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(A Constituent College of Magadh university)

B.Sc (H)Physics Part I

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Third Law of Thermodynamics

1 Introduction

In previous topics, we studied about an important state function ‘entropy’ of the thermodynamic systems and calculated the change in this function during some reversible/irreversible processes. We had been familiarized with the fact that entropy (of the universe) remains the same during a reversible process and always increases whenever the process occurs irreversibly. Let us consider a thermodynamic system which absorbs an infinitesimal amount of heat dQ reversibly at temperature T , then, from the definition, the change in the entropy of the system is given by equation

$$dS = dQ/T \dots\dots\dots (1)$$

Now, for the processes involving unit mass occurring at constant pressure dQ may be written as;

$$dQ = \frac{C_p dT}{T} \dots\dots\dots (2)$$

And, the entropy S can be obtained by integration, so that

$$S = \int \frac{C_p}{T} dT + \text{Constant of integration} \dots\dots(3)$$

Writing above equation as a definite integral, we have that the entropy of a system measured at some temperature T is given by;

$$S(T) = \int_{T_0}^T \frac{C_p}{T} dT + S(T_0) \dots\dots\dots(4)$$

or

$$S(T) - S(T_0) = \int_{T_0}^T \frac{C_p}{T} dT \dots\dots\dots (5)$$

where T_0 is some different temperature. Thus from above equation, it seems that we are only able to find the *change in entropy* and not the absolute measurement of entropy itself at a given temperature. On the other hand, with the fact that the entropy decreases with temperature, what value will it take when temperature is absolute zero? The answer of this question is given by the third law of thermodynamics. Below are given some of the statements of the third law.

2 Statements of the third law

While Walter Nernst's ingenious intuition was led to the establishment of third law of thermodynamics, some other distinguished people, most notably Max Planck, Albert Einstein, and Simon contributed significantly in the development of this important scientific venture. The third law of thermodynamics has evolved from the Nernst observations on the chemical thermodynamics of electro-chemical cells. After his statement of third law, the discussions were made between him, Planck and Einstein regarding his analysis on an entropy change in a reacting system at temperatures approaching absolute zero. Even after 100 years since this discussion took place, there is still no satisfactory universal formulation of the third law thermodynamics. The development of the understanding about the third law by different scientists based on their own experimental/theoretical analysis is briefly presented below.

Walter H. Nernst (1864-1941) had carried out some experiments on electro-chemical cells and analyzed the data based on chemical thermodynamics. His conclusions were mainly concerned with the changes in enthalpy (ΔH) and Gibbs' function (ΔG). According to the relation: $G = H - TS$, the change in the Gibbs' free energy could be obtained as $\Delta G = \Delta H - T\Delta S$ so that, theoretically, $\Delta G \longrightarrow \Delta H$ as $T \longrightarrow 0$. Experimentally, it was found true, but he observed that ΔG and ΔH not only came closer together on cooling, but they approached each other asymptotically. He also postulated that $\Delta S \longrightarrow 0$ as $T \longrightarrow 0$.

Max Planck (1858-1947) made a hypothesis in 1911 that the entropy of a perfect crystal is zero and further it is believed to be true about any system which is in **internal equilibrium**. For example, the systems such as ^4He and ^3He which are liquids at very low temperature, and electrons in a metal can be treated as a gas even at temperature down to $T = 0$. Here, the zero entropy could be understood by taking into account its statistical definition *i.e.* $S = k_B \log \Omega$. $S=0$ implies that $\Omega=1$, meaning by at absolute zero, the system is in its ground state which is non-degenerate.

Einstein (1879-1955) was first to investigate the entropy of quantum systems at low temperatures. He, on the basis of theoretical calculations, proposed that heat capacities should vanish at absolute zero which implies that S is finite as T tends to 0. Later on, Nernst and his group at University of Berlin undertook experimental investigation of physical properties at low temperatures and the results were in agreement (almost) with Einstein's prediction. The quantum theory of heat capacity led by Einstein was later corrected by Debye to produce a better quantitative match with Nernst's experimental results.

Now, let us discuss one by one the statements made by different physicists about the third law of thermodynamics;

Planck's statement: The entropy of any pure crystalline substance tends to a universal constant (which can be taken to be zero) When temperature falls to absolute zero *i. e.*

$$S \longrightarrow 0 \text{ as } T \longrightarrow 0$$

Explanation: As we have learned from the previous lessons that entropy is related with the degree of ordering of the constituents of a system *i.e.* lower the ordering, higher the entropy and vice-versa. For a solid substance, the lowest-energy (highest ordering) phase, which could be achieved by cooling it down to zero, is the perfect crystal. Planck chose zero value for the entropy of a perfect crystal. It was further motivated by the development of statistical mechanics, according to which entropy can also be defined as $S = k_B \log \Omega$. From this definition of entropy, zero entropy is equivalent to $\Omega = 1$ which implies that, at absolute zero temperature, a system finds its ground state (lowest energy state) and this ground state is non-degenerate. Planck actually made his statement about third law for perfect crystals. However, with the condition that all parts of a system being in the **internal equilibrium** with each other, it could be true about any system *e.g.* electrons in metal and liquid helium (^3He , ^4He) at temperatures down to zero.

One can have an **apparent objection** on the Planck's formulation of third law. Consider a system of N spinless atoms forming a perfect crystal. According to the Planck statement, the entropy of the considered system, being a perfect crystal, should be zero. However, if we assume that the nucleus of each atom possesses angular momentum I and in the absence of applied magnetic field, the degeneracy of the nuclear spin will be $(2I + 1)$. Now, if $I > 0$, the degeneracy will not be equal to 1 and we will have $S = Nk_B \log(2I + 1) \neq 0$ which contradicts the statement ($S = 0$) for perfect crystals. The **answer** to above contradiction is hidden in the term *internal equilibrium*. It implies that the individual components of the system must be able to exchange energy with each other *i.e.* to interact with each other. So, for the above example, the nuclear spins feel a tiny magnetic field due to their dipolar fields and this lifts the degeneracy of the system to give non-degenerate ground state at absolute zero which corresponds to ($S = 0$).

Simon's statement: In internal thermodynamic equilibrium, the contribution to the entropy by each aspect of the system tends to zero as temperature (of the system) approaches to 0.

Explanation: Here the term "aspect" indicates about different sub-systems of the main thermodynamic system under study. For a crystal, the subsystems like electrons, nuclear spins, and nucleons *etc.* are called as aspects. The introduction of the term aspect by Simon made his statement convenient by allowing one to focus on a particular aspect of interest while ignoring the aspects that we do not care about. When we cool a crystal, we extract energy from the lattice and its entropy drops towards zero as temperature approaches to zero. However, the nuclear spins may still retain their entropy and it require further cooling to a much lower temperature to have zero entropy. Moreover, if we find method of cooling the nuclei, there might still be some residual entropy associated with the individual nucleons.

Einstein's statement: As the temperature falls to absolute zero, the entropy of any substance remains finite.

$$S(T, y) \longrightarrow S_0(y) \text{ Where } |S_0| < \infty \text{ as } T \longrightarrow 0, |y| < \infty \quad \dots(6)$$

The limiting value S_0 may depend on y ; which is supposed to remain finite at $T \longrightarrow 0$.

Explanation: In his theory about heat capacities of solids, Einstein proposed that the heat capacities should vanish at absolute zero. Considering expression for the entropy change in a constant pressure heating process;

$$S = \int_0^T \frac{C_P}{T} dT \quad \dots\dots\dots (7)$$

In above equation, C_P stands for y and equation (7) presumes heat capacity to vanish *i.e.* $C_P \longrightarrow 0$, as $T \longrightarrow 0$,

Since otherwise, S will diverge to $-\infty$ as $T \longrightarrow 0$. A similar conclusion can be obtained for C_V by considering the heating process with constant volume.

Nernst's statement: According to Nernst, the change in entropy of a system undergoing any reversible isothermal process approaches to zero as temperature tends to 0 °K. In other words, All reactions in a system being in internal equilibrium occur without any change in entropy at temperature near to absolute zero.

Mathematically, we can express it as:

$$\lim_{T \rightarrow 0} \Delta S \rightarrow 0$$

Consequences of the third law

Having familiarized with the third law of thermodynamics in terms of the statements given by different learned physicists, let us discuss some of its consequences;

1 Heat capacities near absolute zero?

It can be easily shown that the value of any heat capacity will tend to 0, as temperature approaches absolute 0°K *e.g.*

The heat capacity C can be expressed in terms of entropy as;

$$C = T \left(\frac{\partial S}{\partial T} \right)$$

$$C = T \left(\frac{\partial S}{\partial \ln T} \right)$$

Now from above equation, when $T \rightarrow 0$, $\ln T \rightarrow -\infty$ and hence C will tend to zero. Recall that this result differs from the classical predictions according to which $C = R/2$ per mole per degree of freedom (for gases). However, the classical theory based on equipartition theorem is a high temperature phenomenon which fails at low temperatures. The quantum mechanical treatment by Debye conveniently explained the behavior of heat capacities for

both high and low temperature limits. Variation of heat capacity as T^3 at low temperatures predicted by Debye is known as **T^3 Law**.

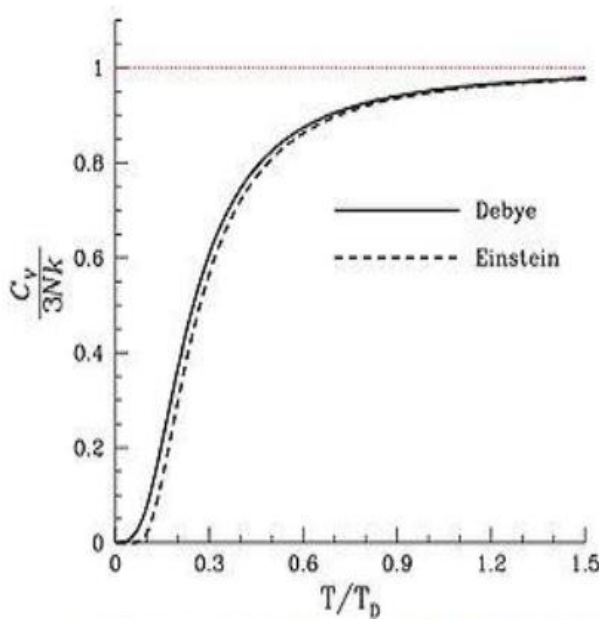


Figure 1 (taken from Wikipedia): Variation of dimensionless heat capacity as a function of temperature as predicted by classical (red line), quantum mechanically (the Debye model and by Einstein's models). The horizontal axis is the temperature divided by the Debye temperature. Note that, the dimensionless heat capacity is zero at absolute zero, and rises to a value of three as the temperature becomes much larger than the Debye temperature.

3.2 No gases remain ideal as

We are familiar with the fact that no any real gas behaves as an ideal gas. The concept of ideal gas is just a combination of some idealized conditions extracted from the theoretical/experimental observations made by some scientists such as Boyle, Charles, and Gay-Lussac. However, the ideal gas equation describes the real gases quite well under quite a wide range of conditions.

We know that for a mole of mono-atomic ideal gas, the difference between its heat capacities equals a constant *i.e.*

$C_p - C_v = R$; However, both C_p and $C_v \rightarrow 0$ as $T \rightarrow 0$ and the relation can not be satisfied. Moreover, from the expression for the entropy for an ideal gas;

$$S = C_v \ln T + R \ln V + \text{constant} \quad (10.10)$$

As $T \rightarrow 0$, the above equation yields $S \rightarrow -\infty$ which is as far from zero as you can get! Thus the third law limits the ideal gas model when temperature approaches zero. Of course, at low temperatures, the interactions between gas molecules become important which were ignored during ideal gas modeling. It requires more sophisticated models describing the behavior of gases at low temperatures.

3.3 Thermal expansion stops as $T \rightarrow 0$

$$\left(\frac{\partial S}{\partial p}\right)_T = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$$

where $\frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p = \beta_p$ is the isobaric expansivity. It is clear that $\beta_p \rightarrow 0$ as $T \rightarrow 0$ (because

$S \rightarrow 0$ when $T \rightarrow 0$ and when $S \rightarrow 0$, $\left(\frac{\partial S}{\partial p}\right)_T \rightarrow 0$ which implies the result).

3.4 Curie's law breaks down as $T \rightarrow 0$

This law states that the magnetic susceptibility (χ) is inversely proportional to temperature

$$\chi = \frac{M}{B} = \frac{C}{T} \quad \dots\dots\dots(2)$$

Where M is magnetization, B applied magnetic field and C is a material specific constant. From equation (2), it is clear that $\chi \rightarrow \infty$ as $T \rightarrow 0$. However, third law implies that i.e.

$$\left(\frac{\partial S}{\partial B}\right)_T \rightarrow 0$$

and hence

$$\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial m}{\partial T}\right)_B = \frac{VB}{\mu_0} \left(\frac{\partial \chi}{\partial T}\right)_B \rightarrow 0$$

Thus $\left(\frac{\partial \chi}{\partial T}\right) \rightarrow 0$, this is in disagreement with Curie's law. The reason to this disagreement lies in the development of the law itself. Curie's law is derived by assuming the magnetic moments to be entirely independent and their properties were determined by considering only the interactions between the applied magnetic field (to align the moments) and the temperature (which randomize the moments). The magnetic susceptibility χ is a measure of responses of these independent moments to the applied magnetic field which will, obviously, become infinite (maximum) in the complete absence of randomizing force *i.e.* at $T = 0$.

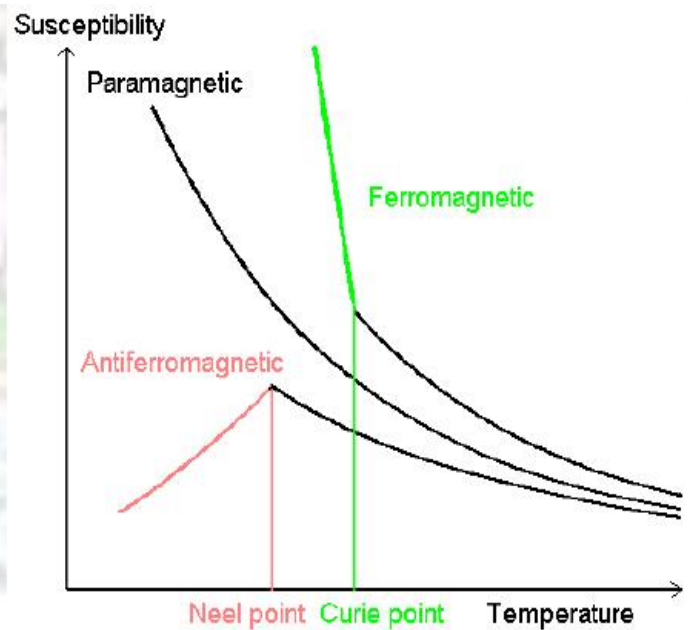


Figure 2: Variation of magnetic susceptibility with temperature (image taken from Wikipedia)

However, at very low temperatures ($T \rightarrow 0$), for the real magnetic systems, the interactions between the magnetic moments can not be ignored. Due to their mutual non-zero interactions these magnetic moments will be driven into some partially ordered state by each other and an applied magnetic field will have much less of an effect. It could be briefly stated as: the microscopic constituents of a system can behave independently at higher temperatures where the thermal energy ($k_B T$) is much larger than any interaction energy. The mutual interactions between the microscopic constituents become significant and their independence breaks down at low temperatures.

3.5 Unattainability of absolute zero

It is the main consequence of the third law, according to which “It is impossible to cool any system to $T = 0$ °K in finite number of steps”.

Let us understand above statement by considering the cooling behavior of a system in terms of the parameters entropy (S) and Temperature (T). Figure 3(a) shows the plot of S against T for different parameter X of the system.

Here, the cooling is produced by isothermal increase and adiabatic decrease in X respectively. If the third law were not to be followed, it would be possible to cool the system to absolute zero by proceeding according to figure 3 (a). However, due to the restriction caused by the third law (*i.e.* $S \rightarrow 0$, as $T \rightarrow 0$), the situation will be like as given in figure 3 (b). Clearly, the number of steps (isothermal increase and adiabatic decrease) needed to get absolute zero becomes infinite.

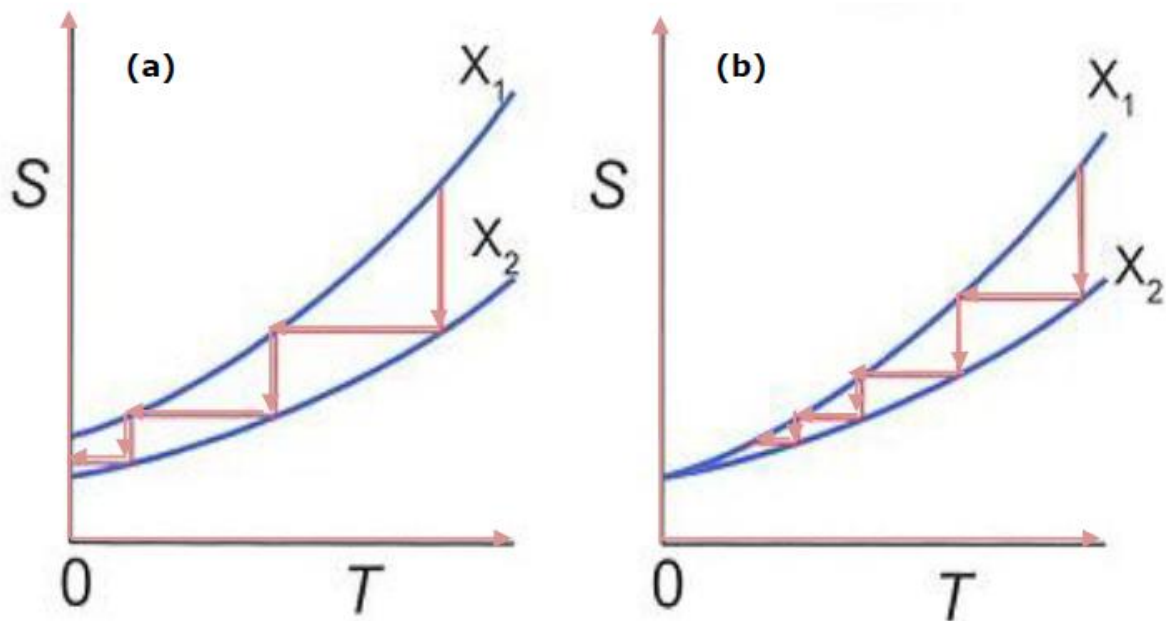


Figure 3: The entropy of as a function of temperature for two different values of a parameter X of a system.

Interesting fact

Is third law a consequence of the second law?

In above discussion, we have been familiarized with the fact that we can not attain absolute zero in a finite number of steps as a consequence of the third law. This makes a constraint on the maximum efficiency of the Carnot engine. Let us consider a Carnot engine operating between reservoirs with temperatures T_S and T_H where the subscripts S and H represents the low temperature *i.e.* sink and high temperature heat reservoirs respectively. Now, from the expression for the efficiency of Carnot engine *i.e.* $\eta = 1 - \frac{T_H}{T_S}$, if $T_S \rightarrow 0$, the efficiency η will tend to 1 (maximum value). The Carnot engine when operated under this condition, we will have a complete conversion of heat into work, in violation of Kelvin's statement of the second law. From here, it seems at first sight that un-attainability of absolute zero (an outcome of third law) is simply a consequence of the second law itself.

Explanation: We have considered in above example, the Carnot engine operating between two reservoirs, one of which is at absolute zero. The difficulty lies in our consideration *i.e.* how can one perform an isothermal process at absolute zero. Once a system is at absolute zero, it is not possible to change its state without heating it. Thus, the third law is indeed a separate postulate independent from the second law.