

Class \Rightarrow B.Sc.(Hons.) Part-II
Subject \Rightarrow Chemistry
Chapter \Rightarrow Second law of
Thermodynamics

Topic \Rightarrow Clapeyron Equation
and Clausius-Clapeyron
Equation and its applications.

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Clapeyron Equation

An important equation for one-component two-phase systems was derived by Clapeyron from the second law of thermodynamics and is called the Clapeyron Equation.

Let the system be $\text{L} \rightleftharpoons \text{V}$

Liquid \rightleftharpoons vapour

Consider one gm mole of a liquid confined in a cylinder by a frictionless piston. Let the volume of the liquid be V_1 and its vapour pressure equal to P . Now allowed the liquid to evaporate reversibly at a constant temperature T and when the whole of it has vaporised, let the volume of the vapour be V_2 .

\therefore Work done during evaporation,

$$W = P(V_2 - V_1) \quad \text{--- (1)}$$

Differentiating equation (1) with respect to temp at constant $(V_2 - V_1)$, we get

$$\frac{dW}{dT} = (V_2 - V_1) \frac{dP}{dT} \quad \text{--- (2)}$$

Heat absorbed from the surroundings is the

(2)

latent heat of vaporization L which on substitution in the first law of equation gives us

$$\Delta E = \omega - L \quad \text{--- (3)}$$

On substitution of expressions (2) and (3) in the Gibbs-Helmholtz equation, we have

$$\omega + \Delta E = T \frac{d\omega}{dT}$$

$$\omega + (L - \omega) = T \frac{dP}{dT} (V_2 - V_1)$$

$$\therefore \frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

This is the Clapeyron equation in its general form, may be written as

$$\frac{dP}{dT} = \frac{\Delta H}{T(V_2 - V_1)}$$

where ΔH is the heat of transition when a volume V_1 of a definite weight of one form changes to a volume V_2 of the same weight of other form at the temperature T .

Clausius-Clapeyron Equation

The Clapeyron equation is simplified by neglecting the small volume of the liquid in comparison with the volume of the vapour. The Clapeyron equation becomes

$$\frac{dP}{dT} = \frac{\Delta H}{TV}$$

supposing the vapour obeys the ideal gas laws

$$V_2 = \frac{RT}{P}$$

$$\frac{dP}{dT} = \frac{\Delta H \cdot P}{RT^2}$$

(3)

$$\text{or } \frac{1}{P} \times \frac{dP}{dT} = \frac{\Delta H}{RT^2}$$

$$\text{But } \frac{1}{P} \times \frac{dP}{dT} = d \log_e P$$

$$d \log_e P = \frac{\Delta H}{RT^2}$$

This equation is known as Clausius-Clapeyron equation.

If ΔH is regarded as constant, we may integrate the above equation

$$d \log_e P = \frac{\Delta H}{RT^2} dT$$

$$\int d \log_e P = \frac{\Delta H}{R} \int \frac{dT}{T^2}$$

$$\log_e P = -\frac{\Delta H}{RT} + \text{constant}$$

$$\log_{10} P = \frac{-\Delta H}{2.303 RT} + C$$

If P_1 is the vapour pressure at T_1 and P_2 the vapour pressure at T_2 , we have

$$\log_{10} P_1 = \frac{-\Delta H}{2.303 RT_1} + C \quad (1)$$

$$\text{and } \log_{10} P_2 = \frac{-\Delta H}{2.303 RT_2} + C \quad (2)$$

Subtracting (1) from (2)

$$\log_{10} \frac{P_2}{P_1} = \frac{\Delta H}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\text{or, } \log_{10} \frac{P_2}{P_1} = \frac{\Delta H}{2.303 R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

(4)

Applications of Clapeyron-Clausius Equation

(1) Calculation of Latent Heat of vaporization \Rightarrow

If the vapour pressure of a liquid at two temperatures T_1 and T_2 be P_1 and P_2 respectively, the molar heat of vaporisation ΔH_v can be calculated by substituting these values in Clapeyron-Clausius equation.

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(2) Calculation of Boiling point or freezing point \Rightarrow

If the freezing point or the boiling point of a liquid at one pressure is known, it is possible to calculate it at another pressure by the use of the Clapeyron-Clausius equation.

(3) Calculation of vapour pressure at another temp \Rightarrow

If the mean heat of vaporisation is available, it is possible to calculate the vapour pressure of a liquid at given temperature if the vapour pressure at another temperature is known.

(4) Molal elevation constant K_b is calculated using Clapeyron - Clausius equation.

(5) Molal depression constant K_f is calculated using Clapeyron - Clausius equation.