Clausius - Clapeyron Equation

If the two phases of a pure substance A and B are in equilibrium with each other they have the same molar free energies at that temperature and pressure. When the pressure is changed at constant temperature or temperature is changed at constant pressure, one of the phases will disappear. However, if both pressure and temperature are changed in such a way so as to keep the two molar free energies equal to each other the two phase will continue & coexist. i.e

$$\text{Phase A} \rightleftharpoons \text{Phase B}$$

then the change in free energy must be same in each phase

$$dG_A = dG_B$$

For any pure substance in a single phase such as liquid or gaseous water any variation in free energy is given by equation

$$dG = V\cdot dP - S\cdot dT$$

Applying the above equation for both the phases

$$dG_A = V_A\cdot dP - S_A\,dT \quad - \text{①}$$

$$dG_B = V_B\cdot dP - S_B\,dT \quad - \text{②}$$

Equating these expressions, we get

$$V_B\cdot dP - S_B\cdot dT = V_A\cdot dP - S_A\,dT$$

$$(V_B - V_A)\cdot dP = (S_B - S_A)\cdot dT$$

or

$$\frac{dP}{dT} = \frac{S_B - S_A}{V_B - V_A} = \frac{\Delta S}{\Delta V} \quad - \text{③}$$

Further $\Delta S = \frac{\Delta H}{T}$

Making this substitution in equation

$$\boxed{\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}} \quad ④$$

which is generally known as Clapeyron equation. It gives the variation of the equilibrium pressure with temperature for any two phases of a given substances

This equation may be applied to vaporisation, sublimation, fusion or the transition between two solid phases of a pure substance. The enthalpies of sublimation, fusion and vaporisation at a given temperature are related by

$$\bar{\Delta H}_{sub} = \bar{\Delta H}_{fus} + \bar{\Delta H}_{vap} \quad ⑤$$

Since the heat required to vaporise a given amount of the solid is the same whether the process is carried out directly or by first melting the solid and then vaporising the liquid.

For vaporisation and sublimation, Clausius showed how the Clapeyron equation may simplified by assuming that the vapour obeys the ideal gas law and by neglecting the volume of 1 mol of liquid in comparison with 1 mol of va

Writing eq 4. as

$$\frac{dP}{dT} = \frac{\Delta H}{T(V_v - V_l)}$$ (for liquid and vapour phase)

replacing $V_v - V_l \simeq V_v$.

$$\frac{dP}{dT} = \frac{\Delta H}{T V_v} \quad - ⑥$$

If the gas law is applicable then

$$PV_v = RT$$

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

Hence eq 6 converts

$$\frac{dP}{dT} = \frac{\Delta H}{T} \frac{P}{RT}$$

$$\frac{dP}{P} = \frac{\Delta H}{T} \frac{dT}{RT}$$

$$\boxed{\text{or} \quad \frac{d(\ln P)}{dT} = \frac{\Delta H}{RT^2}} \quad - ⑦$$

→ This is known as

Clausius – Clapeyron Equation.

Now Integrated form of eq 7.

If ΔH remain constant over a small range of temperature, the eq 7 can be integrated between limits of P_2 at T_2 and P_1 at T_1 as follows: —

$$\int_{P_1}^{P_2} d\ln P = \frac{\Delta H}{R}\int_{T_1}^{T_2} T^{-2}\,dT.$$

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

$$= -\frac{\Delta H}{R}\left[\frac{T_1-T_2}{T_1T_2}\right]$$

$$\boxed{\text{or}\quad \log\frac{P_2}{P_1} = -\frac{\Delta H.}{2.303R}\left[\frac{T_1-T_2}{T_1T_2}\right]} \quad ⑧$$

Numericals !

what is the b.p. of H_2O on a mountain where the barometer ~~provided~~ # reading is 660Torr ? The heat of vaporisation of H_2O may be taken to be 40.670 KJ/mol.

$P_1 = 660$Torr

$T_1 = ?$

$R = 8.314\ JK^{-1}mol^{-1}$

$P_2 = 760$Torr.

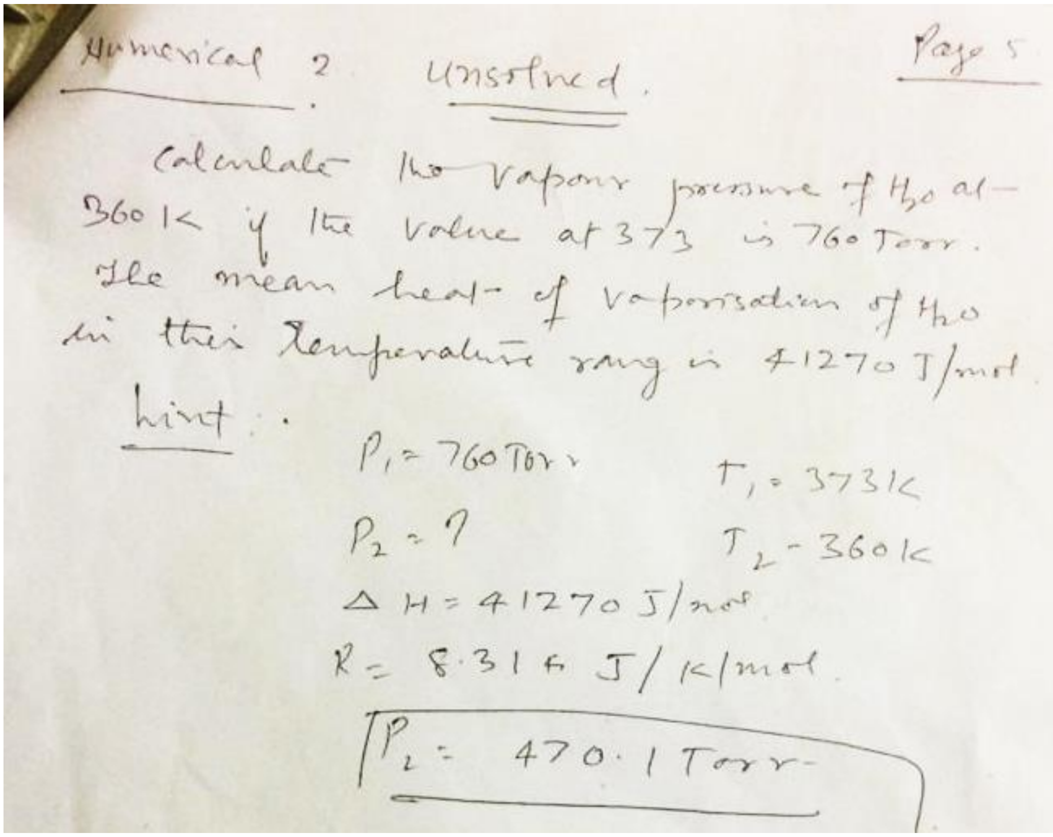
$T_2 = 373K$
(273+100)

$\Delta H_v = 40670\ J/mol.$

$$\log\frac{P_2}{P_1} = \frac{\Delta H}{2.303R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

$$\log\frac{760.}{660} = \frac{40670.}{2.303\times8.314}\left(\frac{1}{T_1}-\frac{1}{373}\right)$$

$T_1 = 369.01K.$ b.p of H_2O on mountain



Numerical 2. Unsolved.

Calculate the vapour pressure of H_2O at 360 K if the value at 373 is 760 Torr. The mean heat of vaporisation of H_2O in this temperature rang is 41270 J/mol.

hint :

$P_1 = 760$ Torr $T_1 = 373K$

$P_2 = ?$ $T_2 = 360K$

$\Delta H = 41270$ J/mol

$R = 8.314$ J/K/mol

$$\boxed{P_2 = 470.1 \text{ Torr}}$$