

# CHAPTER 6

## Thermodynamics – II

### ❖ Clausius-Clapeyron Equation

The Clausius-Clapeyron equation was initially proposed by a German physics Rudolf Clausius in 1834 and then further developed by French physicist Benoît Clapeyron in 1850. This equation is extremely useful in characterizing a discontinuous phase transition between two phases of a single constituent.

#### ➤ Derivation of Clausius-Clapeyron Equation

In order to derive the Clausius-Clapeyron equation, consider a system at equilibrium i.e. the free energy change for the ongoing process is zero ( $\Delta G = 0$ ). However, we know from the principles of thermodynamics that the variation of free energy with temperature and pressure can be formulated by the following differential equation.

$$dG = VdP - SdT \quad (1)$$

For typical single-constituent equilibria, we have

$$\text{Phase I} \rightleftharpoons \text{Phase II} \quad (2)$$

Where phase I can be solid, liquid, or gas; whereas phase II can be liquid or vapor depending upon the nature of the transition whether it is melting, vaporization or sublimation, respectively.

Now consider a system at pressure  $P$  and temperature  $T$ ; and the free energies of phase I and phase II of the same system are  $G_1$  and  $G_2$ , respectively. Moreover, if we change the temperature from  $T$  to  $T+dT$  and pressure from  $P$  to  $P+dP$ ; the free energy changes in phase I and phase II will be  $dG_1$  and  $dG_2$ , respectively. Mathematically, we can formulate the situation as given below.

$$dG_1 = V_1dP - S_1dT \quad (3)$$

$$dG_2 = V_2dP - S_2dT \quad (4)$$

Where  $V_1$  and  $S_1$  represent the molar volume and entropy of phase I, while  $V_2$  and  $S_2$  represent the molar volume and entropy of phase II. However, if the phase I and phase II are in equilibrium with each other, we have

$$\Delta G = 0 \quad (5)$$

$$G_2 - G_1 = 0 \quad (6)$$

Now recalling the fact that  $G_1$  and  $G_2$  are simply the free energies of the phase I and phase II at temperature  $T$  and pressure  $P$ ; we can say the same must also be true at temperature  $T+dT$  and pressure  $P+dP$  i.e.

$$(G_2 + dG_2) - (G_1 + dG_1) = 0 \quad (7)$$

$$(G_2 - G_1) + (dG_2 - dG_1) = 0 \quad (8)$$

Since  $G_2 - G_1 = 0$  from equation (6), the above equation takes the form

$$dG_2 - dG_1 = 0 \quad (9)$$

$$dG_2 = dG_1 \quad (10)$$

After putting the values of  $dG_1$  and  $dG_2$  from equation (3, 4) in equation (10), we get

$$V_2 dP - S_2 dT = V_1 dP - S_1 dT \quad (11)$$

or

$$V_2 dP - V_1 dP = S_2 dT - S_1 dT \quad (12)$$

$$(V_2 - V_1) dP = (S_2 - S_1) dT \quad (13)$$

$$\Delta V \cdot dP = \Delta S \cdot dT \quad (14)$$

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} \quad (15)$$

Now if the  $\Delta H$  is the latent heat of phase transformation occurring at temperature, the entropy change is

or

$$\Delta S = \frac{\Delta H}{T} \quad (16)$$

After using the value of  $\Delta S$  from equation (16) into equation (15), we get

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V} \quad (17)$$

The equation was first developed by Calpeyron in 1834 and therefore is named after him Calpeyron equation.

Now if phase I is solid while phase II is vapor i.e. solid  $\rightleftharpoons$  melt equilibria, the equation (17) takes the form

$$\frac{dP}{dT} = \frac{\Delta_{fus}H}{T_f \Delta V} \quad (18)$$

Where  $\Delta_{fus}H$  is the latent heat of fusion and  $T_f$  is the melting point. The term  $\Delta V = V_l - V_s$  i.e. the difference in the volume of melt and solid phase. Therefore, equation (18) can also be written as

$$\frac{dP}{dT} = \frac{\Delta_{fus}H}{T_f (V_l - V_s)} \quad (19)$$

For vaporisation equilibrium i.e. liquid  $\rightleftharpoons$  vapour,

$$\frac{dP}{dT} = \frac{\Delta_{vap}H}{T_b(V_v - V_l)} \quad (20)$$

Where  $\Delta_{vap}H$  is the latent heat of vaporization and  $T_b$  is the boiling point. The term  $\Delta V = V_v - V_l$  i.e. the difference in the volume of vapor and liquid phases. Now since the volume of the liquid is very small in comparison to the gaseous phase, the term  $V_l$  in equation (20) can simply be neglected for simplicity i.e.

$$\frac{dP}{dT} = \frac{\Delta_{vap}H}{TV_v} \quad (21)$$

If the vapor act as an ideal gas i.e.  $PV_v = RT$  or  $V_v = RT/P$ , the above equation can be written as

$$\frac{dP}{dT} = \frac{\Delta_{vap}H}{RT^2} \cdot P \quad (22)$$

or

$$\frac{1}{P} \cdot \frac{dP}{dT} = \frac{\Delta_{vap}H}{RT^2} \quad (23)$$

or

$$\frac{d \ln P}{dT} = \frac{\Delta_{vap}H}{RT^2} \quad (24)$$

The above equation is popularly known as the Clausius-Clapeyron equation.

One more popular form of Clausius-Clapeyron Equation is the integrated one which can easily be derived by using the rearranged form of equation (24) as given below.

$$d \ln P = \frac{\Delta_{vap}H}{RT^2} dT \quad (25)$$

If the temperature changes from  $T_1$  to  $T_2$  and pressure is varied from  $P_1$  to  $P_2$ , then we can say that

$$\int_{P_1}^{P_2} d \ln P = \int_{T_1}^{T_2} \frac{\Delta_{vap}H}{RT^2} dT \quad (26)$$

or

$$\ln \frac{P_2}{P_1} = \frac{\Delta_{vap}H}{R} \int_{T_1}^{T_2} \frac{1}{T^2} dT \quad (27)$$

$$\ln \frac{P_2}{P_1} = \frac{\Delta_{vap}H}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \quad (28)$$

After converting to the common logarithm, we get

$$2.303 \log \frac{P_2}{P_1} = \frac{\Delta_{vap}H}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \quad (29)$$

or

$$\log \frac{P_2}{P_1} = \frac{\Delta_{vap}H}{2.303 R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \quad (30)$$

Which is the integrated form of Clausius-Clapeyron equation.

### ➤ Applications of Clausius-Clapeyron Equation

There are many applications of Clausius-Clapeyron equation ranging from chemistry to meteorology and climatology as well. Some of the most important applications in chemistry are given below.

i) For transitions between a gas and a condensed phase (liquid or solid), the Clausius-Clapeyron equation can be given as

$$\ln P = -\frac{L}{R} \left( \frac{1}{T} \right) + C \quad (31)$$

Where  $C$  represents a constant. The symbol  $L$  represents the specific latent heat for a liquid-gas transition whereas specific latent heat of sublimation for a solid-gas transition. If the latent heat is known, then knowledge of one point on the coexistence curve determines the rest of the curve. Conversely, as the plot  $\ln P$  vs  $1/T$  is linear with the zero intercept, the simple linear fitting is used to estimate the latent heat of phase change. The latent heat of vaporization of any liquid can also be determined if the vapor pressures of the same are known at two different temperatures.

ii) The boiling point of a liquid at any temperature can be determined if the boiling point at a particular temperature and latent heat of vaporization of the same are known.

iii) If the latent heat of vaporization and the vapor pressure of a liquid at a particular temperature are known, the vapor pressure of the same liquid at any other temperature can be known.

iv) One more application of this equation is to check if a phase transition will occur via compression or expansion in solid  $\rightleftharpoons$  melt equilibria. To understand this, recall the

$$\frac{dP}{dT} = \frac{\Delta_{fus}H}{T_f \Delta V} \quad (32)$$

The sign for  $dP/dT$  can be positive or negative for expansion and compression, respectively.

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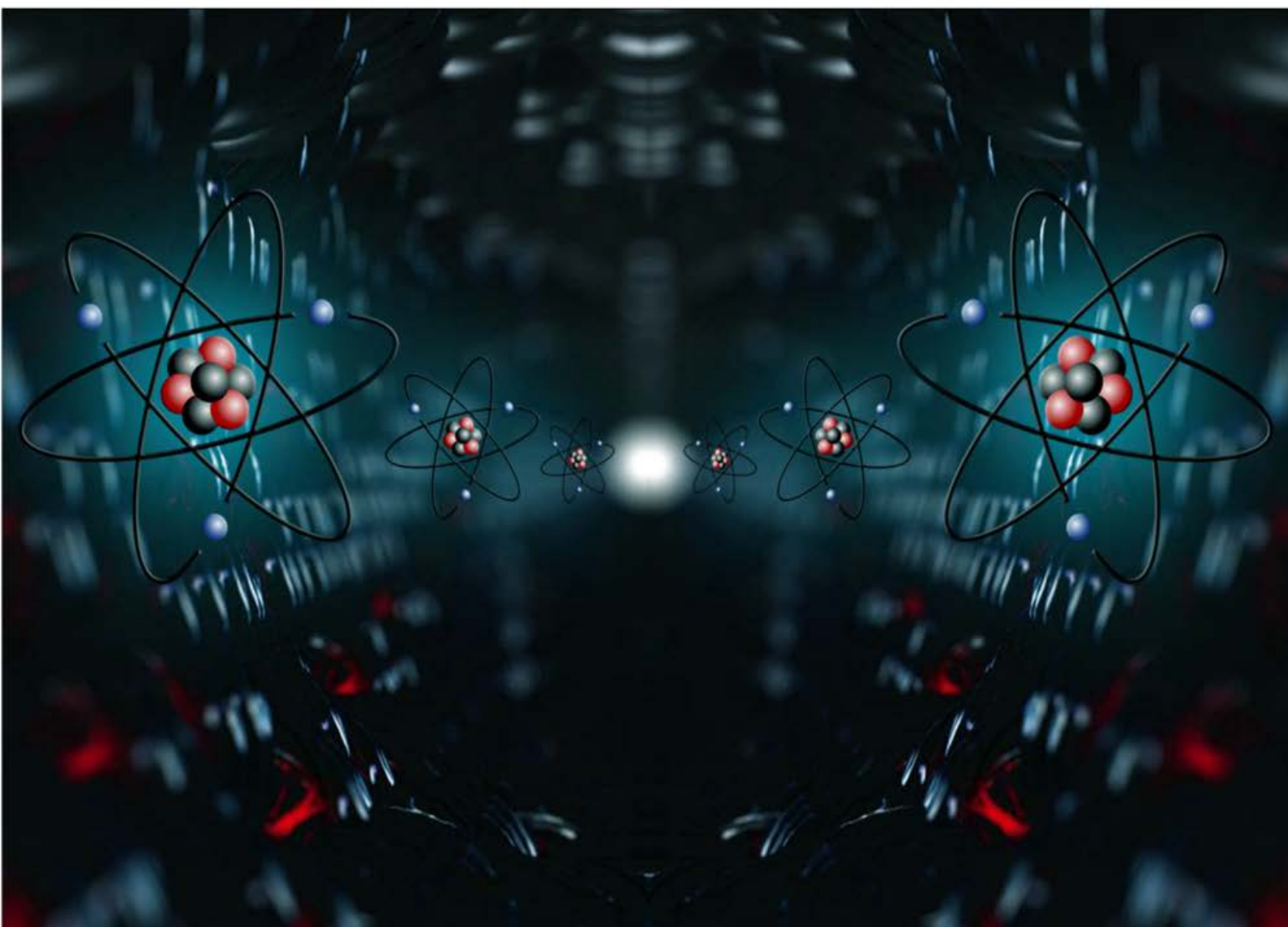
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**Volume I**

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