The Clausius-clapeyron Equation

By

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- The Clausius-Clapeyron equation is of great importance for calculating the effect of change of pressure (P) on the equilibrium transformation temperature (T) of a pure substance, and may be represented as:-

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V} \qquad (1)$$

- where ΔH is the heat of transformation and ΔV is the volume change associated with the transformation.

Application of Clausius-Clapeyron Equation to Phase Changes

1) Liquid-Vapour (Vaporization) Equilibria

Applying Eq.(1) to a liquid-vapour equilibrium, we have

$$\frac{dP}{dT} = \frac{\Delta H_v}{T(V_{vap} - V_{liq})} \qquad (2)$$

Where

ΔH_v is the molar heat of vaporization or latent heat of evaporation,

V_{vap} is the molar volume of vapour, and

V_{liq} is the molar volume of liquid.

Since the molar volume of vapour is *very* much larger than the molar volume of liquid, V_{liq} is negligible as compared to V_{vap} and hence

$$\frac{dP}{dT} = \frac{\Delta H_v}{T\,V_{vap}} \qquad (3)$$

Assuming that the vapour behaves as an ideal gas, the volume V_{vap} may be related to

$$V_{vap} = \frac{RT}{P} \qquad (4)$$

Substituting Eq. (4) in Eq. (3)

$$\frac{dP}{dT} = \frac{P\Delta H_v}{RT^2} \qquad (5)$$

The equation can be rearranged in the most generally used differential form

$$\frac{d(\ln P)}{dT} = \frac{\Delta H_v}{RT^2} \qquad (6)$$

If we assume as an approximation, however, that over the interval in question ΔH_v remains constant, then integration of Eq.(6) yields

$$\ln P = -\frac{\Delta H_v}{RT} + C' \qquad (7a)$$

or

$$\log P = \frac{-\Delta H_v}{2.303\,RT} + C \qquad (7b)$$

where C’ and C are integration constants.

It is evident from Eq.(7b) that if log P for any liquid metal is plotted against 1/T, the plot should be a straight line . The slope (m) of the straight line will be given by

$$m = \frac{-\Delta H_v}{2.303\,R}$$

The intercept of the line with Y-axis will give the value of constant C. From the slope of line, the heat of vaporization of liquid may be calculated.

However, the heat of vaporization of a liquid metal calculated in this way will be the mean value over the temperature interval concerned.

Eq(6) may also be integrated between the limits P_1 and P_2 corresponding to temperatures T_1 and T_2 respectively. Assuming that the temperature range is small enough so that ΔH_v is independent of temperature, integration of Eq.(6) yields

$$\int_{P_1}^{P_2} d(\ln P) = \frac{\Delta H_v}{R}\int_{T_1}^{T_2}\frac{dT}{T^2}$$

or

$$\log\frac{P_2}{P_1} = \frac{-\Delta H_v}{2.303\ R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) \qquad (8)$$

Eq.(8) may be used to calculate the vapour pressure at any temperature if the vapour pressure at another temperature and the mean heat of vaporization over that temperature range are known.

Example (1)

The vapour pressure of liquid titanium at 2227 °C is 1.503 mm Hg. The heat of vaporization at the normal boiling point of titanium is 104 kcal/mole. Calculate its normal boiling point.

2) Solid-Vapour (Sublimation) Equilibria

On the basis of assumptions similar to those made in liquid-vapour equilibria, an expression similar to Eq.(6) may also be obtained for solid-vapour equilibria.

$$\frac{d(\ln P)}{dT} = \frac{\Delta H_s}{RT^2}$$

where ΔH_s is the heat of sublimation.

3) Solid-Liquid (Fusion) Equilibria

Applying the Clausius-Clapeyron equation to solid-liquid equilibria,

$$\frac{dP}{dT} = \frac{\Delta H_f}{T(V_{liq} - V_{solid})}$$

or

$$\frac{dT}{dP} = \frac{T(V_{liq} - V_{solid})}{\Delta H_f}$$

where ΔH_f is the molar heat of fusion, V_{liq} and V_{solid} are the molar volumes of liquid and solid respectively.

Example (2)

The melting point of gallium is 30 °C at 1 atm. The densities of solid and liquid gallium are 5.885 and 6.08 g/cm^3 respectively. The heat of fusion of gallium is 18.5 cal/g. Calculate the change in melting point of gallium for an increase of pressure of 1 atm.

4) Solid-Solid Equilibria

The rate of change of transition temperature at which two crystalline forms of a solid are in equilibrium with pressure is given by an equation similar to that discussed earlier.

If α is the stable form above the transition temperature, and β is the stable form below the transition temperature T, then according to Eq.(1)

$$\frac{dP}{dT} = \frac{\Delta H_{tr}}{T(V_\alpha - V_\beta)}$$

or

$$\frac{dT}{dP} = \frac{T(V_\alpha - V_\beta)}{\Delta H_{tr}}$$

where ΔH_{tr} is the molar heat of transition, V_α and V_β are the molar volumes of the indicated forms, all measured at temperature T.

Trouton's Rule

Trouton's rule states that the ratio of latent heat of evaporation to the temperature of normal boiling T_b is constant for all liquids, and is approximately 21 cal/deg/mole, i.e.

$$\frac{\Delta H_v}{T_b} = 21 \text{ cal/deg/mole}$$

Example (3)

The normal boiling point of zinc is 907 °C. Calculate its vapour pressure at 800 °C, assuming that zinc follows Trouton's rule.