

First and Second laws of thermodynamics have led to new concepts of energy content and entropy. The Third law, however, does not lead to any new concept. It only places a limitation on the value of the entropy of a crystalline solid. Some scientists hesitate to call it a 'law' at all. All the same, its applications do lead to conclusions which are borne out by experience and hence, in accordance with scientific terminology, it is a law, like the other two laws of thermodynamics.

Nernst Heat Theorem. Before passing on to the Third law of thermodynamics, we may consider briefly the Nernst heat theorem. This is an old generalisation but still has relevance as the forerunner of the Third law of thermodynamics.

From the Gibbs-Helmholtz equation, viz.,

$$\Delta G - \Delta H = T (\partial(\Delta G)/\partial T)_P \quad \dots(1)$$

where ΔG is the change in free energy and ΔH is the change in enthalpy accompanying any process including a chemical reaction, it is seen that at the absolute zero (i.e., $T=0$), $\Delta G = \Delta H$.

Richards, by measuring EMFs of cells at different temperatures, found that the value of $\partial(\Delta G)/\partial T$ decreases with decrease in temperature and, therefore, concluded that ΔG and ΔH tend to approach each other more and more closely as the temperature is lowered. Nernst, relying on this data, made an important suggestion that the value of $\partial(\Delta G)/\partial T$ approaches zero gradually as the temperature is lowered towards the absolute zero. This is known as the **Nernst heat theorem**. According to this theorem, ΔG and ΔH not only become equal to each other at absolute zero but also approach each other asymptotically, that is, gradually at temperatures close to absolute zero. This is illustrated in Fig. 1. Thus, the approach of ΔG and ΔH towards each other is as represented by the full lines and not as represented by the dotted lines.

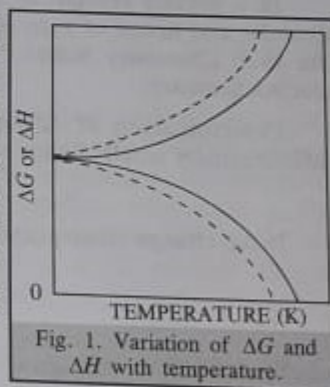


Fig. 1. Variation of ΔG and ΔH with temperature.

Mathematically, the theorem may be expressed as

$$\lim_{T \rightarrow 0} [\partial(\Delta G)/\partial T]_P = \lim_{T \rightarrow 0} [\partial(\Delta H)/\partial T]_P = 0 \quad \dots(2)$$

where Lt stands for the limiting value.

We also know from the Second law of thermodynamics that

$$(\partial(\Delta G)/\partial T)_P = -\Delta S \quad \dots(3)$$

and

$$(\partial(\Delta H)/\partial T)_P = \Delta C_P \quad \text{(Kirchhoff equation)} \quad \dots(4)$$

where ΔS is the entropy change of the reaction and ΔC_P is the difference in the heat capacities of the products and the reactants.

It follows from Eqs. 2, 3 and 4 that

$$\lim_{T \rightarrow 0} \Delta S = 0 \quad \dots(5)$$

and

$$\lim_{T \rightarrow 0} \Delta C_p = 0 \quad \dots(6)$$

The significance of these equations is that the entropy change of a reaction tends to approach zero and that the difference between the heat capacities of products and reactants also tends to approach zero as the temperature is lowered towards the absolute zero.

The Nernst theorem holds good only in the case of pure solids.

Third Law of Thermodynamics. According to Eq. 6, ΔC_p tends to approach zero at 0 K. This means that at absolute zero, the heat capacities of products and reactants in solid state are identical. This leads to the suggestion that at absolute zero, all substances have the same heat capacity. The quantum theory, as applied to heat capacities of solids, has shown that heat capacities of solids tend to become zero at 0 K. The Nernst heat theorem may, therefore, be written as

$$\lim_{T \rightarrow 0} C_p = 0 \quad \dots(7)$$

According to Eq. 5, ΔS becomes zero at absolute zero, i.e., the entropy change of a process involving solids becomes zero at 0 K. In other words, the absolute entropies of products and reactants in the solid state are identical. Planck, therefore, suggested that entropies of all pure solids approach zero at 0 K, i.e.,

$$\lim_{T \rightarrow 0} S = 0 \quad \dots(8)$$

This statement has led to the following enunciation of the **Third law of thermodynamics** :

At the absolute zero of temperature, the entropy of every substance may become zero and it does become zero in the case of a perfectly crystalline solid.

In a perfect crystal, at absolute zero temperature, there is a state of perfect order, i.e., zero disorder and hence of zero entropy. Walther Nernst (1864-1941), the German chemist, was awarded the 1920 Chemistry Nobel Prize for his work in thermochemistry. He also did pioneering work in electrochemistry.

Determination of Absolute Entropies of Solids, Liquids and Gases. We know that for an infinitesimally small change of state of a substance or a system, the entropy change is given by

$$dS = dq/T \quad \dots(9)$$

If the change takes place at constant pressure, then

$$(\partial S)_p = (\partial q)_p/T \quad \dots(10)$$

$$(\partial S/\partial T)_p = (\partial q/\partial T)_p \times 1/T \quad \dots(11)$$

$$(\partial q/\partial T)_p = C_p \quad \dots(12)$$

$$(\partial S/\partial T)_p = C_p \times 1/T \quad \dots(13)$$

or at constant pressure, $dS = (C_p/T)dT$... (14)

For a perfectly crystalline substance, the absolute entropy $S=0$ at $T=0$. Therefore, we may write

$$\int_{S=0}^{S=S} dS = \int_{T=0}^{T=T} (C_p/T)dT \quad \dots(15)$$

or

$$S_T = \int_0^T \frac{C_p dT}{T} = \int_0^T C_p d(\ln T) \quad \dots(16)$$

where S_T is the absolute entropy of the crystalline solid under examination at the temperature T .

The integral in Eq. 16 can be evaluated by measuring C_p at various temperatures between $T=0$ and the desired temperature T and then plotting C_p against $\ln T$ and determining the area under the curve between $T=0$ and the required temperature T . This area gives directly the value of S_T . Since it is not possible to obtain the value of C_p at the absolute zero, heat capacities are measured up to as low a temperature as possible, usually up to 15 K and the value at the absolute zero is obtained by extrapolation. This method, therefore, consists in determining heat capacities of the substance under examination at temperatures varying from approximately 15 K to the required temperature T . A graph of C_p vs $\ln T$ is then plotted and extrapolated to the absolute zero of temperature, as shown in Fig. 2. The area under the graph gives the required value of S_T , the absolute entropy of the substance at temperature T .

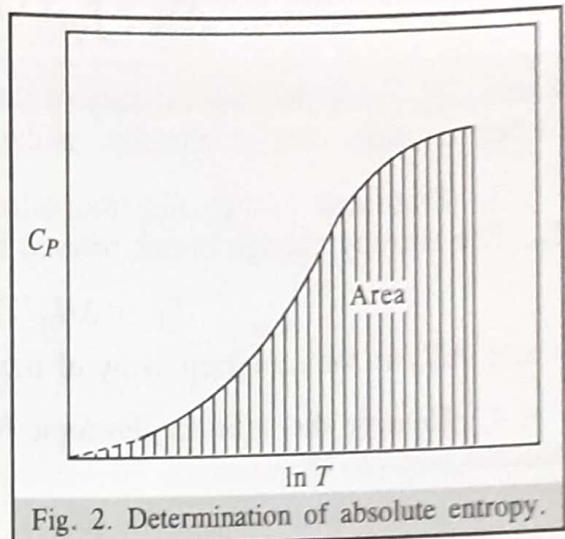


Fig. 2. Determination of absolute entropy.

Eq. 16. is thus written as follows :

$$S_T = \int_0^{T^*} C_p \frac{dT}{T} + \int_{T^*}^T C_p \frac{dT}{T} \quad \dots(17)$$

where $0 < T^* < 15$ K.

The first integral is evaluated with the help of the Debye theory of heat capacities of crystalline substances according to which, at very low temperatures ($0 < T < 15$ K),

$$C_p \approx C_v \approx aT^3 \quad \dots(18)$$

where a is an empirical constant. Eq. 18 is known as the Debye T^3 law.

Accordingly, Eq. 17 may be written as

$$S_T = \int_0^{T^*} aT^3 \frac{dT}{T} + \int_{T^*}^T C_p \frac{dT}{T} = \frac{1}{3}a(T^*)^3 + \int_{T^*}^T C_p \frac{dT}{T} \quad \dots(19)$$

The second integral in Eq. 17 is evaluated from experimental measurements of heat capacities. Combining the heat capacity data with the enthalpy data on phase transformations, the absolute entropy of a substance, whether solid, liquid or gas, at temperature T , can be determined, as illustrated below. In every case, the start is made with the substance in the crystalline solid state at the absolute zero when its absolute entropy is taken as zero. Then the total absolute entropy of the substance in the given state and at a given temperature is taken as the sum of all the entropy changes that the substance has to undergo in order to acquire the given state at the given temperature starting from the crystalline solid at absolute zero.

Suppose, it is required to determine absolute entropy of a gas at 25°C under atmospheric pressure. This would be equal to the sum of the entropy changes involved in the following processes each of which is brought about reversibly. It is assumed for general discussion that the substance in solid state exists in two allotropic forms α and β .

1. Heating the crystalline solid from absolute zero to temperature T^* , where $0 < T^* < 15$ K and evaluating the entropy change with the aid of the Debye's theory. Let the entropy change be ΔS_1 . Then,

$$\Delta S_1 = \int_0^{T^*} aT^3 \frac{dT}{T} = \frac{1}{3}a(T^*)^3 \quad \dots(20)$$

2. Heating the crystalline solid from T^* to T_{tr} where T_{tr} is the transition temperature at which the crystalline solid changes from allotropic form α to allotropic form β . The entropy change in this

process is given by

$$\Delta S_2 = \int_{T^*}^{T_r} C_{P,s}(\alpha) dT \quad \dots(21)$$

where $C_{P,s}(\alpha)$ is the heat capacity of the solid in allotropic form α . ΔS_2 is evaluated by the integration of heat capacity data graphically, as described above.

3. Transition of the solid from allotropic form α to allotropic form β at the transition temperature T_{tr} . The entropy change in this process is given by

$$\Delta S_3 = \Delta H_{tr}/T_{tr} \quad \dots(22)$$

where ΔH_{tr} is the molar enthalpy of transition.

4. Heating the solid in allotropic form β up to its fusion point, T_{fus} . The entropy change in this process is given by

$$\Delta S_4 = \int_{T_{tr}}^{T_{fus}} C_{P,s}(\beta) dT \quad \dots(23)$$

where $C_{P,s}(\beta)$ is the heat capacity of the solid in allotropic form β .

5. Changing the solid in allotropic form β into the liquid state at the fusion temperature T_{fus} . The entropy change of this process (entropy of fusion) is given by

$$\Delta S_5 = \Delta H_{fus}/T_{fus} \quad \dots(24)$$

where ΔH_{fus} is the molar enthalpy of fusion of the substance.

6. Heating the liquid from its freezing point (T_{fus}) to its boiling point (T_b). The entropy change involved in this case is given by

$$\Delta S_6 = \int_{T_{fus}}^{T_b} C_{P,l} d \ln T \quad \dots(25)$$

where $C_{P,l}$ is the heat capacity of the substance in the liquid state. This can be evaluated by plotting $C_{P,l}$ vs $\ln T$ between temperatures T_{fus} and T_b and noting the area below the graph, as described before.

7. Changing the liquid into the gaseous state at the temperature T_b . The entropy change involved here, ΔS_7 , is the molar entropy of vaporisation and is given by

$$\Delta S_7 = \Delta H_{vap}/T_b \quad \dots(26)$$

where ΔH_{vap} is the enthalpy of vaporisation per mole of the substance.

8. Heating the gas from T_b to the required temperature, *i.e.*, 25°C (298.15 K). The entropy change involved in this process is given by

$$\Delta S_8 = \int_{T_b}^{298.15} C_{P,g} d \ln T \quad \dots(27)$$

where $C_{P,g}$ is the heat capacity of the substance in the gaseous state at constant pressure. ΔS_8 is evaluated by plotting $C_{P,g}$ vs $\ln T$ between temperatures T_b and 298.15 K and noting the area below the curve.

The absolute entropy of the gas at 298.15 K (25°C), S_T , is equal to the sum of all the entropy changes listed above. Thus,

$$S_T = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5 + \Delta S_6 + \Delta S_7 + \Delta S_8$$

Experimental Verification of the Third Law of Thermodynamics

The heat capacity and enthalpy data on substances that exist in two different crystalline forms may serve to verify the Third law of thermodynamics. For reversible isothermal transition, $\alpha \rightarrow \beta$, we can write

$$\Delta S = S_{\beta} - S_{\alpha} = \Delta H_{tr}/T_{tr} \quad \dots(28)$$

where ΔH_{tr} and T_{tr} are the experimentally determined enthalpy of transition and the temperature of transition, respectively.

$$\Delta S = S_0(\beta) + \int_0^{T_{tr}} \frac{C_{P,S}(\beta)}{T} dT - S_0(\alpha) - \int_0^{T_{tr}} \frac{C_{P,S}(\alpha)}{T} dT = \Delta H_{tr}/T_{tr} \quad \dots(29)$$

If an experiment proves that

$$\int_0^{T_{tr}} \frac{C_{P,S}(\beta)}{T} dT - \int_0^{T_{tr}} \frac{C_{P,S}(\alpha)}{T} dT = \frac{\Delta H_{tr}}{T_{tr}} \quad \dots(30)$$

then it will also prove that $S_0(\beta) = S_0(\alpha)$.

Thus, both the crystalline modifications α and β would have equal entropies at 0 K, in accordance with Third law of thermodynamics.

Experiments carried out on systems such as sulphur, tin and phosphine have demonstrated the validity of the Third law.

The following results have been obtained on phosphine :

$$\Delta S_{tr} = \frac{\Delta H_{tr}}{T_{tr}} = \frac{185.7 \text{ J mol}^{-1}}{49.43 \text{ K}} = 15.73 \text{ J K}^{-1} \text{ mol}^{-1} \quad \dots(31)$$

In respect of phosphine, the difference of the two integrals in Eq. 30 is experimentally found to be $15.69 \text{ J K}^{-1} \text{ mol}^{-1}$, i.e.,

$$\int_0^{T_{tr}} \frac{C_{P,S}(\beta)}{T} dT - \int_0^{T_{tr}} \frac{C_{P,S}(\alpha)}{T} dT = 15.69 \text{ J K}^{-1} \text{ mol}^{-1} \quad \dots(32)$$

A comparison of the two results shows that, within the limits of experimental error, the Third law is valid for phosphine.

Entropies of Real Gases

From one of the Maxwell relations

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad \text{or} \quad dS = -\left(\frac{\partial V}{\partial T}\right)_P dP \quad \dots(33)$$

Integrating between pressures P_1 and P_2 at constant T , we get

$$\int_1^2 dS = -\int_{P_1}^{P_2} \left(\frac{\partial V}{\partial T}\right)_P dP \quad \dots(34)$$

A real gas behaves ideally at low pressures. Let this pressure be P . Let $(S_r)_1$ be the entropy of the real gas at 1 atm pressure and $(S_r)_P$ be the entropy at pressure P , the temperature remaining constant. Then, Eq. 34 becomes

$$(S_r)_1 - (S_r)_P = -\int_P^1 \left(\frac{\partial V}{\partial T}\right)_P dP \quad \dots(35)$$

For an ideal gas, $(\partial V/\partial T)_P = R/P$. If $(S)_1$ and $(S)_2$ are the entropies of an ideal gas at 1 atm and P atm, respectively, then, Eq. 35 can be written as

$$(S)_2 - (S)_1 = \int_P^1 (R/P) dP \quad \dots(35)$$

We can equate $(S)_2$ with $(S)_1$ because at the low pressure P , the real gas behaves ideally.

Adding Eqs. 35 and 36, we get

$$(S)_1 - (S)_2 = S^\circ - S = \int_P^1 \left[\left(\frac{\partial V}{\partial T} \right)_P - \frac{R}{P} \right] dP \quad \dots(36)$$

where S° is the standard entropy and S is the entropy of real gas both determined at 1 atm. We have to determine S° . Here S is given by

$$S = \frac{1}{3} a(T^*)^3 + \int_{T^*}^{T_1} \frac{C_{p,S}}{T} dT + \frac{\Delta H_{fus}}{T_{fus}} + \int_{T_1}^{T_2} \frac{C_{p,l}}{T} dT + \frac{\Delta H_v}{T_b} + \int_{T_b}^T \frac{C_{p,g}}{T} dT \quad \dots(37)$$

Though the integrals in Eq. 38 can be evaluated graphically, it is more convenient to do so with the use of Berthelot's equation of state, viz.,

$$\left(P + \frac{a}{TV^2} \right) (V - b) = RT \quad \dots(38)$$

which is more appropriate to use than the van der Waals equation of state.

Multiplying and rearranging, we get

$$PV = RT + Pb - \frac{a}{TV} + \frac{ab}{TV^2} \quad \dots(39)$$

The term ab/TV^2 in the above equation is negligible as compared to other terms since the Berthelot constants a and b are small.

$$PV = RT + Pb - a/TV = \left[1 + \frac{Pb}{RT} - \frac{aP}{R^2T^2} \right] \quad (\because V \approx RT/P) \quad \dots(40)$$

For Berthelot's equation of state, the constants a , b and R can be written in terms of the critical constants. Accordingly,

$$a = (16/3) P_c V_c^2 T_c; \quad b = V_c/4; \quad R = (32/9) P_c V_c/T_c \quad \dots(41)$$

Hence, Eq. 41 becomes

$$PV = RT \left[1 + \frac{9}{128} \frac{PT_c}{P_c T} \left(1 - \frac{T_c^2}{6T^2} \right) \right] \quad \dots(42)$$

Dividing by P , we have

$$V = \frac{RT}{P} + \frac{9}{128} \frac{RT_c}{P_c} - \frac{27}{64} \frac{RT_c^3}{P_c T^2} \quad \dots(43)$$

$$\therefore \left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{P} + \frac{27}{32} \frac{RT_c^3}{P_c T^3} \quad \dots(44)$$

Substituting for $(\partial V/\partial T)_P$ in Eq. 37, we get

$$S^\circ = S + \frac{27}{32} \frac{RT_c^3}{P_c T^3} \int_P^1 dP = S + \frac{27}{32} \frac{RT_c^3}{P_c T^3} (1 - P) = S + \frac{27}{32} \frac{RT_c^3}{P_c T^3} \quad (\because P \ll 1) \quad \dots(45)$$

As mentioned earlier, S is given by Eq. 38. In Eq. 46, the second term is the correction term that should be added to S to give S° , the standard entropy for a real gas.

Entropy Changes in Chemical Reactions

We can calculate ΔS° for a chemical reaction from the tabulated standard entropy values for the reactants and products at 298 K. This is one of the most important applications of the Third law of thermodynamics. For a reaction



occurring in the standard state, the standard entropy change, ΔS° , is given by

$$\begin{aligned} \Delta S^\circ &= [lS_L^\circ + mS_M^\circ + \dots] - [aS_A^\circ + bS_B^\circ + \dots] \\ &= \sum S_{\text{products}}^\circ - \sum S_{\text{reactants}}^\circ \end{aligned} \quad \dots(47)$$

where S° s are the molar standard entropies of the species involved and a, b, l, m , etc., are the stoichiometric coefficients.

From the tabulated values of S° , ΔS° for the reaction at 298 K can be calculated. The ΔS° value at any other temperature can be calculated by the Kirchoff-type equation, viz.,

$$\left[\frac{d(\Delta S^\circ)}{dT} \right]_P = \sum \left(\frac{\partial S_{\text{products}}^\circ}{\partial T} \right)_P - \sum \left(\frac{\partial S_{\text{reactants}}^\circ}{\partial T} \right)_P \quad \dots(48)$$

Since $(\partial S/\partial T)_P = C_P/T$, we have

$$\left[\frac{d(\Delta S^\circ)}{dT} \right]_P = \sum (C_P/T)_{\text{products}} - \sum (C_P/T)_{\text{reactants}} \quad \dots(49)$$

Rearranging and integrating between 298 K and T K, we have

$$\begin{aligned} \int_{298}^T d(\Delta S^\circ) &= \int_{298}^T (\Delta C_P/T) dT = \int_{298}^T \Delta C_P d \ln T \\ \Delta S_T^\circ &= \Delta S_{298}^\circ + \int_{298}^T \Delta C_P d \ln T \end{aligned} \quad \dots(50)$$

Eq. 50 is applicable to chemical reactions involving solids, liquids or gases.