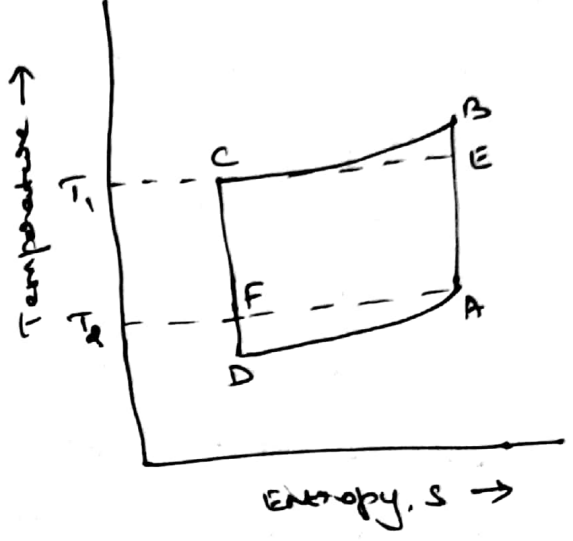
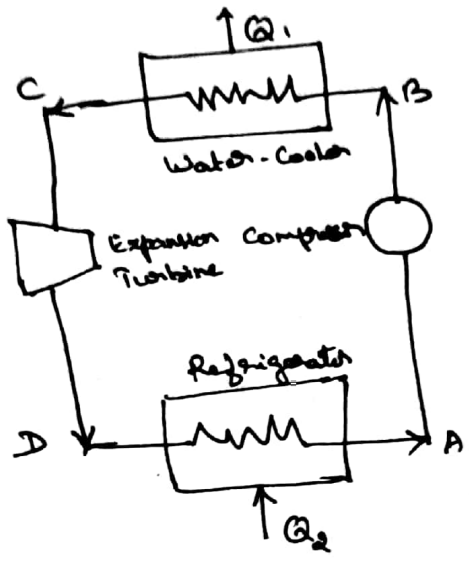


15. (a) Air - refrigeration cycle



The air-refrigeration cycle is illustrated in figure. Here, the working fluid is air, which undergoes no phase change in the unit. The air is compressed adiabatically to a pressure P_1 and temperature T_1 in the compressor (AB). In the cooler, it is then cooled at constant pressure P_1 (BC). The air at pressure P_1 is expanded in an engine or a turbine to a pressure P_2 , which is an ideal case, is equal to the pressure of air at the compressor intake (CD). The work output of the expander contributes a part of the work requirement of the compressor. The gas leaving the expander is passed through the refrigerator, where it absorbs heat at constant pressure P_2 (DA). The gas leaving the refrigerator enters the compressor, and the cycle is repeated.

On the T-s diagram, T_1 is the temperature of the cooling water and T_2 is the temperature to be maintained in the refrigerator. The area under the

(23)

Curve DA down to the S-axis is the heat absorbed in the refrigerator and the enclosed area ABCD is the work required for the removal of heat. It can be easily shown that, an ideal Carnot refrigerator operating between temperature levels T_1 and T_2 removes greater amount of heat with less work than an air-refrigeration machine.

Let the rate of air circulation be m . Assume that the heat capacity of air remains constant during the cycle. Then, heat absorbed is

$$Q_2 = m c_p (T_A - T_D)$$

and the heat rejected is

$$Q_1 = m c_p (T_B - T_C)$$

The net work required is

$$W = Q_1 - Q_2 = m c_p [(T_B - T_C) - (T_A - T_D)]$$

The coefficient of performance of an air-refrigeration machine is

$$COP = \frac{Q_2}{W} = \frac{T_A - T_D}{(T_B - T_C) - (T_A - T_D)} \quad \text{--- (1)}$$

The initial and final temperatures of the fluid undergoing adiabatic process are related to the initial and final pressures.

$$\frac{T_B}{T_A} = \left(\frac{P_1}{P_2} \right)^{\frac{\gamma-1}{\gamma}} = \frac{T_C}{T_D} \quad \text{--- (2)}$$

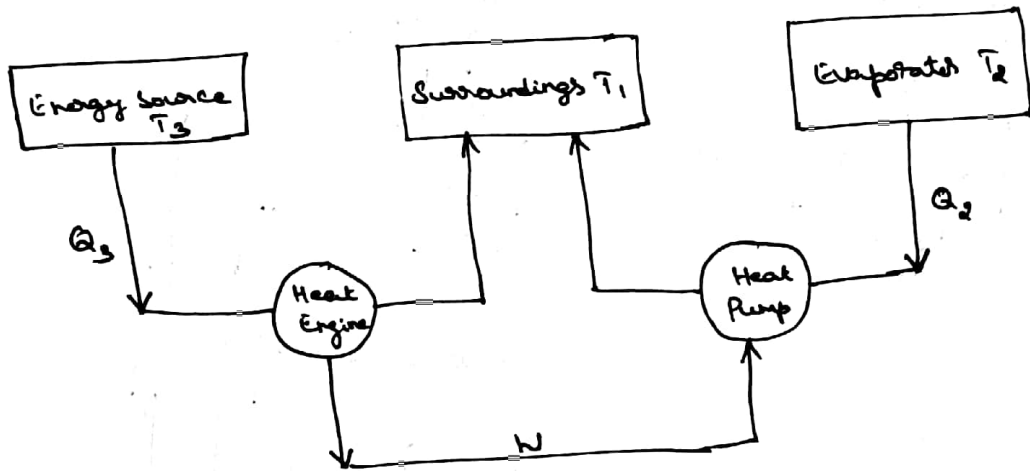
Using equation (2),

$$T_B - T_C = (T_A - T_D) \left(\frac{P_1}{P_2} \right)^{\frac{\gamma-1}{\gamma}} \quad \text{--- (3)}$$

Substitute (3) into (1)

$$\text{COP} = \frac{1}{\left(\frac{P_1}{P_2} \right)^{\frac{\gamma-1}{\gamma}} - 1} = \frac{T_A}{T_B - T_A} \quad \text{--- (4)}$$

(b) Absorption Refrigeration



The principle behind absorption refrigeration is illustrated in figure. For a refrigeration rate of Q_2 kJ/h, the minimum work required when the refrigerator and the condenser are at temperatures T_2 and T_1 respectively is given by

$$W = Q_2 \frac{T_1 - T_2}{T_2} \quad \text{--- (1)}$$

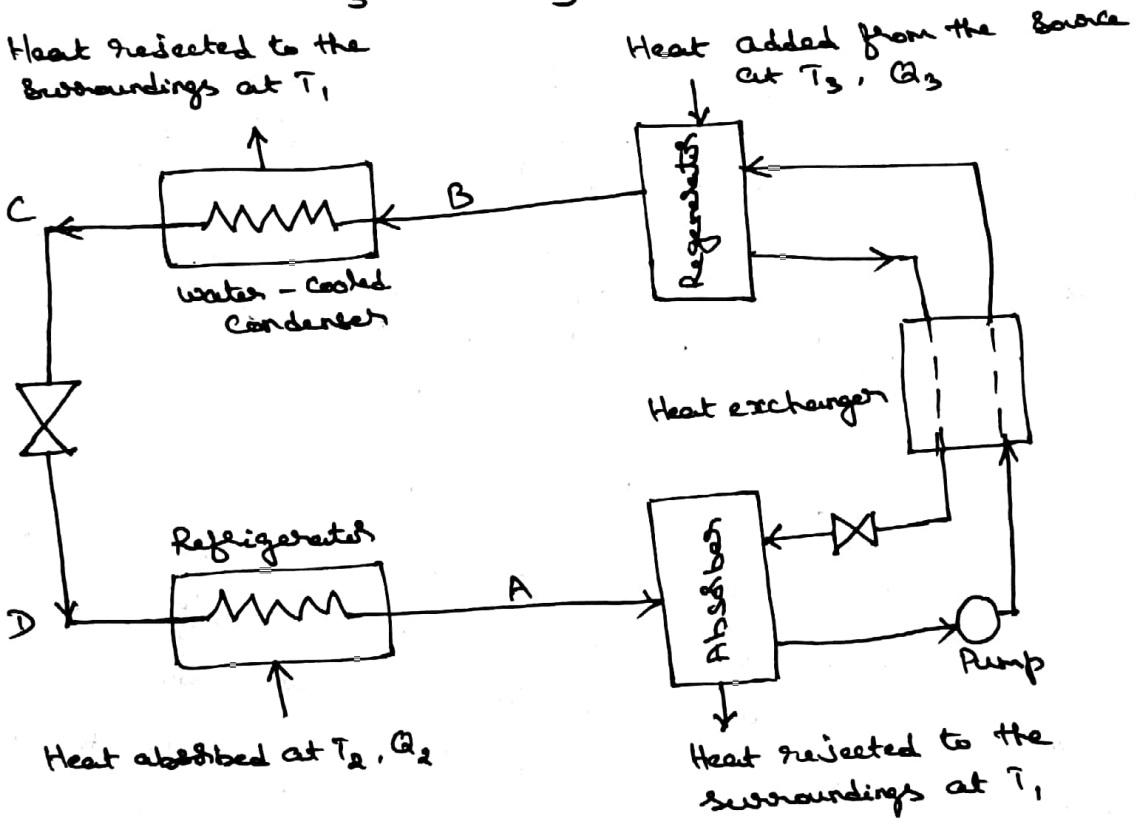
In order to deliver a work equal to W , a heat engine operating between a high-temperature source at T_3 and the surroundings at T_1 should absorb a quantity of heat Q_3 , where

$$Q_3 = W \frac{T_3}{T_3 - T_1} \quad \text{--- (2)}$$

Sub eqn (1) in (2); $Q_3 = Q_2 \frac{T_1 - T_2}{T_2} \frac{T_3}{T_3 - T_1} \quad \text{--- (3)}$

Equation (3) gives the amount of heat from a high temperature source required to obtain a refrigeration capacity of Q_2 . The ratio (Q_2/Q_3) , which is the refrigeration obtained per unit quantity of high temperature heat, is known as the efficiency of an absorption refrigeration cycle.

$$\frac{Q_2}{Q_3} = \frac{T_3 - T_1}{T_3} \frac{T_2}{T_1 - T_2} \quad \text{--- (4)}$$

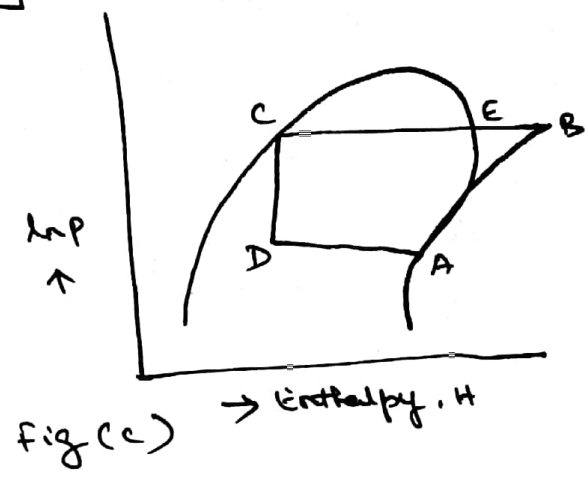
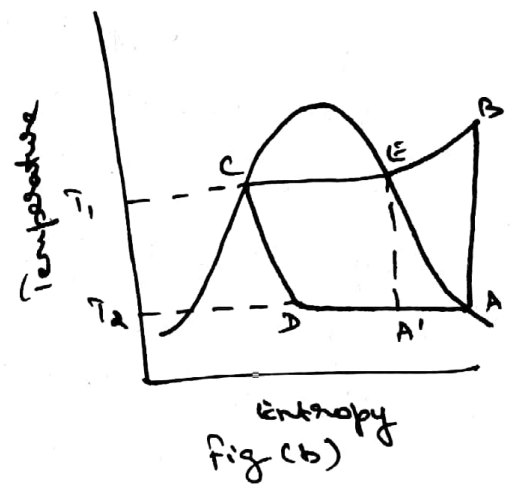
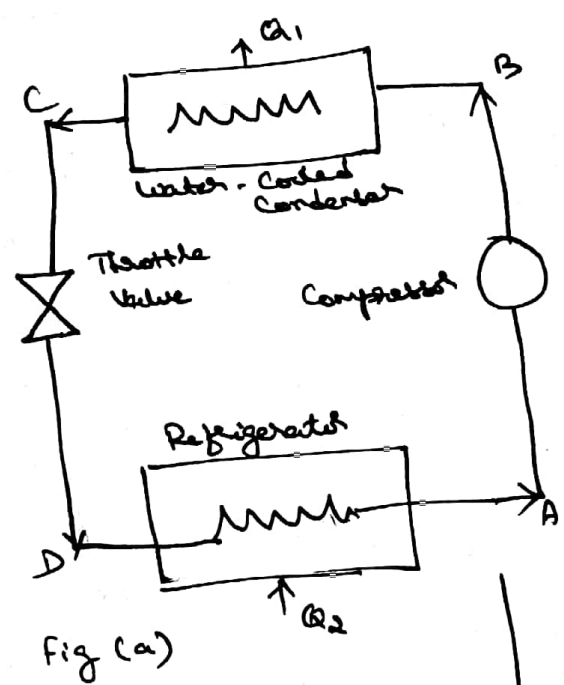


The compressor unit is replaced by an absorber - regenerator combination as shown in figure. Heat is liberated when the refrigerant vapour is absorbed in a non-volatile solvent. A typical absorption refrigeration cycle for moderate temperature applications uses water as the refrigerant and lithium bromide solution as the absorbent. For lower temperatures, ammonia is used as the absorbent and water as the solvent. The heat liberated during absorption is discarded to the surroundings at temperature T_1 . The liquid leaving

(26)

the absorber is a solution of the refrigerant in a relatively non-volatile solvent. It is pumped through a heat exchanger as shown in figure. The temperature and pressure of the solution increase when the liquid reaches the regenerator. Regeneration of the refrigerant is achieved by evaporating it from the solution and the heat required for this is absorbed from the source at T_3 . Low-pressure steam is usually used as the source. The regenerated absorbent liquid, which is almost free of the refrigerant, is cooled by passing through the heat exchanger. The heat given off by the solvent is utilized to raise the temperature of the solution leaving the absorber. The solvent is recycled to the absorber.

(C) Vapour - Compression Cycle



(27)

In the vapour compression cycle shown in Fig. (a), the refrigerant vapour is compressed (AB) to such a pressure that the available cooling water can condense the vapour in a condenser (BC) operated at this pressure which is maintained constant. The vapour, during condensation rejects heat to the cooling medium. By passing through a throttling valve, the pressure of the liquid leaving the condenser is reduced (CD) to the pressure maintained in the evaporator. The liquid then evaporates (DA), absorbing heat at constant temperature T_2 . The vapour thus produced enters the compressor, and the cycle is repeated. The process is represented on the T-s diagram as shown in Fig. (b). The liquid portion of the refrigerant leaving the throttling valve is vaporized at constant pressure P_2 and constant temperature T_2 in the refrigerator. The vapour leaving the refrigerator is saturated (A). It is possible that the vapour leaving the refrigerator may get slightly superheated & may be slightly unsaturated. On adiabatic compression, the vapour gets superheated (B) and this vapour enters the condenser at pressure P_1 . The reversible adiabatic compression is an isentropic process and is represented by the vertical line AB. In the condenser, the vapour is first cooled and the superheat is removed from the vapour, as shown by the line BE, and then it is condensed at constant temperature T_2 . The saturated

liquid (c) leaving the Condenser is expanded by throttling. The throttling is a constant enthalpy process and is represented by the curve CD. Throttling results in the partial vaporisation of the liquid, and the point (D) representing the mixture leaving the valve lies in the two-phase region. Fig (c) shows the Vapour - Compression Cycle on a pressure - enthalpy diagram.

As the heat absorption in the refrigerator occurs at constant pressure, the heat absorbed during vaporisation is equal to the change in the enthalpy of the refrigerant.

$$Q_2 = H_A - H_D \quad \text{--- (1)}$$

The heat rejected is

$$Q_1 = H_B - H_C \quad \text{--- (2)}$$

Since the work required, $w = Q_1 - Q_2$, and $H_D = H_C$ (the process CD is isenthalpic),

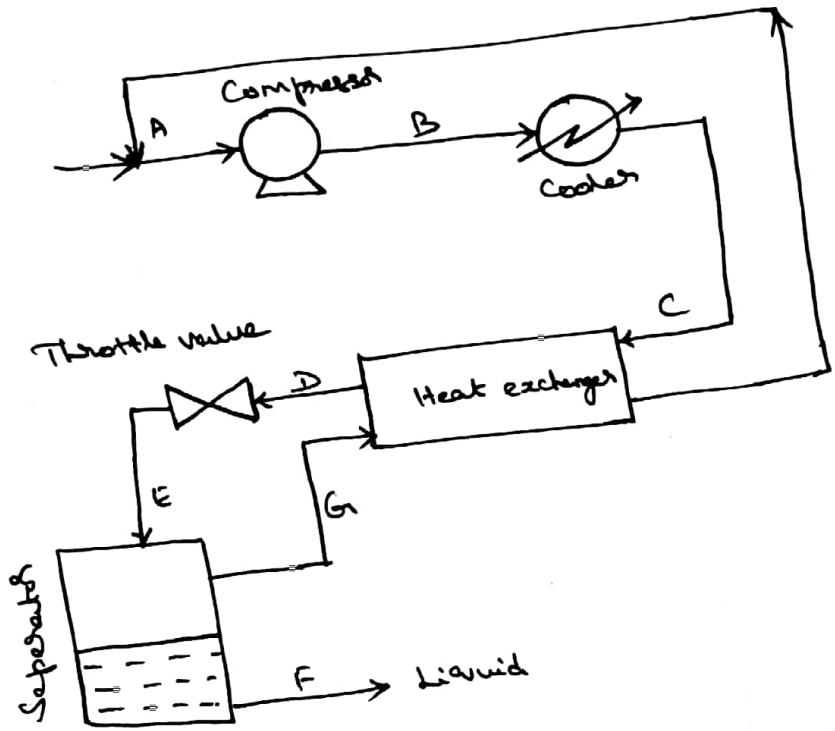
$$w = H_B - H_A \quad \text{--- (3)}$$

The Coefficient of performance is

$$COP = \frac{Q_2}{w} = \frac{H_A - H_D}{H_B - H_A} \quad \text{--- (4)}$$

16. (a) The Linde Process for gas-liquefaction:

The Linde process for gas liquefaction works on the principle of Joule - Thomson expansion. The Linde process for liquefaction of air is shown in the figure.

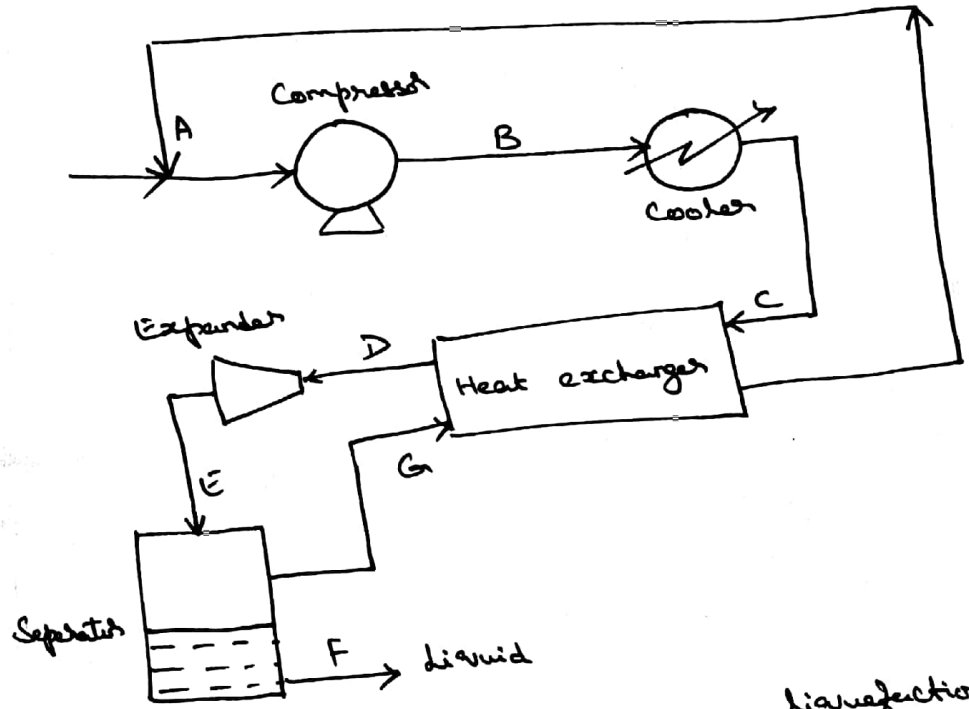


The temperature of the air at the upstream side of the throttle valve is reduced to a sufficiently low value so that the constant enthalpy lines cut into the two-phase region. The cooling of air is achieved by passing it counter-currently to the unliquefied part of the air leaving the throttling valve. Fresh air and the unliquefied air form the input to the compressor. Air leaving the compressor is cooled by ambient air & by cooling water and subsequently by counter-current heat exchange with the recycled air. In the throttling valve, a fraction of the gas is liquefied. By applying the first law, it can be shown that the fraction x of the liquefied air is given by

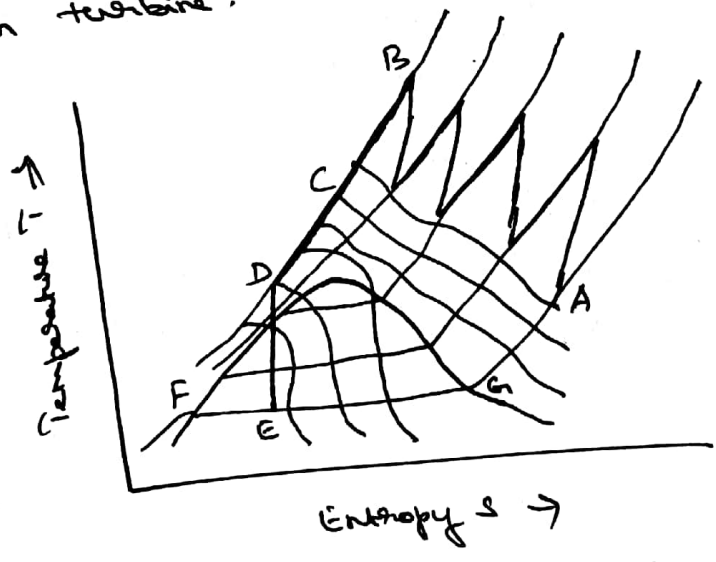
$$H_c = x H_f + (1-x) H_a$$

$$x = \frac{H_c - H_a}{H_f - H_a}$$

(b) The Claude process for gas liquefaction:



The Claude process for gas liquefaction utilizes isentropic expansion of a compressed gas. The throttle valve, in the Linde process will be replaced by an expansion turbine.



The process can be followed on the T-s diagram as shown in the figure. The vertical line DE represents the isentropic expansion. The fraction of gas liquefied can be determined as follows.

An energy balance around the heat exchanger, turbine and the separator gives

$$\alpha H_c = (1-\alpha) H_A + \alpha H_F + W_s \quad \text{--- (1)}$$

where W_s is the work delivered by the turbine. If the turbine operated adiabatically, the shaft work W_s is equal to the decrease in enthalpy of the gas during expansion

$$W_s = H_D - H_E \quad \text{--- (2)}$$

The fraction of the gas liquefied in an isentropic expansion is clearly greater than that in a free expansion. However, since the turbine is to be operated with a two-phase mixture, the isentropic expansion process has certain practical difficulties. To overcome these, only a portion of the gas leaving the compressor may be expanded isentropically. The remaining portion is cooled in a heat exchanger before it is expanded in a throttle valve. The saturated gas leaving the turbine is used to cool the portion of the gas that is throttled. In this way, the inlet stream to the valve can be cooled to a very low temperature, which will result in greater liquefaction.

17. (a) Maxwell's relation:

These are relations between measurable parameters like T, P, v and entropy S . There are four such relations which can be derived from the four thermodynamic potentials.

If Z is a state function, the following relations are to be satisfied:

$$dZ = Mdx + Ndy \quad \text{--- (1)}$$

where $M = \left(\frac{\partial Z}{\partial x}\right)_y$ and $N = \left(\frac{\partial Z}{\partial y}\right)_x$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \quad \text{--- (2)}$$

(i) Maxwell's relation from internal energy relations:

$$dU = Tds - PdV \quad \text{--- (3)}$$

Comparing eqn (1) and (3)

$$Z = U; \quad M = T; \quad x = s; \quad N = -P; \quad y = V$$

By eqn (2) $\Rightarrow \left(\frac{\partial T}{\partial V}\right)_s = - \left(\frac{\partial P}{\partial s}\right)_V$ --- (4)

(ii) From enthalpy relation:

$$dH = Tds + VdP \quad \text{--- (5)}$$

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial V}{\partial s}\right)_P \quad \text{--- (6)}$$

(iii) From Gibbs free energy relation:

$$dG = -SdT + VdP \quad \text{--- (7)}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = - \left(\frac{\partial S}{\partial P}\right)_T \quad \text{--- (8)}$$

(iv) From Helmholtz work function relation:

$$dA = -SdT - PdV \quad \text{--- (9)}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \quad \text{--- (10)}$$

(b) Fundamental property relations :

The first law for non-flow process is

$$dU = dQ - dW \quad \text{--- (1)}$$

The heat and work terms are related to the properties of the system as

$$dQ = Tds \text{ and } dW = PdV \quad \text{--- (2)}$$

Substitute eqn (2) in (1)

$$\boxed{dU = Tds - PdV} \quad \text{--- (3)}$$

WKT,

$$H = U + PV$$

$$dH = dU + d(PV)$$

$$dH = Tds - PdV + PdV + VdP \quad \left[\because \text{eqn (3)} \right]$$

$$\boxed{dH = Tds + VdP} \quad \text{--- (4)}$$

WKT,

$$A = U - TS$$

$$dA = dU - d(TS)$$

$$= Tds - PdV - Tds - SdT$$

$$\boxed{dA = -PdV - SdT} \quad \text{--- (5)}$$

WKT,

$$G = H - TS$$

$$dG = dH - d(TS)$$

$$= Tds + VdP - Tds - SdT$$

$$\boxed{dG = VdP - SdT} \quad \text{--- (6)}$$

Eqns (3), (4), (5) & (6) are the fundamental property relations.

18. Clausius Clapeyron Equation:

The Clapeyron equation predicts the dependence of equilibrium pressure on temperature when two phases of a given substance coexist. It is given by

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V} \quad \text{--- (1)}$$

If the temperature is not too near the critical point, the volume of the liquid is small in comparison with the volume of vapour. The volume change accompanying vaporisation $\Delta V = V_G - V_L$ is therefore approximately equal to V_G , the molar volume of vapour. Eqn (1) now

becomes

$$\frac{dP}{dT} = \frac{\Delta H}{T V_G} \quad \text{--- (2)}$$

The vapour pressures in regions well below the critical point is relatively small so that the vapour can be assumed to behave as an ideal gas.

The molar volume, V_G , can now be replaced by RT/p^s so that eqn (2) becomes

$$\frac{dP^s}{dT} = P^s \frac{\Delta H}{RT^2} \quad \text{--- (3)}$$

$$\frac{d \ln P^s}{dT} = \frac{\Delta H}{RT^2} \quad \text{--- (4)}$$

(35)

This result is known as Clausius-Clapeyron equation. Assuming that the heat of vaporisation remains constant in the temperature range T_1 to T_2 , equation (4) can be integrated to give the following equation.

$$\ln \frac{P_2^s}{P_1^s} = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \text{--- (5)}$$

P_2^s and P_1^s are the saturation pressures at temperatures T_2 and T_1 respectively.

19. S.T $ds = \frac{C_v}{T} dT + \left(\frac{dP}{dT} \right)_v dv$

Proof:

Let $S = f(T, v)$

$$ds = \left(\frac{ds}{dT} \right)_v dT + \left(\frac{ds}{dv} \right)_T dv \quad \text{--- (1)}$$

WKT, $ds = \frac{dq}{T} \quad \text{--- (2)}$

For a constant volume process $dq = C_v dT$

Sub the above equation in eqn (2)

$$\text{(2)} \Rightarrow ds = \frac{C_v dT}{T}$$

$$\left(\frac{ds}{dT} \right)_v = \frac{C_v}{T} \quad \text{--- (3)}$$

By Maxwell's Helm-holtz work function relation

$$\left(\frac{dP}{dT} \right)_v = \left(\frac{ds}{dv} \right)_T \quad \text{--- (4)}$$

Substitute (3) and (4) in eqn (1)

$$\text{(1)} \Rightarrow ds = \frac{C_v}{T} dT + \left(\frac{dP}{dT} \right)_v dv \quad \text{--- (5)}$$

Hence it is proved.

36
 20. (a) P.T $dH = C_p dT + V(1 - \beta T) dP$

Proof:

Let $H = f(P, T)$

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT \quad \text{--- (1)}$$

WKT, $dH = Tds + VdP$ --- (2)

$$\text{(2)} \Rightarrow \left(\frac{\partial H}{\partial P}\right)_T = T \left(\frac{\partial s}{\partial P}\right)_T + V$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_P \quad \text{--- (3)}$$

∴ Maxwell's Gibbs Free Energy Relation

By definition, Coefficient of volume expansion (β):

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad \text{--- (4)}$$

Substitute eqn (4) in eqn (3)

$$\text{(3)} \Rightarrow \left(\frac{\partial H}{\partial P}\right)_T = V - TV\beta = V(1 - \beta T) \quad \text{--- (5)}$$

$$\text{(2)} \Rightarrow \left(\frac{\partial H}{\partial T}\right)_P = T \left(\frac{\partial s}{\partial T}\right)_P \quad \text{--- (6)}$$

WKT, $ds = \frac{dq}{T}$

For a constant pressure process, the above

equation becomes

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

$$\left(\frac{\partial s}{\partial T}\right)_P = \frac{C_p}{T} \quad \text{--- (7)}$$

Substitute eqn (7) in (6)

$$\text{(6)} \Rightarrow \left(\frac{\partial H}{\partial T}\right)_P = T \cdot \frac{C_p}{T} = C_p \quad \text{--- (8)}$$

Substitute equation (5) and (8) in equation (1)

$$(1) \Rightarrow dH = C_p dT + v(1-\beta T) \frac{dP}{T}$$

Hence it is proved.

$$(b) \quad P.T \, ds = C_p \frac{dT}{T} - \beta V dP$$

Proof:

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

$$ds = \left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP \quad \text{--- (1)}$$

$$\text{WKT, } ds = \frac{dQ}{T}$$

For a constant pressure process, the above equation becomes

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

$$\left(\frac{\partial S}{\partial T} \right)_P = \frac{C_p}{T} \quad \text{--- (2)}$$

By Maxwell's Gibbs free energy relation

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P \quad \text{--- (3)}$$

By definition, coefficient of volume expansion (β):

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad \text{--- (4)}$$

Substitute equation (4) in (3)

$$(3) \Rightarrow \left(\frac{\partial S}{\partial P} \right)_T = -\beta V \quad \text{--- (5)}$$

Substitute eqn (2) and (5) in eqn (1)

(1) $\Rightarrow ds = \frac{C_p}{T} dT - \beta v dP$. Hence it is proved.

Q1. P.T $C_p - C_v = \frac{\gamma v \beta^2}{k}$

Proof:

WKT,

$$\left(\frac{ds}{dT}\right)_P = \frac{C_p}{T} ; \left(\frac{ds}{dT}\right)_V = \frac{C_v}{T} \quad \text{--- (1)}$$

WKT,

$$ds = \frac{C_p}{T} dT - \left(\frac{dv}{dT}\right)_P dP \quad \text{--- (2)}$$

\therefore (2) by dT and imposing the constant volume restriction

$$\left(\frac{ds}{dT}\right)_V = \frac{C_p}{T} - \left(\frac{dv}{dT}\right)_P \left(\frac{dP}{dT}\right)_V \quad \text{--- (3)}$$

Substitute equation (1) in (3)

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

which can be rearranged as

$$C_p - C_v = T \left(\frac{dv}{dT}\right)_P \left(\frac{dP}{dT}\right)_V \quad \text{--- (4)}$$

let $v = f(P, T)$

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

At constant volume, $dv = 0$ so that the above

equation becomes

$$\left(\frac{dv}{dP}\right)_T dP = - \left(\frac{dv}{dT}\right)_P dT \quad \text{(at constant volume)}$$

This on rearrangement gives

$$\left(\frac{\partial P}{\partial T}\right)_V = - \frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = - \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T \quad \text{--- (5)}$$

Equation (5) can be used to replace $\left(\frac{\partial P}{\partial T}\right)_V$ from

the equation (4).

$$(4) \Rightarrow C_p - C_v = -T \left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T \quad \text{--- (6)}$$

By definition, $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$; $k = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$

$$\therefore (6) \Rightarrow C_p - C_v = \frac{\beta^2 V T}{k} \quad \text{--- (7)}$$

Hence it is proved.