Thermodynamics.

★. Based on law of conservation of energy.

★. Energy nor be created and neither be destroyed only convert into one form to another.

★. In close system undergoing any thermodynamic cycle the cyclic integral of work and heat are proportional to each other.

Point function :-

A path function is a function whose value depends on path followed by the thermodynamic process.

example :- work.

Point function :-

A point function is a function whose value depends on final and initial states.

example :- density, enthalpy, internal energy.
entropy.

Extensive properties :-

Depend on the amount of matter. ex:- volume. mass energy.

Intensive properties :-

Doesnot depend on the amount of matter ex:- density. melting, Boiling point. Temperature.

Isobaric Process.

Constant Pressure. $P_1 = P_2$

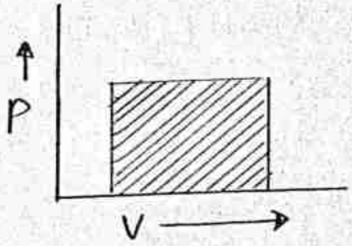
PVT Relationship.

$$P_1V_1 = nRT_1$$
$$P_2V_2 = nRT_2$$

$$\frac{P_1V_1}{P_2V_2} = \frac{n\cancel{R}T_1}{\cancel{n}RT_2}$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

PV - diagram.



Work done.

$$\delta W = PdV$$
$$= P(V_2 - V_1)$$

change in internal energy.

$$dv = mC_pdt.$$

Heat transfer.

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

Isochoric Process.

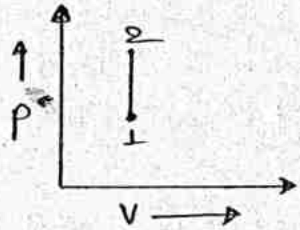
Volume = constant.

$V_1 = V_2$.

PVT Relationship.

$$\frac{P_1}{P_2} = \frac{T_1}{T_2}$$

PV diagram.



$$\text{slope} = \frac{dP}{dv}$$

$dv = 0$.

slope = ∞

change in internal energy.

$dV = m C_v dT$.

Work done.

$$\delta W = P dV = P(V_2 - V_1)$$

$\delta W = 0$.

Heat transfer.

$\delta Q = \delta W + dU$

$\delta Q = dU$.

Isothermal Hyperbolic Process.

Temperature = constant

$T_1 = T_2$

No change in Internal energy.

Extremely slow.

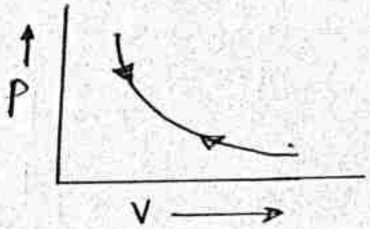
Ideal Process.

PVT Relationship.

$PV = \text{constant}.$

$P_1V_1 = P_2V_2.$

PV-diagram.



Heat transfer.

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

$$\delta Q = \delta W.$$

change in Internal energy.

$$dV = 0 = mC_v dT.$$

$$= mC_v(T_2 - T_1) = 0$$

Work done.

$$\delta W = P_1V_1 \ln \frac{V_2}{V_1}$$

$$= RT \ln \frac{V_2}{V_1}$$

or

$$P_1V_1 \ln \frac{P_2}{P_2}$$

$$RT \ln \frac{P_1}{P_2}.$$

Adiabatic | Isentropic Process.

No heat transfer. $\delta Q = 0$

Extremely fast.

Ideal Process.

PVT Relationship.

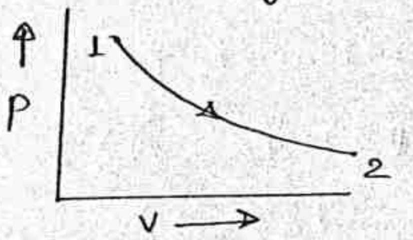
$$PV^{\gamma} = C$$

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

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

$$\frac{T_1}{T_2} = \left(\frac{P_1}{P_2}\right)^{\frac{\gamma-1}{\gamma}}$$

PV diagram.



change in internal energy

$$dV = MC_v dT.$$

Work done

$$dW = PdV$$

$$\delta W = PdV$$

$$\delta W = \frac{P_1V_1 - P_2V_2}{\gamma - 1}$$

$$\delta W = \frac{R(T_1 - T_2)}{\gamma - 1}$$

Heat transfer.

$$dQ = 0$$

Polytropic.

$$PV^{n} = C.$$

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A 2kW. 40 litre water heater is switched on for 20min. The heat capacity (C_p) for water is 4.2 kJ/kg·k assuming all electrical energy has gone into heating the water increases of temperature.

Energy supply = $du = mC_v\,dT$

$$2\,\frac{kJ}{s} \times 20\,min \times 60\,sec = 40 \times 4.2 \times dT$$

$$\Delta T = \underline{14.2\,K}.$$

A monoatomic ideal gas with $\gamma = 1.67$ m.wt = 40 is compressed adiabalically from 0.15MPa. 500K to 0.2 MPa. The work of compression of the gas in kJ/kg.

$P_1 = 0.1\,MPa.$ $P_2 = 0.2\,MPa.$

$T_1 = 300\,K$

$$\delta W = \frac{P_1V_1 - P_2V_2}{\gamma - 1}$$

$$= \frac{MR(T_1 - T_2)}{\gamma - 1}$$

	slope.	sp. h.
P = constant.	$n = 0$	C_p.
V = constant	$n = \infty$	C_v
T = constant	$n = 1$	cr
Adiabatic	$n = \gamma$	$C_v = 0$

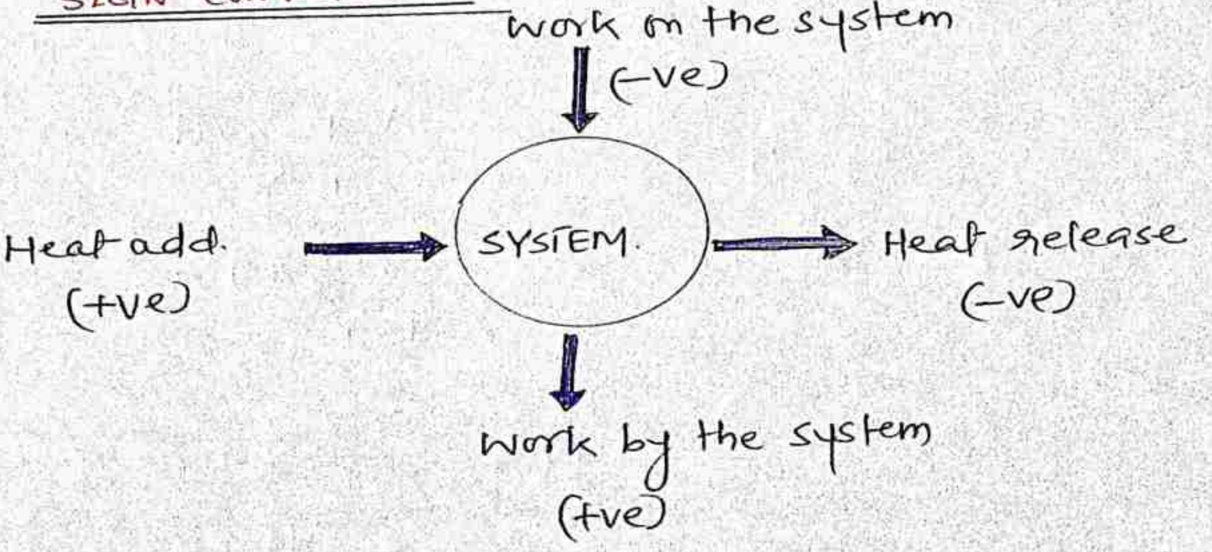
ENTHALPY.

sum of internal energy and flow energy

$U + PV = H$ = total energy.

open system → H
closed system → U

SIGN CONVERSION.



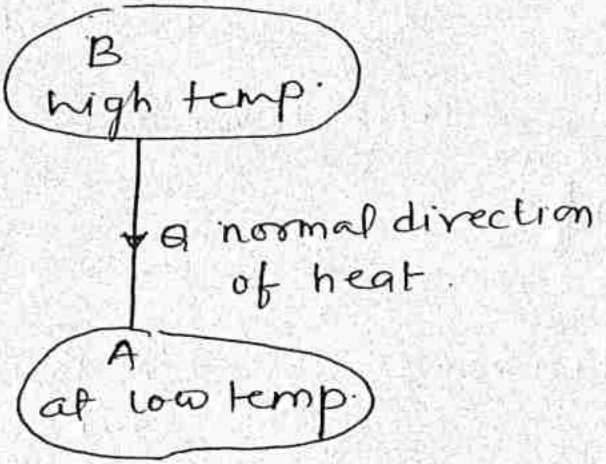
SECOND LAW OF THERMODYNAMICS.

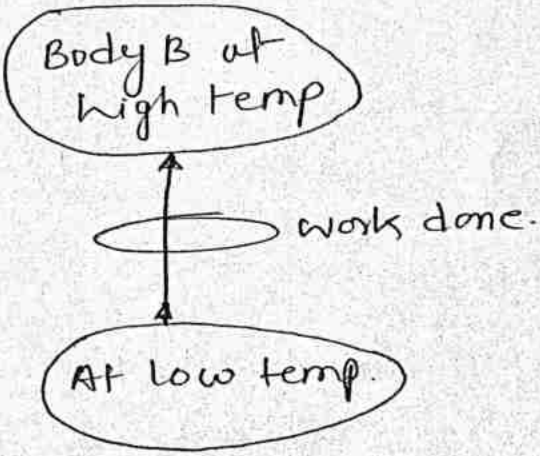
claussius statement :-

It is impossible to convert. operate in a thermodynamic cycle and produce no effect than transfer af heat from at low temperature to a body at high temperature.

Kelvin Plank statement.

It is impossible to construct a heat engine which would absorb heat from a reservior and convert 100% of the heat absorbed into work.





Thermal Reservior.

It is a body from which or to which any amount of heat is transferred without affecting it temperature.

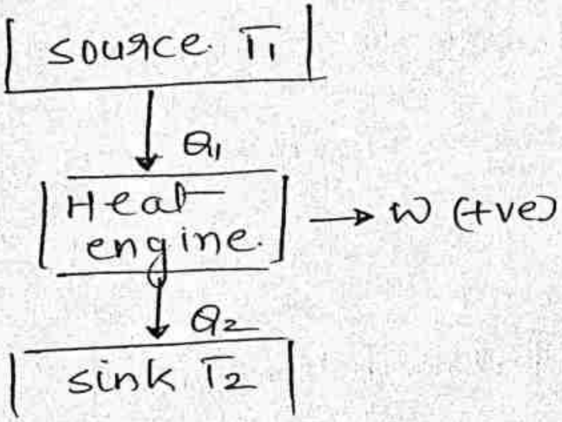
Type.
- source. maintain at high temp.
- sink. maintain at low temp.

Mean heat capacity of Reservior.

= Mass x specific heat

= M Cp.

Heat engine.



Thermal efficiency (η)

$$\eta = \frac{\text{output}}{\text{input}}$$

$$\eta = \frac{\text{work output}}{\text{heat input}}$$

$$\eta = \frac{W}{Q_1}$$

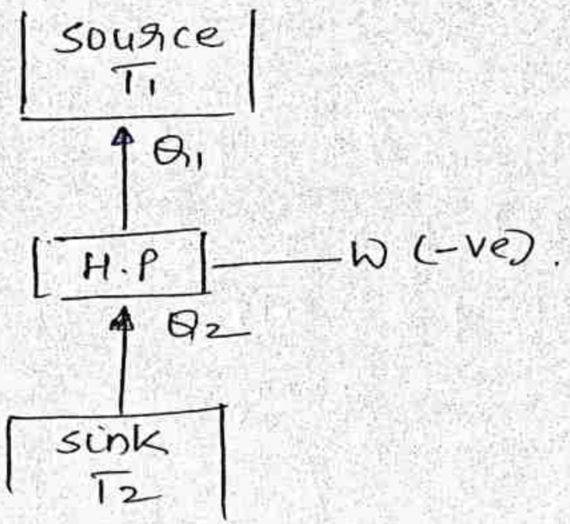
$$\eta = \frac{Q_1 - Q_2}{Q_1}$$

$$\eta = \frac{\cancel{Q_1}}{\cancel{Q_1}} - \frac{Q_2}{Q_1}$$

$$\eta = 1 - \frac{Q_2}{Q_1}$$

$$\eta = 1 - \frac{T_2}{T_1}$$

Heat Pump.



Aim :- To increase the temperature of source.

COP = coefficient of Performance

$$COP_{H.P} = \frac{\text{Desired effect}}{\text{work input}}$$

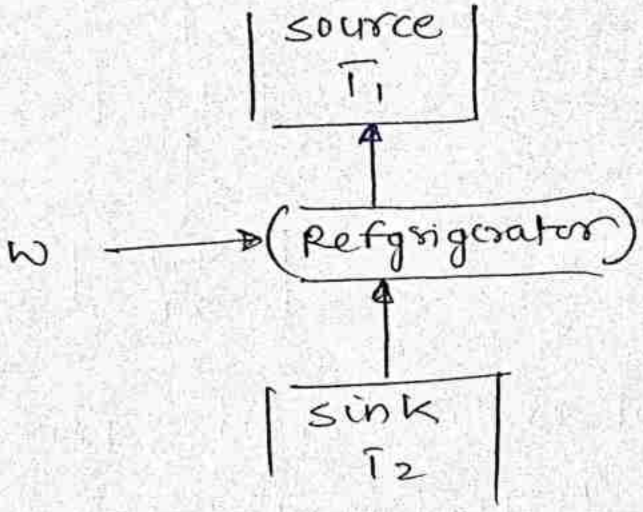
$$= \frac{Q_1}{W}$$

$$= \frac{Q_1}{Q_1 - Q_2}$$

$$= 1 - \frac{Q_1}{Q_2}$$

Refrigerator.

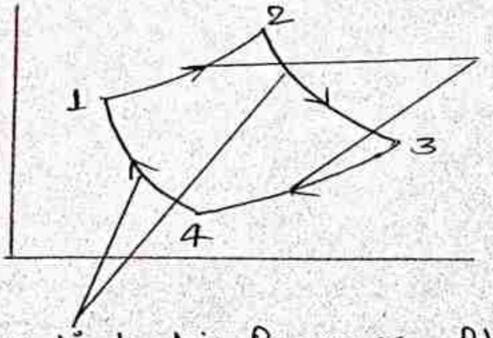
Aim :- To decrease the temperature of sink or lower temperature.



$$COP = \frac{\text{Desire effect}}{\text{work input}}$$

Carnot cycle.

- Used as heat engine
- Reversible or ideal or frictionless.



1 - 2 Reversible isothermal

$$Q = P_1 V_1 \ln \frac{V_2}{V_1}$$

2-3. Reversible adiabatic Process.

No heat transfer.

3- 4 Reversible isothermal Process.

$$Q = P_3 V_3 \ln \frac{V_4}{V_3}$$ (-ve) heat.

4 - 1 Reversible adiabatic Process.

No heat transfer.

$$Q_{net} = Q_1 - Q_2.$$

$$= P_1 V_1 \ln \frac{V_3}{V_1} - P_3 V_3 \ln \frac{V_4}{V_3}$$

Efficiency.

$$(\eta)\ \text{cycle} = \frac{W_{net}}{\text{Heat supplied.}}$$

$$= \frac{Q_1 - Q_2}{Q_1}$$

$$\eta = 1 - \frac{Q_2}{Q_1}$$

Entropy (S).

It is the property which will be increase in temp and decrease with decrease in temperature. remain constant when no heat supplied.

$$ds = \frac{dQ}{T} \quad (dQ \propto T)$$

$\frac{dQ}{T}$ → Independent of path.

It is a point function.

Thermodynamic property. extensive.

Perfect differential.

$\delta Q = +ve$.	$ds = +ve$
$\delta Q = -ve$.	$ds = -ve$.
$\delta Q = 0$	$ds = 0$.

1. $\oint \frac{dQ}{T} < 0$ for actual system.
Irreversible system due to friction.

2. $\oint \frac{dQ}{T} = 0$ claussius inequality.
for reversible system or frictionless.
for ideal system.

3. $\oint \frac{dQ}{T} > 0$ It is impossible.

Heat supply ↑ entropy ↓

Heat ↓ entropy ↓

Isobaric → Pressure = constant

$$ds = \frac{dQ}{T} = \frac{C_p dT}{T}$$

$$ds = C_p \ln \frac{T_2}{T_1}$$

$$\text{slope} = \frac{dT}{ds} = +ve.$$

Isochoric → volume = constant

$$ds = \frac{dQ}{T} = \frac{C_v dT}{T}$$

$$ds = C_v \, lm \frac{T_2}{T_1}$$

$$\text{slope} = \frac{dT}{ds} = +ve.$$

Isothermal → Temperature = constant.

$$ds = \frac{dQ}{T} = \frac{dW}{T}$$

$$= \frac{PdV}{T}$$

$$ds = \frac{R\cancel{T} \ln \frac{V_2}{V_1}}{\cancel{T}} \qquad ds = R \ln \frac{V_2}{V_1}$$

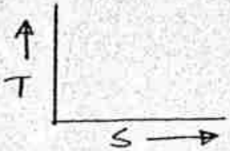
$$\text{slope} = \frac{dT}{ds} = \frac{0}{ds} = 0$$

Adiabatic

Entropy remain constant.
Because in this process. no heat supply and no heat rejected.

slope = ∞

entropy - T-s diagram.



A heat engine operate at 75% of max speed possible efficiency ratio at heat source temp to heat sink temp is 5|3.

(a) 0.2 [✓ (b) 0.3] (c) 0.4 (d) 0.6

$$\frac{T_1}{T_2} = \frac{5}{3} \quad \eta = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}$$

$$1 - \frac{3}{5} = 0.4$$

$$\eta = \frac{W}{0.75H}$$

$$0.4 = \frac{W}{0.75H}$$

$$W = 0.3 \times H$$

For a carnot refrigerator operating between 40°C and 25°C the COP is .

(a). 1 b (1.67) [✓ c 19.88] d 39.44.

$T_2 = 273 + 25 = 298\,K.$

$T_1 = 273 + 40 = 313\,K.$

$$COP = \frac{T_2}{T_1 - T_2} = \frac{298}{313-298} = \frac{298}{15} = 19.88.$$

Qus. A cyclic heat engine exchange heat with two reservior maintain at 100°C and 300°C respectively The maximum amount of work in Joule that can be obtain from 1000 Joule of feed. extracted from hot reservior is.

[✓ (a) 349] (b) 651 (c) 667 (d) 1000.

$$\eta = \frac{W}{Q_1} = \frac{T_1 - T_2}{T_1}$$

$$W = Q_1 \frac{T_1 - T_2}{T_1}$$

$$W = 1000\left(\frac{573 - 373}{573}\right)$$

$W = 349$

Ist law based on intenal energy.

IInd law entropy, flow of heat in opposite direction.

Zeroth law :- If two system are in thermal equilibrium.
with a third system. then they are in
thermal equilibrium with each other.

IIIrd law :- At absolute zero temperature, absolute
entropy is minimum for all the system.

★. Entropy $\propto$ irreversible process.
★. Entropy increases for closed system.
★ microscopic property = study about gas molecule.
★ macroscopic property = effect of action of molecule.

★ for incompressible fluid - PVT are not applicable.

★ Two parameter theorem - Temperature falls.
decreases.
Pressure decreases.
Temperature increase. Pressure increase.

★ Three parameter theorem - Reduce temperature.
Reduce pressure
Reduce eccentric factor.

Ecentric factor (ω).

$-1-\log_{10}(P_r)_{\text{saturation}}$ $\qquad r = 0.7$

for single fluid $\omega = 0$.

- ★ for ideal gas law - high temperature and low pressure.
- ★ latent heat of vapourisation at constant temp. is always zero.
- ★ Two reversible adiabatic path cannot be intersect with each other.

Relationship between critical temperature and latent heat.

$$\frac{\lambda_2}{\lambda_1} = \frac{1 - T_{r_2}}{1 - T_{r_1}}$$

λ_2, λ_1 = latent heat.

T_{r_1}, T_{r_2} = critical temp.

<u>Thermal expansion coefficient.</u>

$$\beta = \frac{\left(\frac{\partial v}{\partial T}\right)_P}{V}$$

for ideal gas $\beta = \frac{1}{T}$

Density $(\alpha) = -\frac{1}{\rho}\left(\frac{d\rho}{dT}\right)_P$

incompressible fluid $\alpha, \beta = 0$

Relationship between: U H S A and G.

for I st law. $dQ = dW + dU$

$ds = \frac{dQ}{T}$

$dQ = Tds$.

$dw = PdV$

$$Tds = PdV + dU$$

$$\left(\frac{dT}{dV}\right)_s = \left(\frac{dP}{ds}\right)_V$$

for enthalpy $H = U + PV$

$$dH = dU + PdV + VdP$$

$\therefore dU = Tds - PdV$

$$= Tds - PdV + PdV + VdP$$

$$Tds = dH - VdP$$

$$\left(\frac{dT}{dP}\right)_s = -\left(\frac{dV}{ds}\right)_P$$

From. Gibbs. free. energy $G = H - TS$.

$$dG = dH - Tds - SdT$$

$$dG = \cancel{Tds} + VdP - \cancel{Tds} - SdT$$

$$dG = VdP - SdT$$

$$-VdP = dG + SdT$$

$$\left(\frac{dV}{dT}\right)_P = \left(\frac{ds}{dP}\right)_T$$

Helmolthz free energy A | E

$$A = U - TS.$$

$$dA = dU - Tds - sdT$$

$$dA = \cancel{Tds} - PdV - \cancel{Tds} - SdT$$

$$dA = -PdV - sdT$$

$$\left(\frac{dP}{dT}\right)_s = + \left(\frac{ds}{dv}\right)_T$$

Relationship between. Cp. Cv α and β.

Cp = specific heat at constant Pressure.

Cv = specific heat at constant volume.

β = Thermal expansion.

α = Thermal compressibility.

$$C_p = \left(\frac{dH}{dT}\right)_p \quad \text{or} \quad T\left(\frac{ds}{dT}\right)_p$$

$$C_v = \left(\frac{dU}{dT}\right)_v \quad \text{or} \quad T\left(\frac{ds}{dT}\right)_v$$

$$C_p - C_v = R.$$

$$C_p - C_v = T\left(\frac{ds}{dT}\right)_p - T\left(\frac{ds}{dT}\right)_v$$

$$= T\left(\frac{ds}{dT}\right)_p - \left(\frac{ds}{dT}\right)_v$$

$$C_p - C_v = \frac{T\beta^2 V}{\alpha}.$$

Relationship PVT AS GV and M

$$T = \left(\frac{dU}{ds}\right)_V \quad T = \left(\frac{dH}{ds}\right)_P$$

$$P = -\left(\frac{dU}{dV}\right)_s \quad P = -\left(\frac{dA}{dV}\right)_T$$

$$V = \left(\frac{dH}{dP}\right)_s \quad V = \left(\frac{dG}{dP}\right)_T$$

$$S = -\left(\frac{dG}{dT}\right)_P \quad S = -\left(\frac{dA}{dT}\right)_V$$

Tds. equation.

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

$$ds = \left(\frac{dT}{ds}\right)_V + \left(\frac{dv}{ds}\right)_T$$

multiply with T

$$Tds = T\left(\frac{dT}{ds}\right)_V + T\left(\frac{dv}{ds}\right)_T$$

$$Tds = C_v dT + T\left(\frac{dP}{dT}\right)_T dV$$

$$Tds = C_p dT - T\left(\frac{dv}{dT}\right)_P dP.$$

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$$Tds = \left(\frac{dT}{dP}\right)_v C_v dP + \left(\frac{dT}{dv}\right)_P C_p dv$$

$$\left(\frac{ds}{dP}\right)_\mu = \frac{-v}{T}$$

$$\left(\frac{ds}{dv}\right)_u = \frac{P}{T}$$

Joule Thomson co.efficient.

$$\mu = \left(\frac{dT}{dP}\right)_h.$$

$\mu > 0$ temp increases

$\mu = 0$ temp constant

$\mu < 0$ temp decreases.

Clapeyorn equation.

Determine the enthalpy change associate with phase change.

$$\left(\frac{dP}{dT}\right) = \left(\frac{ds}{dv}\right)_T = \frac{s_f - s_g}{v_f - v_g}.$$

s_f = entropy of liquid v_f = volume of liquid.

s_g = entropy of gas. v_g = volume of gas.

During the phase change process. the pressure. saturation pressure which depend upon the temperature only and independent of volume.

$$\left(\frac{dP}{dT}\right) = \frac{h_{f,g}}{T, v_{fg}}$$

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{h_{fg}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

<u>Claypleyon. claussius. equation</u>

$$\frac{dP}{dT} \rightarrow \text{slope}$$

for isolated system :-

saturation entropy is total energy of system and volume remain constant.

Partial molar Properties

$$G = f(P.T, n_1, n_2 \ldots n_i)$$

n_i = no. of moles.

$$dG = \left(\frac{dG}{dT}\right)_{P\, n_1, n_2 \ldots} dT + \left(\frac{dG}{dP}\right)_{T\, n_1, n_2 \ldots} dP + \left(\frac{dG}{dN_i}\right)_{T.P} dN_i$$

$$\overline{G_i} = \left(\frac{dG}{dT}\right)_{P, n_1, n_2}$$ Partial molar Properties.

If temp and pressure constant

$$dG_{P.T} = \Sigma \overline{G_i}\, dn_i$$

Gibbs Phase Rule.

When the equillibrium between no. of phase is influence by only temperature, pressure and composition but not by gravity magnetic force etc.

Gibbs. Helmoltz equation

$$\frac{d}{dT}\left(\frac{\Delta G}{T}\right) = \frac{-\Delta H}{T^2}$$

$$\ln \frac{k_2}{k_1} = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

K = Rate constant.
thermal constant.

Equillibrium.

mechanical equillibrium.

At which there are all forces are in balance. condition.

Thermal equillibrium

Temperature = constant

chemical equillibrium.

forward reaction = backward reaction.

Take place in close system.

$\Delta G = 0$.

applicable only for reversible.

Has dynamic nature.

$$aA + bB \rightleftharpoons cC + dD$$

rate of forward reaction $= K_f [A]^a [B]^b$.

rate of backward reaction $= K_b [C]^c [D]^d$.

at equilibrium

$$K_f [A]^a [B]^b = K_b [C]^c [D]^d.$$

$$K_c = \frac{K_f}{K_b} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$K_p = K_c [RT]^{\Delta n}$. $\Delta n = (c+d) - (a+b)$

Δn : +ve $K_p > K_c$

$\Delta n = 0$ $K_p = K_c$

~~$\Delta n <$~~

Δn = −ve $K_p < K_c$

$K_p = K_x P^{\Delta r}$

$K_c = K_x \left(\frac{n}{V}\right)^{\Delta r}$

Enthalpy depend on temperature and independent on volume.

CCl4 boils at 76°C and 101 kPa. The latent heat of vapourisation for CCl4 is 195 kJ/kg and gas constant R = 0.55 kJ/kg·k find the boiling temperature of CCl4 at 202 kPa.

$T = 76°C$ $P = 101 \cdot kPa$. $h_{fg} = 195\ kJ/kg$.

$T_2 = ?$ $P_2 = 202\ kPa$.

$$\ln \frac{P_1}{P_2} = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$T = 1374.5\ K$.

Sensible heat. $Q = Mc_p dT$.

Latent heat $= \Delta h = m\lambda$.

−10°C Ice (solid) $\xrightarrow{\text{heat}}$ 0°C Ice solid.

sensible heat of ice can be measured by thermometer.

0°C Ice (solid) $\xrightarrow{\text{heat}}$ water (liquid)

latent heat of melting.

0°C water (liquid) $\xrightarrow{\text{heat}}$ 100 water (liquid)

sensible heat of liquid.

100°C water $\xrightarrow{\text{heat}}$ 100°C dry and saturated steam. (gaseous)

latent heat of vapourisation.

100°C Dry and saturated (steam) gaseous. $\xrightarrow{\text{heat}}$ sensible heat and super heated system.

$\Delta G < 0$ Process is spontaneous in forward direction.

$\Delta G > 0$ Process is spontaneous in backward direction.

$\Delta G = 0$ Process is reversible not change in chemical Potential is zero.

<u>Ideal gas</u> — There is no interaction between molecules.

<u>Real gas</u> - Just opposite of ideal gas.

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Fugasity (F) $dG = VdP - SdT$

$PV = RT$

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

at isothermal condition

$$dG = VdP$$

$$dG = \frac{RT}{P}\,dP$$

for Ideal gas.

$$dG = RT\,d\,(\ln P)$$

$$\int_{G_1}^{G_2} dG = RT \int_{P_1}^{P_2} d\,\ln P$$

$$\Delta G = G_1 - G_2 = RT \ln\left(\frac{P_2}{P_1}\right)$$

for Real gas.

$$dG = RT\,d\,(\ln F)$$

$$dG = RT\,d\,(\ln F) = \int_{G_1}^{G_2} dG = RT \int_{F_1}^{f_2} d\,(\ln F)$$

$$\Delta G = RT \ln\left(\frac{f_2}{f_1}\right)$$

equation (i) and (ii)

$$\frac{f_2}{f_1} = \frac{P_2}{P_1}$$

fugasity $\propto$ Pressure $f \uparrow$ $p \uparrow$

$$f = cP$$

$$\frac{f}{P} = c$$

for ideal gas = $c = 1$ $f = P$

fugacity co.efficient (ϕ)

$$= \frac{\text{fugasity of gas}}{\text{Pressure of ideal gas}}$$ same temperature

$$\phi = \frac{f}{P} \qquad f = \phi P$$

for Real gas.

compressibility factor (z) = $\dfrac{\text{volume of real gas}}{\text{volume of ideal gas.}}$

$$z = \frac{V}{\frac{RT}{P}}$$

$$\ln(\phi) = \int_0^P \left(\frac{z-1}{P}\right) dP$$

suppose $\phi = 1$ $f = P$

* $P \longrightarrow 0$ $\phi \Longrightarrow 0$

Real gas → ideality

$P \longrightarrow \infty \quad \phi \longrightarrow 0$

Real gas ⟶ Away from ideality.

Activity (a) => Ratio of fugacity to fugacity in standard state for pure substance.
(Relative fugasity)

$$a = \frac{f}{f^\circ}$$

$$\Delta G = RT \ln \left(\frac{f}{f^\circ}\right)$$

$$\Delta G = RT \ln a.$$

Lewis Randall. Model.

fugasity of component in an ideal solution is directly proportional to molar fraction of the component in solution.

$$\hat{f}_i \propto x_i$$

$$\hat{f}_i = x_i f_i$$

for a liquid $\hat{f}_i$ = fugasity of i in ideal solution.

x_i = molar fraction of i in ideal solution.

f_i° = fugacity of i in pure state.

Validity ✯ At low Pressure.

✯ component concentration is present in excess condition.

✯ When physical property of all component are nearly same.

Limitation :— is not applicable for high Pressure

✯. valid only for gaseous mixture at low Pressure.

✯. Not valid for all the liquid mixture.

Raults law :- The partial Pressure of the component in the ideal solution directly proportional to the mole fraction in the liquid solution.

$\bar{P_i} \propto y_i$ $\qquad \hat{f_i} = x_i f_i$

fugacity of i in ideal

For dilute ideal solution :- The fugacity of component is directly proportional to molar fraction of component in solution.

$\hat{f_i} \propto x_i$

Activity: $a_i = \frac{\hat{f}_i}{f_i}$

for ideal solution $a_i = x_i$

Real solution $a_i \propto x_i$

$a_i = \gamma_i x_i$ $\frac{a_i}{x_i} = \gamma_i$

γ_i = activity coefficient.

Phase Rule | Gibbs Phase Rule.

Relation between no. of phase, no. of species · no. of intensive property

for Non. reacting system.

$F = C - \pi + 2$

F = degree of freedom.
C = no. of chemical species.
π = no. of phase present in the system.
2 = no. of intensive property.

$F < 0$ = system is in dis.equilibrium.

for Reacting system.

$F = C - \pi + 2 - r$

r = no. of independent chemical reaction.

Solution. (4) X_1 = initial moisture content on dry basis

$x_1 = \frac{67}{100} = 0.67$

$$X_1 = \frac{0.67}{1-0.67} = 2.03$$

X_2 = final moisture content on dry basis

$x_2 = \frac{25}{100} = 0.25$

$$X_2 = \frac{0.25}{1-0.25} = 0.333$$

X^* = eq. moisture content

$x^* = \frac{1}{100} = 0.01$

$$X^* = \frac{0.01}{1-0.01} = 0.0101$$

X_c = critical moisture content

$x_c = \frac{40}{100} = 0.40$

$$X_c = \frac{0.40}{1-0.40} = 0.67$$

R_c = Rate of drying in the const. rate period
= 1.5 kg/m²h (given)

$$\frac{A}{W'} = 0.5 \Rightarrow \frac{W'}{A} = 2$$

The time req. for drying is given by

$$t = \frac{W'}{AR_c}\left[(X_1 - X_c) + (X_c - X^*) \ln \frac{X_c - X^*}{X_2 - X^*}\right]$$

$$t = \frac{2}{1.5}\left[(2.03 - 0.67) + (0.67 - 0.0101) \ln \frac{0.67 - 0.0101}{0.333 - 0.0101}\right]$$

t = 2.44 Hrs. Ans.

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Solution(6) Basis 100 kg of feed solution

It contains 48 kg $Na_2S_2O_3$ and 52 kg of water

Let "c" be the yield of crystal

m_1 = mol. wt. of $Na_2S_2O_3$ = 158

m_2 = mol. wt. of $Na_2S_2O_3 \cdot 5H_2O$ = 248

x'_f = wt fraction of solution in the feed solution

$$= \frac{wt\%}{100} = \frac{48}{100} = 0.48$$

M.B. of water

water in feed = water in crystals + water in mother liq.

$$52 = c\,\frac{m_2 - m_1}{m_2} + L'$$

$$L' = 52 - c\,\frac{m_2 - m_1}{m_2}$$

$$L' = 52 - c\left[\frac{248-158}{248}\right]$$

M.B. of solute :—

Solute in feed = solute in crystals + solute in M.L.

$$0.48 \times 100 = c\left(\frac{m_1}{m_2}\right) + L'x'$$

$$0.48 \times 100 = c\left(\frac{158}{248}\right) + \left[52 - c\left[\frac{248-158}{248}\right]\right] \times \frac{70}{100}$$

$$48 = 0.637c + [52 - 0.363c] \times 0.70$$

$$c = 30.3 \text{ kg}$$

Yield of $Na_2S_2O_3 \cdot 5H_2O$ crystals = 30 kg

$Na_2S_2O_3 \cdot 5H_2O$ in the feed solution $= 48 \times \frac{248}{158} = 73.34$ kg

% yield of hydrated crystals $= \frac{30.3}{73.34} \times 100 = 41.31\%$

Ans

Abhishek Sao

Solution
(4)

Basis - 1000 kg of solution at 353 K (80°C)

$f = 1000$ kg

x'_f = weight fraction of $MgSO_4$ in feed

$= \frac{64.2}{164.2} = 0.391$

Water in the feed solution

$= f(1 - x'_f)$

$= 1000(1 - 0.391) = 609$ kg

V = kg of water evaporated during cooling

$= 609 \times \frac{10}{100} = 60.9$ kg

x' = Solubility of $MgSO_4$ at 303 K = 40.8 kg/100 kg of water

M_1 = mol. wt. of $MgSO_4$ = 120

M_2 = mol. wt of $MgSO_4 \cdot 7H_2O$ = 246

C = yield of $MgSO_4 \cdot 7H_2O$ crystal from feed soluti

$M_2 - M_1$ = water of crystallisation

$246 - 120 = 126$

Material Balance of $MgSO_4$

$$x'_f f = C\frac{M_1}{M_2} + \left[f(1-x'_f) - V - C\left(\frac{M_2-M_1}{M_2}\right)\right]x'$$

$MgSO_4$ in feed = $MgSO_4$ in hydrated crystal + $MgSO_4$ in mother liquor

$$0.391(1000) = C\left(\frac{120}{246}\right) + \left[1000(1-0.391) - 60.9 - C\left(\frac{126}{246}\right)\right]\frac{40.8}{100}$$

$$391 = 0.488C + [609 - 60.9 - 0.512C](0.408)$$

$MgSO_4 \cdot 7H_2O$ yield $(C) = 599.7$ kg Ans