Lecture-7

Contents

- Statistical view of entropy
    - Entropy and Probability
    - Boltzmann-Plank Equation
    - Configuration and weight of configuration (*W*)
    - A brief illustration of *W*

Entropy and Probability

Entropy

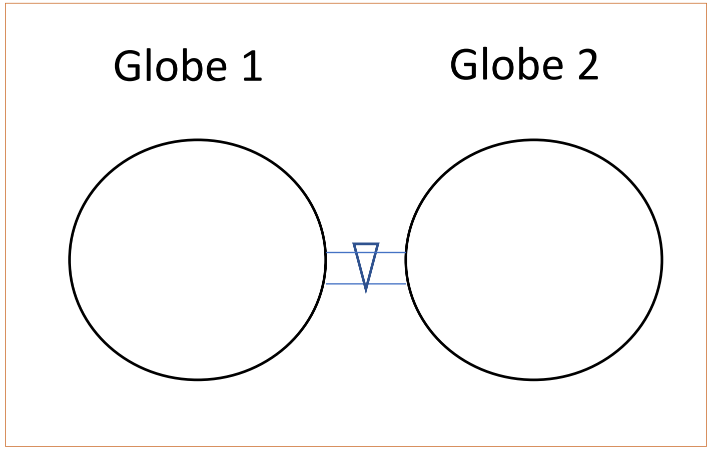
The entropy of a system is a measure of the disorder prevailing in it.

Probability

The thermodynamic probability of a system is defined as the total number of different ways in which the given system in the specified thermodynamic state may be realized. It is denoted by W.

Probability and spontaneity

- Let us consider a single molecule in the system. This molecule may be either in globe 1 or in globe 2. The probability of finding this molecule in one of this globe is ½ or 50%.



- If a second molecule is introduced, the probability of finding both molecules in the same globe is $\frac{1}{2} \times \frac{1}{2} = (\frac{1}{2})^2$.
- Similarly, the probability of finding all the N molecules in the same globe is $(\frac{1}{2})^N$.
- As N is very large, this probability is very low.
- On the other hand, the probability of uniform distribution is very high.

All spontaneous process represent changes from a less probable to a more probable state.

Boltzmann-Plank Equation

A functional relationship exists between the entropy S and the thermodynamic probability W of a system.

It is possible to write,

$$S = f(W)$$

Let us consider two systems 1 and 2. If the systems are combined.

For the combined system

Entropy = $S_1 + S_2$
Probability = $W_1 \times W_2$

[Because entropy is additive but the probability is multiplicative.]

Thus, $S_{12} = S_1 + S_2 = f(W_1 \times W_2)$

Also, $S_1 + S_2 = f(W_1) + f(W_2)$

Therefore, $f(W_1) + f(W_2) = f(W_1 \times W_2)$

Such a function relationship is obeyed only if

$$S = k\ lnW + C$$

where *k* and *C* are constants. This relation was first put forward by L. Boltzmann who left *k* and *C* undetermined.

M. Plank proposed that *C* is zero and hence

$$S = k\ lnW$$

Boltzmann-Plank Equation

where, *k* = Boltzmann constant = 1.38065×10^{-23} J K^{-1}

Configuration and weight of configuration

- We consider a closed system composed of N molecules. At any instant, there will be N_0 molecules in the state with energy ε_0, N_1 with ε_1, and so on. The instantaneous **configuration** of the system is $\{N_0, N_1, \ldots\}$. The instantaneous configuration fluctuates with time because the populations change.

- The weight of a configuration, W is the number of ways that molecules can be distributed over the available states.

- The weight of the configuration $\{N_0, N_1, \ldots\}$ is given by the expression

$$\mathcal{W} = \frac{N!}{N_0!N_1!N_2!\ldots}$$

A brief illustration of *W*

To calculate the number of ways of distributing 20 identical objects with the arrangement 1, 0, 3, 5, 10, 1, we note that the configuration is {1,0,3,5,10,1} with $N = 20$; therefore the weight is

$$\mathcal{W} = \frac{20!}{1!0!3!5!10!1!} = 9.31 \times 10^{8}$$

Self-test

Calculate the weight of the configuration in which 20 objects are distributed in the arrangement 0, 1, 5, 0, 8, 0, 3, 2, 0, 1. [4.19×10^{10}]

Lecture-8

Contents

- Nernst Heat Theorem
- Third Law of Thermodynamics
- Residual Entropy

The Nernst Heat Theorem

The entropy change accompanying any physical or chemical transformation approaches zero as the temperature approaches zero: $\Delta S \rightarrow 0$ as $T \rightarrow 0$ provided all the substances involved are perfectly ordered.

Conclusion of Nernst Heat Theorem

If we arbitrarily ascribe the value zero to the entropies of elements in their perfect crystalline form at $T = 0$, then all perfect crystalline compounds also have zero entropy at $T = 0$ (because the change in entropy that accompanies the formation of the compounds, like the entropy of all transformations at that temperature, is zero).

Third Law of Thermodynamics

The entropy of all perfect crystalline substances is zero at $T = 0$.

Justification of the third law of thermodynamics

Entropy, $S = k \ln W$

where, W is the number of microstates. In most cases, $W = 1$ at $T = 0$ because there is only one way of achieving the lowest total energy: put all the molecules into the same, lowest state.

Therefore, $S = 0$ at $T = 0$, in accord with the Third Law of thermodynamics

Residual Entropy

The entropy possessed by a substance even at absolute zero is known as residual entropy.

In certain cases, W may differ from 1 at $T = 0$. This is the case if there is no energy advantage in adopting a particular orientation even at absolute zero.

For instance, for a diatomic molecule AB there may be almost no energy difference between the arrangements . . . AB AB AB . . . and . . . BA AB BA . . . , so $W > 1$ even at $T = 0$.

If $S > 0$ at $T = 0$ we say that the substance has a **residual entropy.**

Ice has a residual entropy of 3.4 J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$.

Calculation of Residual Entropy

The entropy arising from residual disorder can be calculated readily by using the Boltzmann formula,

$$S = k \ln W.$$

To do so, suppose that two orientations are equally probable, and that the sample consists of N molecules.

Because the same energy can be achieved in 2^N different ways (because each molecule can take either of two orientations), the total number of ways of achieving the same energy is $W = 2^N$.

It follows that, $S = k \ln 2^N = Nk \ln 2 = nR \ln 2$

A residual molar entropy of $R \ln 2 = 5.8\ \mathrm{J\ K^{-1}\ mol^{-1}}$ is expected for solids composed of molecules that can adopt either of two orientations at $T = 0$.

If *s* orientations are possible, the residual molar entropy is

$$S_m(0) = R\ ln\ s$$

For CO, the measured residual entropy is 5 J K^{-1} mol^{-1}, which is close to $R \ln 2$ (5.8 J K^{-1} mol^{-1}), the value expected for a random structure of the form ...CO CO OC CO OC OC... .

Exercise

For H_2O molecules, the average number of permitted orientations is $\frac{3}{2}$. Calculate (i) the residual molar entropy for H_2O and (ii) the residual entropy for 100 H_2O molecules.