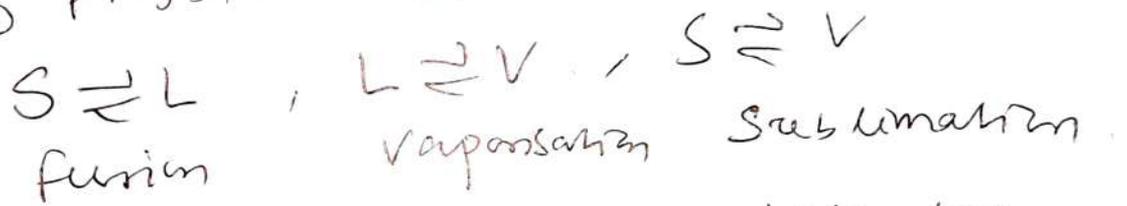


Dear students sharing what I tried to explain.

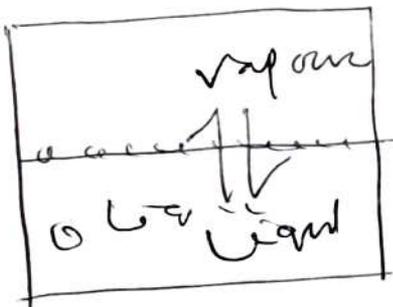
Clapeyron Eqn \rightarrow It is 2nd law of thermodynamics but it has its application in phase transition of one component system and colligative properties.

We calculate no of components when a system in equilibrium.

In one component there can be three kind of equilibrium possible in terms of physical states.



For simplification example let us take water (1 component) system.



Let us take a close container in which liquid water is in eqm with water vapor

We know $\Delta G = 0$

Let us take



Let us find the energy of reaction & find out the Gibbs free energy

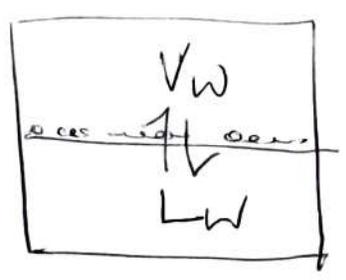
Let the Gibbs free energy of liquid water G_L and Gibbs free energy of water vapor G_V

$$G_V - G_L = \Delta G$$

If $\Delta G = -ve \Rightarrow$ Process spontaneous. ($G_L > G_V$) means the rate of forward rxn is higher. Spontaneously vaporization will take place.

$\Delta G = +ve$ means non spontaneous $G_V > G_L$. More vapour will get condensed into water and more liquid water will be formed. non spontaneously rxn will proceed in reverse direction.

$\Delta G = 0$ ($G_V = G_L$) : System is in equilibrium no change with time. Rate of formation of water = Rate of formation of vapour. Rate of vaporisation = Rate of condensation. process will be dynamic but no change in states.



Let liquid water is in equilibrium with vapour.

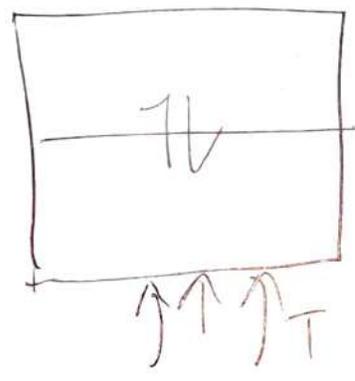
$$G_L = G_V$$

At equilibrium Gibbs free energy of liquid water = Gibbs free energy of water vapour.

Now let the equilibrium is disturbed by increasing the temperature (T) means system is heated i.e. the equilibrium is disturbed.

According to Le-Chatelier principle when ever a equilibrium is disturbed by ~~high~~ changing its temp, pressure or concentration, the system adjust itself to annul the change and a new equilibrium is re-established.

Now

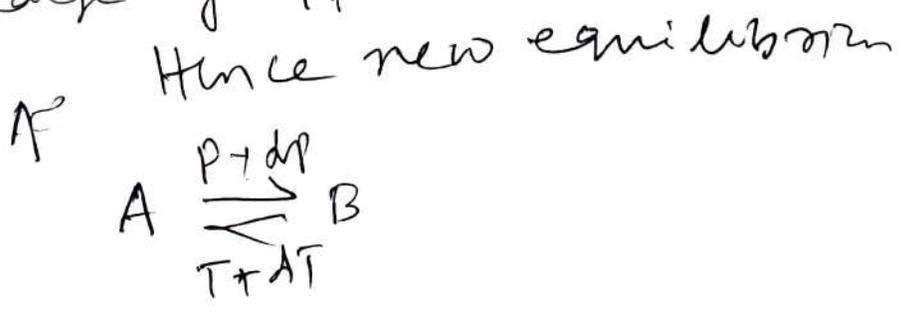


By ~~supp~~ heating the equilibrium is disturbed & the a new equilibrium is established with a new T & p

Let us write A & B for simplification



with increas in T or p by dT pressure also change by dp .



with increase in temp there will be change
in ~~an~~ increase in energy. (4)

Let- the system be new eqm.

Gibb's free energy change dG .

$$G_A + dG_A = G_B + dG_B :$$

When the system is again in
eqm

$$\Rightarrow G_A + dG_A = G_B + dG_B \quad (2)$$

$$\text{Since } \boxed{G_A = G_B}$$

$$\text{Hence } dG_A = dG_B \quad (3)$$

According to Maxwell eqn.
 $dG = V \cdot dp - S \cdot dT$.

$$\text{Hence } dG_A = V_A dp - S_A dT \quad (4)$$

$$dG_B = V_B dp - S_B dT \quad (5)$$

Since $dG_A = dG_B$ (R.H.S of 4 = 5).

$$V_A dp - S_A dT = V_B dp - S_B dT \quad (6)$$

$$V_A dp - V_B dp = S_A dT - S_B dT \quad (7)$$

$$(V_A - V_B) dp = (S_A - S_B) dT \quad (8)$$

$$\therefore \frac{dp}{dT} = \frac{(S_A - S_B) dT}{(V_A - V_B) dT} \quad \text{--- (8)}$$

$$\therefore \frac{dp}{dT} = \frac{-(S_B - S_A) dT}{-(V_B - V_A) dT} \quad \text{--- (9)}$$

[In order to make final eqn]

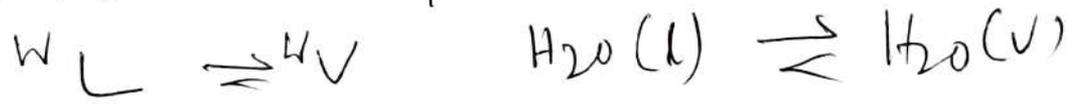
$$\therefore \frac{dp}{dT} = \frac{(S_B - S_A)}{(V_B - V_A)} = \frac{\Delta S}{\Delta V} \quad \text{(Clapeyron eqn)}$$

Since system is reversible (A ⇌ B)
 $\Delta S = \frac{q}{T}$ by defn of ΔS .

$$\frac{dp}{dT} = \frac{q}{T \Delta V} = \frac{q}{T (V_B - V_A)}$$

Now let us consider eqm between liquid water & water vapour.

Let 1 mol of liquid water in eqm with its vapour



According to Clapeyron when 1 mol of water heated to vapour at T is the eqm temp.

Then acc to Clapeyron eqn

$$\frac{dp}{dT} = \frac{q}{T (V_B - V_L)} = \frac{\Delta H_{vap}}{T (V_V - V_L)}$$

When 1 mol of liquid water attains eqm at eqm Temp T.
 the heat supplied = Enthalpy of vaporisation for 1 mole
 Molar enthalpy of vaporisation.

$$\frac{dp}{dT} = \frac{\Delta H_m^{vap}}{T(V_v - V_L)} \quad \text{--- (*)}$$

(ΔH_m^{vap}) = molar enthalpy of vaporisation

Since in case of water $V_v \gg \gg V_L$.
 (22.4 L for V_v (gas), 18 ml for liquid water).

$$\frac{dp}{dT} = \frac{\Delta H_m^{vap}}{T \times V_v} \quad \text{--- (***)}$$

when gas behaves ideally
 $PV = RT$ (for 1 mole)

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

$$\frac{dp}{dT} = \frac{\Delta H_m^{vap}}{T \times \frac{RT}{P}} = \frac{\Delta H_m^{vap}}{RT^2} \times P \quad \text{--- (****)}$$

$$\frac{dp}{P} = \frac{\Delta H_m^{vap}}{R} \times \frac{dT}{T^2} \quad \text{--- (xxxx)}$$

Integrating $d \ln p = \frac{\Delta H_m^{vap}}{RT^2} \times dT$ (xxxx)

Integrated form of Clapeyron eqn.
from $P_1 - P_2$ & $T_1 - T_2$

$$\int_{P_1}^{P_2} d \ln p = \int_{T_1}^{T_2} \frac{\Delta H_{m \text{ vap}}}{R T^2} dT$$

$\left[\frac{\Delta H_{m \text{ vap}}}{R} \text{ const. at this temp range} \right]$

$$\int_{P_1}^{P_2} d \ln p = \int_{T_1}^{T_2} \frac{\Delta H_{m \text{ vap}}}{R} \frac{dT}{T^2}$$

$$\ln p \Big|_{P_1}^{P_2} = \frac{\Delta H_{m \text{ vap}}}{R} \left[-\frac{1}{T} \right]_{T_1}^{T_2}$$

$$\ln P_2 - \ln P_1 = -\frac{\Delta H_{m \text{ vap}}}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$\ln P_2 - \ln P_1 = \frac{\Delta H_{m \text{ vap}}}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{m \text{ vap}}}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$2.303 \log_{10} \frac{P_2}{P_1} = \frac{\Delta H_{m \text{ vap}}}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\log \frac{P_2}{P_1} = \frac{\Delta H_{m \text{ vap}}}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

(Integrated form)

Equilibrium Between Phases.

1. Thermodynamic Criterion of Phase Equilibria.

A substance distributed between two phases.

Let us consider a system 'B' in which a pure substance B is present in two phases in equilibrium with each other.

Let $\mu_{B(\alpha)}$ and $\mu_{B(\beta)}$ denote the chemical potential of the substance in phase α & β respectively.

The Gibbs's function of the system is given by

$$G = f(T, P, n_{B(\alpha)}, n_{B(\beta)})$$

where $n_{B(\alpha)}$ & $n_{B(\beta)}$ is no. of moles of B in phase α & β respectively.

The change in Gibbs's free energy as a result of change in $T, P, n_{B(\alpha)}$ & $n_{B(\beta)}$ is given by

$$dG = \left(\frac{\partial G}{\partial T} \right)_{P, n_{B(\alpha)}, n_{B(\beta)}} dT + \left(\frac{\partial G}{\partial P} \right)_{T, n_{B(\alpha)}, n_{B(\beta)}} dP + \left(\frac{\partial G}{\partial n_{B(\alpha)}} \right)_{T, P, n_{B(\beta)}} dn_{B(\alpha)}$$

$$+ \left(\frac{\partial G}{\partial n_{B(\beta)}} \right)_{T, P, n_{B(\alpha)}} dn_{B(\beta)} \quad - (1)$$

$$= \left(\frac{\partial G}{\partial T} \right)_{P, n_{B(\alpha)}, n_{B(\beta)}} dT + \left(\frac{\partial G}{\partial P} \right)_{T, n_{B(\alpha)}, n_{B(\beta)}} dP + \mu_{B(\alpha)} dn_{B(\alpha)} + \mu_{B(\beta)} dn_{B(\beta)} \quad - (2)$$

If dn_B of the substance is transferred from phase α to phase β at constant temp & pressure, or 1st two terms will be zero.

$$\therefore dG = \mu_{B(\alpha)} (-dn_B) + \mu_{B(\beta)} dn_B \quad - (3)$$

If the process is reversible $\Delta G = 0$.

$$0 = (\mu_{B(\beta)} - \mu_{B(\alpha)}) dn_B \quad - (4)$$

Since from the eqn

$$[A] [B] = 0$$

\Rightarrow either $[A] = 0$ or $[B] = 0$ or both.

From eqn $(M_{B(\beta)} - M_{B(\alpha)}) dn_B = 0$.

and since dn_B no. of moles of substance can not be zero hence $(M_{B(\beta)} - M_{B(\alpha)}) = 0$.

$$\therefore M_{B(\beta)} = M_{B(\alpha)}$$

Thus if a substance is in equilibrium between two phases, its chemical potential must have the same value in both the phases.

So we can generalize.

$$M_1(\alpha) = M_1(\beta) = M_1(\gamma) = M_1(\delta) = \dots = M_1(z)$$

CLAPEYRON EQUATION:

Let us consider a system in which two phases of the same substance ~~is~~ ~~present in two phases A & B~~ ~~is~~ present in two phases A & B.

Let us consider a system in which a pure substance 'B' is present in two phases α & β respectively.

Let the two phases may be SL, SV or LV
At equilibrium $S \rightleftharpoons L$, $S \rightleftharpoons V$ or $L \rightleftharpoons V$

$$M_{B(\alpha)} = M_{B(\beta)} \quad \text{--- (1)}$$

Let the temperature of the system is changed by an infinitesimal amount δT , then according to Le. Chatelier principle in order to reestablish the equilibrium there is bound to be change in pressure P . It also undergoes a change in infinitesimal amount δP .

(3)

Under these conditions where a new equilibrium is established there will be an infinitesimal change in chemical potential $\mu_{B(\alpha)}$ & $\mu_{B(\beta)}$.

Again a new equilibrium is established. it follows:

$$\mu_{B(\alpha)} + d\mu_{B(\alpha)} = \mu_{B(\beta)} + d\mu_{B(\beta)} \quad - (2)$$

Since from eqn (1) $\mu_{B(\alpha)} = \mu_{B(\beta)}$

$$\text{Hence } d\mu_{B(\alpha)} = d\mu_{B(\beta)} \quad - (3)$$

We know the explicit form of $d\mu$ in terms of dT & dp

$$d\mu_{B(\alpha)} = -S_{m(B)(\alpha)} dT + V_{m(B)(\alpha)} dp \quad - (4)$$

$$d\mu_{B(\beta)} = -S_{m(B)(\beta)} dT + V_{m(B)(\beta)} dp \quad - (5)$$

where $S_{m(B)(\alpha)}$ & $V_{m(B)(\alpha)}$ are molar entropy and molar volume of the substance B in phase α and $S_{m(B)(\beta)}$ & $V_{m(B)(\beta)}$ in phase β respectively.

From eqn (4) & (5)

$$-S_{m(B)(\alpha)} dT + V_{m(B)(\alpha)} dp = -S_{m(B)(\beta)} dT + V_{m(B)(\beta)} dp \quad - (6)$$

$$S_{m(B)(\beta)} dT - S_{m(B)(\alpha)} dT = V_{m(B)(\beta)} dp - V_{m(B)(\alpha)} dp \quad - (7)$$

$$(S_{m(B)(\beta)} - S_{m(B)(\alpha)}) dT = (V_{m(B)(\beta)} - V_{m(B)(\alpha)}) dp \quad - (8)$$

$$\frac{(S_{m(B)(\beta)} - S_{m(B)(\alpha)})}{(V_{m(B)(\beta)} - V_{m(B)(\alpha)})} = \frac{dp}{dT} \quad - (9)$$

$$\frac{\Delta_{\text{trans}} S_{mB}}{\Delta_{\text{trans}} V_{mB}} = \frac{dp}{dT} \quad - (10)$$

$$\frac{dp}{dT} = \frac{\Delta_{\text{trans}} S_{m(B)}}{\Delta_{\text{trans}} V_{m(B)}} \quad - (11)$$

(4)

$\Delta_{\text{trans}} S_m(B)$ and $\Delta_{\text{trans}} V_m(B)$ are the changes in entropy and volume of the system when 1 mol of pure substance B is transferred from phase α to phase β .

$$\frac{dp}{dT} = \frac{\Delta_{\text{trans}} S_m(B)}{\Delta_{\text{trans}} V_m(B)} \quad - (*) \text{ CLAPEYRON EQUATION.}$$

Clapeyron equation finds an extensive application in one component two phase system.

Application of Clapeyron equation in $S \rightleftharpoons L$, $L \rightleftharpoons V$ & $S \rightleftharpoons V$ equilibria.

① $S \rightleftharpoons L$ (Solid Liquid Equilibrium)

$S \rightarrow L$ process ~~is~~ is fusion.

Let one mole of of the substance B is transferred from solid phase to liquid phase.

$$\Delta_{\text{trans}} S_m(B) = S_m(B)(L) - S_m(B)(S) \quad - (1)$$

$$\Delta_{\text{trans}} V_m(B) = V_m(B)(L) - V_m(B)(S) \quad - (2)$$

At equilibrium & $S \rightleftharpoons L$. the transformation of $S \rightarrow L$ is reversible.

We know $\Delta S = \frac{\Delta H}{T}$ (thermodynamic defⁿ of entropy)

$$\Delta S_m \quad \Delta_{\text{fus}} S_m(B) = \frac{\Delta_{\text{fus}} H_m(B)}{T} \quad - (3)$$

According to Clapeyron eqn

$$\frac{dp}{dT} = \frac{\Delta_{\text{fus}} S_m(B)}{\Delta_{\text{fus}} V_m(B)} = \frac{\Delta_{\text{fus}} H_m(B)}{T \cdot \Delta_{\text{fus}} V_m(B)}$$

Since the transformation of $S \rightarrow L$ is always an endothermic process heat is absorbed i.e. supplied.

Hence $S \rightleftharpoons L$ $\Delta H_{\text{fus}} \Delta_{\text{fus}} H_m$ is always positive.

$\Delta_{\text{fus}} V_m$ may be +ve or -ve depends on which one solid or liquid is more dense.

For almost every substance $\rho_s > \rho_L$. (solid is denser than liquid). $\Delta_{\text{fus}} V_m$ is +ve.

Exception water, Bismuth & Antimony $\rho_L > \rho_s$. $\Delta_{\text{fus}} V_m$ is -ve. $\Delta_{\text{fus}} H_m$

Integrated form of Clapeyron Equation.

Clapeyron Equation

$$\frac{dp}{dT} = \frac{\Delta_{\text{fus}} H_m}{T \Delta_{\text{fus}} V_m} \quad \text{--- (1)}$$

$$dp = \frac{\Delta_{\text{fus}} H_m}{\Delta_{\text{fus}} V_m} \frac{dT}{T} \quad \text{--- (2)}$$

Integrating between pressure P_1 to P_2 & Temp T_m & T_m' .

If $\Delta_{\text{fus}} H_m$ & $\Delta_{\text{fus}} V_m$ is considered independent of temp in this range.

$$\int_{P_1}^{P_2} dp = \frac{\Delta_{\text{fus}} H_m}{\Delta_{\text{fus}} V_m} \int_{T_m}^{T_m'} \frac{dT}{T} \quad \text{--- (3)}$$

$$P_2 - P_1 = \frac{\Delta_{\text{fus}} H_m}{\Delta_{\text{fus}} V_m} \ln \frac{T_m'}{T_m} \quad \text{--- (4)}$$

Since $T_m' - T_m$ is usually small.

$$\begin{aligned} \ln \frac{T_m'}{T_m} &= \ln \left(\frac{T_m + T_m' - T_m}{T_m} \right) = \ln \left(1 + \frac{T_m' - T_m}{T_m} \right) \\ &\approx \frac{T_m' - T_m}{T_m} = \frac{\Delta T}{T_m} \quad \left[\ln(1+x) \approx x \right] \end{aligned}$$

$$P_2 - P_1 = \Delta P = \frac{\Delta f_{us} \Delta m}{\Delta f_{us} V_m} \cdot \frac{\Delta T}{T_m} \quad - (5)$$

Infinitesimal change $\frac{dP}{dT}$ is replaced by finite change $\frac{\Delta P}{\Delta T}$.

For a given increase in external pressure (ΔP is +ve) ΔT depends on the sign of $\Delta f_{us} V_m$.

- ΔT is +ve if $\Delta f_{us} V_m$ is +ve
- ΔT is -ve if $\Delta f_{us} V_m$ is -ve.

Integrated form of Clapeyron-Equation:

CLAUDE - CLAPEYRON EQUATION.

$$\text{Clapeyron eqn } \frac{dp}{dT} = \frac{\Delta_{\text{trans}} S_{m,B}}{\Delta_{\text{trans}} V_{m,B}} \quad - (1)$$

$$\text{At transition temperature } T \quad \Delta S = \frac{\Delta_{\text{trans}} H_m}{T} \quad - (2)$$

$$\frac{dp}{dT} = \frac{\Delta_{\text{trans}} H_{m,B}}{T \Delta_{\text{trans}} V_{m,B}} \quad - (2)$$

$$\Delta_{\text{trans}} H_m = \Delta_{\text{fus}} H_m (L \rightleftharpoons S) \quad \Delta_{\text{vap}} H_m (L \rightleftharpoons V) \quad \Delta_{\text{sub}} H_m (S \rightleftharpoons V)$$

In case of $L \rightleftharpoons V$ &

$$\Delta_{\text{trans}} V_{m,B} = V_{m(B)(g)} - V_{m(B)(l)} \quad - (3)$$

Clausius simplifies equation - (3) by introducing the following two approximations.

- $V_{m(B)(g)} - V_{m(B)(l)} \approx V_{m(B)(g)} \ll V_{m(B)(g)}$
- if the gas phase is assumed to be ideal, the molar volume of the gaseous phase is replaced by $\frac{RT}{p}$.

With these approximations.

$$\text{Clapeyron eqn } \frac{dp}{dT} = \frac{\Delta_{\text{trans}} H_{m(B)}}{RT^2} p \quad - (4)$$

$$\text{or } \frac{dp}{p} = \frac{\Delta_{\text{trans}} H_{m(B)}}{R} \cdot \frac{dT}{T^2} \quad - (5) \text{ Clausius Clapeyron Eqn.}$$

Integrated form of Clausius Clapeyron Eqn.

$$\int_{p_1}^{p_2} \frac{dp}{p} = \int_{T_1}^{T_2} \frac{\Delta_{\text{trans}} H_{m,B}}{R} \cdot \frac{dT}{T^2} \quad - (6)$$

where p_1 & p_2 are vapour pressures of condensed phase S & L at temperature T_1 & T_2 respectively $\Delta_{\text{trans}} H_{m(B)}$ is assumed to be independent of temperature.

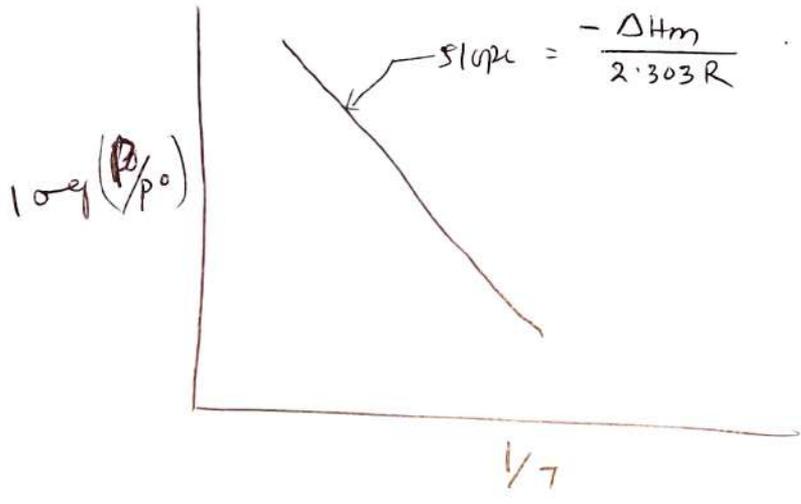
$$\ln \frac{p_2}{p_1} = - \frac{\Delta_{\text{trans}} H_{m(B)}}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

If $P_1 = 1 \text{ bar}$, $T_1 = \text{No sublimation or boiling point of the solid or liquid phase representing } T^*$ (T^* Normal b. p.,

$$\ln\left(\frac{P_2}{1 \text{ bar}}\right) = -\frac{\Delta_{\text{trans}}H_m}{R} \left[\frac{1}{T} - \frac{1}{T^*}\right]$$

If we plot $\ln(P/\text{bar})$ or $\log(P/\text{bar})$ vs $1/T$ we get a linear curve with slope = $-\Delta_{\text{trans}}H_m/R$ or $-\frac{\Delta_{\text{trans}}H_m}{2.303 R}$.
Intercept $1/T = 0$ yields the value $\frac{\Delta_{\text{trans}}H_m}{RT^*}$

or $\frac{\Delta_{\text{trans}}H_m}{2.303 RT^*}$. From the determined values of slope and intercept, we can determine both $\Delta_{\text{trans}}H_m$ & T^* of the substance.



Numericals based on Clapeyron Equation

1. At 100°C , the specific volume of water and steam are 1cm^3 and 1670cm^3 respectively. Calculate the vapour pressure of steam by 5°C change in temperature. The molar heat of vaporisation of water may be taken as 9.70kcal .

$$L \rightleftharpoons V$$

$$\begin{aligned} \text{Molar volume of liquid water} &= V_L = 18\text{cm}^3\text{mol}^{-1} \\ &= 18 \times 10^{-6}\text{m}^3\text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Molar volume of gas/vapour of steam } V_g &= 18 \times 1670\text{cm}^3\text{mol}^{-1} \\ &= 30060 \times 10^{-6}\text{m}^3\text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Heat of vaporisation } \Delta H_{\text{vap}} &= 9700\text{cal mol}^{-1} \times 4.184\text{J cal}^{-1} \\ &= 40584.81\text{J mol}^{-1} \end{aligned}$$

$$\frac{dp}{dT} = \frac{\Delta H_{\text{vap}}}{T (V_g - V_L)} \quad \begin{aligned} dT &= 5\text{K} \\ T &= 273 + 100 = 373\text{K} \end{aligned}$$

$$\begin{aligned} dp &= \frac{40584.81\text{J mol}^{-1} \times 5\text{K}}{373\text{K} (30060 - 18) \times 10^{-6}\text{m}^3} \\ &= \frac{202924\text{J}}{11205660 \times 10^{-6}\text{m}^3} \\ &= 0.018109 \times 10^6\text{Nm}^{-2} \\ &= 0.1789\text{atm} \end{aligned}$$

$$dp = 135.9\text{mmHg}$$

Thus vapour pressure of water increases by 135.9mmHg by 5°C rise in temperature at 100°C .

2. The vapour pressure of water at 94.9°C is found to be 634 mm. What would be the vapour pressure at a temperature of 100°C . The heat of vapourisation in this range of temperature may be taken as ~~40954.5~~ 40593 J mol^{-1} .

Ans.
$$\log \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$T_1 = 273 + 94.9 = 367.9 \text{ K}$ $P_1 = 634 \text{ mm}$
 $T_2 = 273 + 100 = 373 \text{ K}$ $P_2 = ?$

$\Delta H_{\text{vap}} = 40593 \text{ J mol}^{-1}$

$$\log \left(\frac{P_2}{634 \text{ mm}} \right) = \frac{40593 \text{ J mol}^{-1}}{8.314 \text{ J} \times 2.303 \text{ K}^{-1} \text{ mol}^{-1}} \left[\frac{5.1 \text{ K}}{367.9 \text{ K} \times 373 \text{ K}} \right]$$

$P_2 = 759.7 \text{ mmHg}$

3. Suppose solid liquid equilibrium mixture is maintained at triple point temperature (0.0075°C) and triple point pressure (4.6 mm Hg). Calculate the change in temperature that should be made so that the equilibrium is maintained at an external pressure at 1 atm.

Ans. Given $\rho_{\text{ice}} = 0.917 \text{ g cm}^{-3}$ (g cm^{-3})
 $\rho_{\text{liquid}} = \text{~~0.9998~~ } 0.9998 \text{ g cm}^{-3}$
 $\Delta \bar{H}_{\text{fus}} = 6008.5 \text{ J mol}^{-1}$

$$\frac{dp}{dT} = \frac{\Delta \bar{H}_{\text{fus}}}{T(V_{m,l} - V_{m,s})}$$

$$(V_{m,l} - V_{m,s}) = \frac{18 \text{ g mol}^{-1}}{0.9998 \text{ g cm}^{-3}} - \frac{18 \text{ g mol}^{-1}}{0.917 \text{ g cm}^{-3}}$$

 $= -1.6256 \text{ cm}^3 \text{ mol}^{-1}$

Therefore,

$$\frac{dp}{dT} = \frac{6008.5 \text{ J mol}^{-1}}{(273.15 \text{ K})(-1.6256 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})}$$

$$= -1.3538 \times 10^7 \text{ Pa K}^{-1}$$

$$dT = \frac{dp}{-1.3538 \times 10^7 \text{ Pa K}^{-1}}$$

$$dp = 760 \text{ mmHg} - 4.6 \text{ mmHg}$$

$$= 755.4 \text{ mmHg}$$

$$= \frac{755.4}{760} \times 101.325 \times 10^3 \text{ Pa}$$

$$= 1.0071 \times 10^5 \text{ Pa}$$

$$dT = \frac{1.0071 \times 10^5 \text{ Pa}}{-1.3538 \times 10^7 \text{ Pa K}^{-1}}$$

$$dT = -0.00742 \text{ K}$$

— 0 —

4. The specific volume of ice and water at 0°C are 1.0906 cm^3 and 1.0001 cm^3 respectively. Calculate the change in melting point of ice per atm increase of pressure? $\Delta H_{\text{fus}} = 79.8 \text{ cal g}^{-1}$

Ans.

$$V_{m,s} = 18 \times 1.0906 \text{ cm}^3$$

$$= 18 \times 1.0906 \times 10^{-6} \text{ m}^3$$

$$V_{m,l} = 18 \times 1.0001 \text{ cm}^3$$

$$= 18 \times 1.0001 \times 10^{-6} \text{ m}^3$$

$$T = 273 \text{ K}$$

$$\Delta H_{\text{fus}} = 18 \text{ g mol}^{-1} \times 79.8 \text{ cal g}^{-1} \times 4.184 \text{ J cal}^{-1}$$

$$= 6009.9 \text{ J mol}^{-1}$$

$$dp = 1 \text{ atm} = 101325 \text{ Nm}^{-2}$$

$$dT = ?$$

$$\begin{aligned} \frac{dT}{dp} &= \frac{T(V_{m,l} - V_{m,s})}{\Delta H_{fr.}} \\ &= \frac{273 \text{ K} (-0.0906 \times 18 \times 10^{-6} \text{ m}^3)}{6009.9 \text{ J mol}^{-1}} \\ &= \frac{273 \times 18 \times 10^{-6} \times (-0.0906) \text{ m}^3 \times 101325 \text{ Nm}^{-2}}{6009.9 \text{ J mol}^{-1}} \end{aligned}$$

$$\frac{dT}{dp} = -0.0075 \text{ K}$$

M.p. decreases with increase in temperature.

Important conversion factors.

$$1 \text{ cal} = 4.184 \text{ J} = 4.184 \times 10^{-7} \text{ erg} = 41.293 \text{ atm cm}^3$$

$$1 \text{ N} = 10^5 \text{ dynes}$$

$$1 \text{ J} = 10^7 \text{ ergs} = 0.239 \text{ cal}$$

$$1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ Torr} = 101325 \text{ Nm}^{-2} = 101.325 \text{ kPa}$$

$$1 \text{ mm Hg} = 1 \text{ Torr} = 133.322 \text{ Nm}^{-2}$$