Chapter V

Second principle of thermodynamics

Introduction:

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 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.

Formulations

The third law has many formulations, some more general than others, some equivalent, and some neither more general nor equivalent.

The Planck statement: applies only to perfect crystalline substances; as temperature falls to zero; the entropy of any pure crystalline substance tends to a universal constant.

That is, $\lim_{T \to 0} S = S0$ whre S_0 is a universal constant that applies for all possible crystals, of all possible sizes, in all possible external constraints. So it can be taken as zero, giving $\lim_{T \to 0 =} 0$

The Nernst statement: concerns thermodynamic processes at a fixed, low temperature, for condensed systems, which are liquids and solids: The entropy change associated with any condensed system undergoing a reversible isothermal process approaches zero as the temperature at which it is performed approaches 0 K$^{\circ}$.

That is, $\lim_{T \to 0} S(T, X_1) - S(T, X_2) = 0$. Or equivalently,

At absolute zero, the entropy change becomes independent of the process path.

That is,

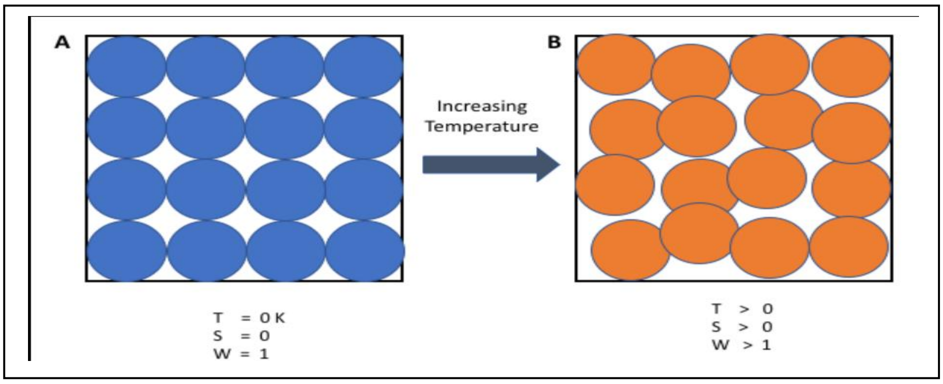
$$\forall x, \lim_{T \to 0} |S(T, x) - S(T, x + \Delta x)| \to 0$$

where Δx represents a change in the state variable x.

The Einstein statement: The entropy of any substance approaches a finite value as the temperature approaches absolute zero.

Explanation of Third Law of Thermodynamics:

In simple terms, the third law states that the entropy of a perfect crystal of a pure substance approaches zero as the temperature approaches zero. The alignment of a perfect crystal leaves no ambiguity as to the location and orientation of each part of the crystal. As the energy of the crystal is reduced, the vibrations of the individual atoms are reduced to nothing, and the crystal becomes the same everywhere.



The third law provides an absolute reference point for the determination of entropy at any other temperature. The entropy of a closed system, determined relative to this zero point, is then the absolute entropy of that system. Mathematically, the absolute entropy of any system at zero temperature is the natural log of the number of ground states times the Boltzmann constant $k_B = 1.38\times10^{-23}$ J K^{-1}.

Mathematical Application:

Let for any solid S^0_0 is entropy at zero kelvin and S is entropy at T kelvin.

So, $\Delta S = S - S_0$

$$\Delta S = \int_0^T \frac{C_p}{T} dt$$

Also, we know Since $S_0 = 0$ at by third law.

$$\Delta S = \int_0^T \frac{C_p}{T} dt$$

So, by this we can calculate the absolute entropy of any solid at temperature T.

Entropy change in a chemical reaction (ΔS_R)

Consider the following chemical reaction:

$$aA + bB \rightarrow cC + dD$$

You should now be able to look at a chemical reaction and predict the entropy change that takes place within the system. In this next section, we will explore one formula, which you can use to calculate this entropy change quantitively.

formed from the elements in the standard state.

The change in entropy of the chemical reaction is equal to the total absolute entropy of all the products, minus the total absolute entropy of all the reactants.

The formula given by the following equation:

$$\Delta S°_R = \sum n_p S_{porducts} - \sum n_R S_{reactants}$$

The entropy variation of a chemical reaction at a new temperature is given by **KIRCHHOFF's** relation:

$$\Delta S_{T_2} = \Delta S_{T_1} + \int_{T_1}^{T_2} \Delta n C_P \frac{dT}{T}$$

$$\Delta n C_P = \sum n_p C_{P_{porducts}} - \sum n_R C_{P_{reactants}}$$

Conclusion:

In the above content, we have discussed the importance of absolute zero and entropy and how these two aspects make up the third law of thermodynamics. This law states that absolute zero temperature is not possible in physics. This is often overlooked whenever anybody tries to attain zero temperature and regains temperature from the external environment and other sources. Hence, this law is highly intuitive to real-life applications.