STUDY MATERIAL

Dumkal College, Basantapur

Subject: Chemistry

Course Code- CHEMHTDSE-3
Topic: Special selected topics

Name of the Teacher: Delwar Ansary

Course Title- Third Law of Thermodynamics

Definition of Third Law-

The third law of thermodynamics states that the entropy of a perfect crystal at a temperature of zero Kelvin (absolute zero) is equal to zero.

Entropy, denoted by 'S', is a measure of the disorder/randomness in a closed system. It is directly related to the number of microstates (a fixed microscopic state that can be occupied by a system) accessible by the system, i.e. the greater the number of microstates the closed system can occupy, the greater its entropy. The microstate in which the energy of the system is at its minimum is called the ground state of the system.

Entropy by definition,

$$S = \int_0^T \frac{\delta q_r}{T} + S_0 \quad \text{Where } S_0\text{- Entropy at 0K}$$

Alternate Statements of the 3rd Law of Thermodynamics

The Nernst statement of the third law of thermodynamics implies that it is not possible for a process to bring the entropy of a given system to zero in a finite number of operations.

The American physical chemists Merle Randall and Gilbert Lewis stated this law in a differentmanner: when the entropy of each and every element (in their perfectly crystalline states) is taken as 0 at absolute zero temperature, the entropy of every substance must have a positive, finite value.However, the entropy at absolute zero can be equal to zero, as is the case when a perfect crystal is considered.

The Nernst-Simon statement of the 3rdlaw of thermodynamics can be written as: for a condensed system undergoing an isothermal process that is reversible in nature, the associated entropy change approaches zero as the associated temperature approaches zero.

Another implication of the third law of thermodynamics is: the exchange of energy between two thermodynamic systems (whose composite constitutes an isolated system) is bounded.

Why is it Impossible to Achieve a Temperature of Zero Kelvin?

For an isentropic process that reduces the temperature of some substance by modifying some parameter X to bring about a change from 'X2' to 'X1', an infinite number of steps must be performed in order to cool the substance to zero Kelvin.

This is because the third law of thermodynamics states that the entropy change at absolute zero temperatures is zero. The entropy v/s temperature graph for any isentropic process attempting to cool a substance to absolute zero is illustrated below.
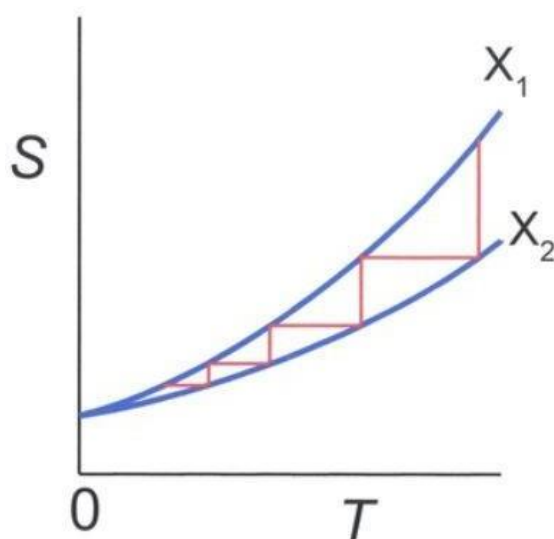
From the graph, it can be observed that – the lower the temperature associated with the substance,the greater the number of steps required to cool the substance further. As the temperature

approaches zero kelvin, the number of steps required to cool the substance further approaches infinity.

Applications of the Third Law of Thermodynamics

An important application of the third law of thermodynamics is that it helps in the calculation of the absolute entropy of a substance at any temperature 'T'. These determinations are based on the heat capacity measurements of the substance. For any solid, let S_0 be the entropy at 0 K and Sbe the entropy at T K, then

$$\Delta S = S - S_0 = \int T_0\, C_p dTT$$

According to the third law of thermodynamics, $S_0 = 0$ at 0 K,

$$S = \int T_0\, C_p T\ dT$$

The value of this integral can be obtained by plotting the graph of C_p/T versus T and then findingthe area of this curve from 0 to T. The simplified expression for the absolute entropy of a solid attemperature T is as follows:

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$$S = \int_{T_0} C_p T \, dT = \int_{T_0} C_p \, d\ln T$$

$$= C_p \ln T = 2.303 \, C_p \log T$$

Here C_p is the heat capacity of the substance at constant pressure and this value is assumed to be constant in the range of 0 to T K.

Nernst Heat Theorem

In 1906, Walther Nernst, a German chemist, studied the variation of enthalpy change and free energy change as a function of temperature.

We know that in Gibbs function $dG = -SdT + Vdp$ …………(i)

At constant pressure equation (i) becomes $\left(\frac{\partial G}{\partial T}\right)_P = -S$ ……..(ii)

We previously know that Gibbs- Helmholtz equation is -

$$G = H - TS = H + T\left(\frac{\partial G}{\partial T}\right)_P \text{ This}$$

$$\Delta G = \Delta H + T\left[\frac{\Delta(\partial G)}{\partial T}\right]_P$$

At absolute temperature we can write that $\Delta G \cong \Delta H$

According to Nernst $\lim_{T \to 0}\left|\frac{\Delta(\partial G)}{\partial T}\right|_P = 0$ $\lim_{T \to 0}\left|\frac{\Delta(\partial H)}{\partial T}\right|_P = 0$

Or we can write

$$\lim_{T \to 0}\left|\frac{\partial(G_2 - G_1)}{\partial T}\right|_P = 0$$

$$\text{or, } \lim_{T \to 0}\left|\left(\frac{\partial G_2}{\partial T}\right)_P - \left(\frac{\partial G_1}{\partial T}\right)_P\right|$$

$$\text{or, } \lim_{T \to 0}(S_1 - S_2) = 0 \quad \text{………(iii)}$$

" All reactions in isothermal process that is reversible in nature, the associated zero as the as the associated temperature approaches zero kelvin"

The sign of the slope of the ΔH vs T and ΔG vs T are proved as follows
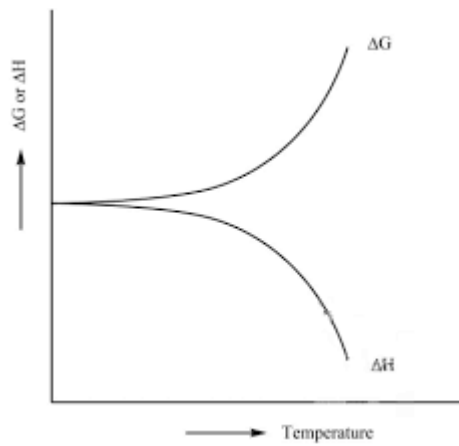
$$\Delta G - \Delta H = T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P$$

$$\text{or, } \frac{\partial(\Delta G)}{\partial T} - \frac{\partial(\Delta H)}{\partial T} = \frac{\partial(\Delta G)}{\partial T} + T\frac{\partial^2(\Delta G)}{\partial T^2}$$

$$\text{or, } -\frac{\partial(\Delta H)}{\partial T} = T\frac{\partial^2(\Delta G)}{\partial T^2} \quad \text{…………(iv)}$$

As near T→0 $T\frac{\partial^2(\Delta G)}{\partial T^2}$ has the same sign that of $\frac{\Delta(\partial G)}{\partial T}$ so from equation iv we can write that

$\frac{\partial(\Delta H)}{\partial T}$ and $\frac{\Delta(\partial G)}{\partial T}$ have opposite sign. Therefore if we plot ΔH vs T and ΔG vs T the we get following curve.

Reference Books:

1.Levine, I. N. Physical Chemistry, TataMcGraw-Hill.
2. Moore, W. J. Physical Chemistry, Orient Longman.
3. Atkins, P. W. & Paula, J. de Atkins', Physical Chemistry, Oxford University Press.
4. McQuarrie, D. A. &Simons, J. D. Physical Chemistry: A Molecular Approach