Paper 3 : Thermodynamics, Bioenergetics and Thermoregulation

Module 4 : The Third Law of Thermodynamics

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Objectives :

1. **Understand what is 3rd law of thermodynamics ?**
2. **Significance of third Law**
3. **Understand the terms, Absolute zero,**
4. **Specific heat**
5. **Thermal expansion coefficient**
6. **Applications of third Law**

Introduction:

"It is interesting to note that the pioneers in the area of thermodynamics, Helmholtz and Julios von Mayer, were actually clinicians. Mayer a German Physicist, is best known for enunciating in 1841 one of the original statements of the conservation of energy or what is now known as one of the first versions of the first law of thermodynamics. Dr. Helmholtz is known for his theories on the conservation of energy, work in electrodynamics, chemical thermodynamics, and on a mechanical foundation of thermodynamics. "(Shahar Dolev andAvshalom C. Elitzur).

Julios von Mayer

Hermann Ludwig Ferdinand von Helmholtz (1821 – 1894)

It is appropriate to remember these two great scientists before we go into other topics of the thermodynamics and its applications

Thermodynamics studies the transformations of energy, and such transformations ceaselessly take place in all living systems (probably with important differences between the states of health and disease). Moreover, thermodynamics studies the elusive notions of order and disorder, which are also, respectively, the very hallmarks of life and death. These similarities suggest that thermodynamics might provide a unifying paradigm for many life sciences, explaining the multitude of life's manifestations on the basis of a few basic physical principles.

What is the Third Law of Thermodynamics ?

The **third law of thermodynamics** is sometimes stated as follows, regarding the properties of systems in equilibrium at absolute zero temperature: The entropy of a perfect crystal at absolute zero is exactly equal to zero.At absolute zero (zero kelvin), the system must be in a state with the minimum possible energy, and the above statement of the third law holds true provided that the perfect crystal has only one minimum energy state. Entropy is related to the number of accessible microstates, and for a system consisting of many particles, quantum mechanics indicates that there is only one unique state (called the ground state) with minimum energy.[1] If the system does not have a well-defined order (if its order is glassy, for example), then in practice there will remain some finite entropy as the system is brought to very low temperatures as the system becomes locked into a configuration with non-minimal energy. The constant value is called the residual entropy of the system.

In the year 1848, Lord Kelvin devised the scale for absolute zero temperature and he concluded that absolute zero temperature meant -273.15 degree Celsius. Later, by the international agreement a new temperature scale was found by the name Kelvin. As per this scale absolute meant 0K or 0 degree Kelvin on Kelvin scale.

The relation between Kelvin and Celsius temperature scale is: K= degree Celsius + 273.

The Third law of thermodynamics

The Third Law of Thermodynamics is the lesser known of the three major thermodynamic laws The Third Law of Thermodynamics refers to a state known as "absolute zero." This is the lowest temperature in the Kelvin temperature scale. In actuality, no object or system can have a temperature of zero Kelvin, because of the Second Law of Thermodynamics. The Second Law, in part, implies that heat can never spontaneously move from a colder body to a hotter body. So, as a system approaches absolute zero, it will eventually have to draw energy from whatever systems are nearby. If it draws energy, it can never obtain absolute zero. So, this state is not physically possible, but is a mathematical limit of the universe.
In short the Third Law of Thermodynamics says: "The entropy of a pure perfect crystal is zero (0) at zero Kelvin (0° K)."Entropy is a property of matter and energy discussed by the Second Law of Thermodynamics. The Third Law of Thermodynamics means that as the temperature of a system approaches absolute zero, its entropy approaches a constant (for pure perfect crystals, this constant is zero). A pure perfect crystal is one in which every molecule is identical, and the

molecular alignment is perfectly even throughout the substance. For non-pure crystals, or those with less-than perfect alignment, there will be some energy associated with the imperfections, so the entropy cannot become zero. There is no entropy and there is no mixing since the crystal is pure. For a mixed crystal containing the atomic or molecular species A and B, there are many possible arrangements of A and B and entropy is associated with the arrangement of the atoms/molecules. Most of the direct use of the Third Law of Thermodynamics occurs in ultra-low temperature chemistry and physics. The applications of this law have been used to predict the response of various materials to temperature changes.

A) Single possible configuration for a system at absolute zero, i.e., only one microstate is accessible.
Thus S = k ln W = 0.
b) At temperatures greater than absolute zero, multiple microstates are accessible due to atomic vibration (exaggerated in the figure).
Since the number of accessible microstates is greater than 1, S = k ln W > 0.

$$S = \int^{T} \frac{đQ}{T} + S_0$$

As long as we deal in differences in entropy, knowledge of S_0 is unnecessary. However, absolute entropy IS important, e.g.

$$F = U - TS$$
$$G = H - TS$$

Statement of Third Law : By different ways by different scientists

1 Gibbs-Helhotz

2 Nernst and 3 Plank

Statements of the third law

- The Gibbs-Helmholtz equation:

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

- For an isothermal process:

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

- These equations imply:

$$\lim_{T\to 0} G = \lim_{T\to 0} H$$
$$\lim_{T\to 0} \Delta G = \lim_{T\to 0} \Delta H$$

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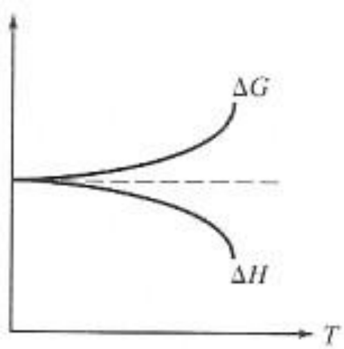

- Nernst postulate implies that:

$$\lim_{T\to 0}\left[\frac{\partial(G_2 - G_1)}{\partial T}\right]_P = \lim_{T\to 0}\left[\frac{\partial G_2}{\partial T} - \frac{\partial G_1}{\partial T}\right] = \lim_{T\to 0}[S_1 - S_2] = 0$$

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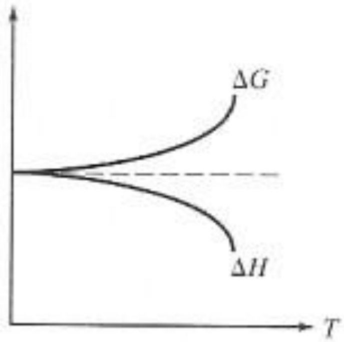

•The Nernst formulation of the Third Law:

'All reactions in a liquid or solid in thermal equilibrium take place with no change of entropy in the neighborhood of absolute zero.'

Statements of the third law

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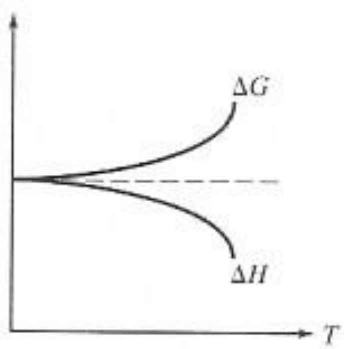

•Planck later postulated that:

$$\lim_{T\to 0}\left(\frac{\partial G}{\partial T}\right)_P = 0, \quad \lim_{T\to 0}\left(\frac{\partial H}{\partial T}\right)_P = 0 \quad \Rightarrow \quad \lim_{T\to 0} S = 0$$

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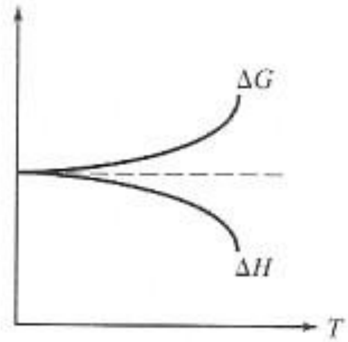

•Planck's statement of the Third Law:

'The entropy of a true equilibrium state of a system at absolute zero is zero.'

Statements of the third law

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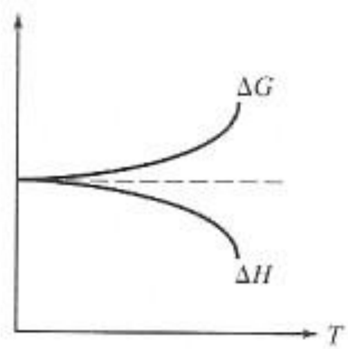


•Another statement of the Third Law is:

'It is impossible to reduce the temperature of a system to absolute zero using a finite number of processes.'

Significance of entropy in biological reactions

In biological systems, very complex but well defined structures arise with high three-dimensional order and, correspondingly, low entropy and high information content. As discussed earlier, water has a strong tendency to form hydrogen bonded structures which make biomolecules to arrange themselves in “tertiary structures” with their polar, hydrophilic groups turned towards the surrounding water. And the hydrophobic, aliphatic groups and tails pack closely together to protect against water contacts. Therefore, it must be remembered that the TΔ S is the dominant term in ΔG for the protein folding reaction. In small systems, surface energies also contribute markedly to the free energy. The spatial fixation of one single amino acid group in chain poly peptide molecule (see proteins in chapter 5) diminishes its entropy by about 0.05 eV ≈1.2 kcal mol-1 at 25° C. Similarly, considerable entropy effects arise due to formation of base pairing in DNA in the cell.

Evolution and Thermodynamics :

To comprehend the evolution from the thermodynamic aspect of energy efficiency:
The ability of living systems to increase complexity is not accidental. Complexity is vital for efficiency. Life was therefore compelled to increase complexity as organisms fought for survival. The course of evolution can be rephrased as “Survival of the most efficient.”

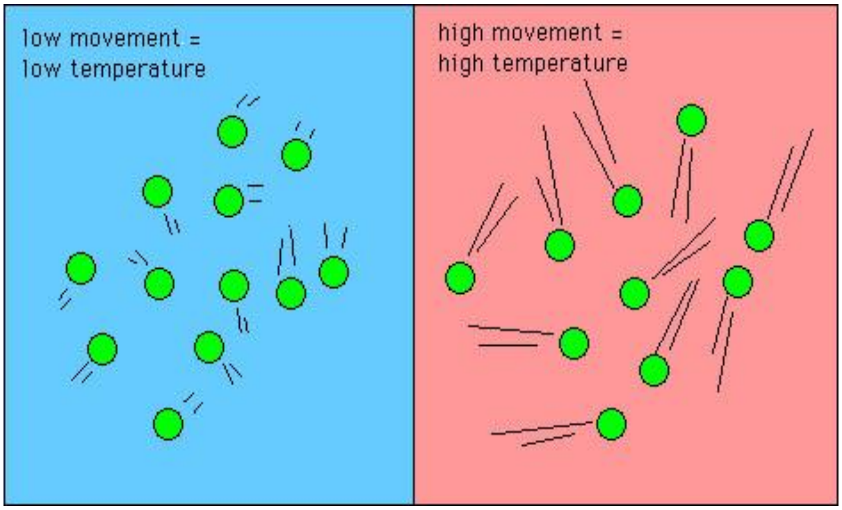
Applications Of Third Law :

1 Response of materials to Temperature changes

Most of the direct use of the Third Law of Thermodynamics occurs in ultra-low temperature chemistry and physics. The applications of this law have been used to predict the response of various materials to temperature changes. These relationships have become core to many science disciplines, even though the Third Law of Thermodynamics is not used directly nearly as much as the other two.

Specific Heat and Heat capacity:

Specific heat is another physical property of matter. All matter has a temperature associated with it. The temperature of matter is a direct measure of the motion of the molecules: The greater the motion the higher the temperature.



The temperature of on gain or loss of heat energy is given by:

The specific heat (S) of the object :

Therefore, the specific heat of an object is defined as: **mass m, x the heat and the temperature rise, then S is given by**

$$S = \frac{x \text{ (in Joules or cal)}}{\text{mass} \times \Delta T}$$

$$\Delta T = \text{change in temperature}$$

Some common specific heats and heat capacities:

Substance	S (J/g 0C)	C (J/0C) for 100 g
Air	1.01	101
Aluminum	0.902	90.2
Copper	0.385	38.5
Gold	0.129	12.9
Iron	0.450	45.0
Mercury	0.140	14.0
NaCl	0.864	86.4
Ice	2..03	203
Water	4.179	417.9

Vapor pressure(v_p)	0.0212 atm at 20°C	
Heat of vaporization, (C_r)	40.63 kJ/mol	High value gives resistance to dehydration
Heat Capacity (C_p)	4.22 kJ/kg.K	High value helps in thermal regulation in the body
Specific heat	4180 J kg-1 K-1 (T=293…373 K)	

Thermal Expansion :

Thermal expansion *is the tendency of matter to change in shape, area, and volume in response to a change in temperature*. Temperature is a monotonic function of the average molecular kinetic energy of a substance. When a substance is heated, the kinetic energy of its molecules increases.

Therefore, the molecules begin vibrating/moving more and usually maintain a greater average separation. Materials which contract with increasing temperature are unusual; this effect is limited in size, and only occurs within limited temperature ranges. The relative expansion or strain divided by the change in temperature is called the material's coefficient of thermal expansion and generally varies with temperature.

Coefficient of Thermal Expansion :

The **coefficient of thermal expansion**(Y) describes how the size of an object changes with a change in temperature. Specifically, it measures the fractional change in size per degree change in temperature at a constant pressure. Several types of coefficients have been developed: volumetric, area, and linear. Which is used depends on the particular application and which dimensions are considered important. For solids, one might only be concerned with the change along a length, or over some area. The volumetric thermal expansion coefficient is the most basic thermal expansion coefficient, and the most relevant for fluids. In general, substances expand or contract when their temperature changes, with expansion or contraction occurring in all directions. Substances that expand at the same rate in every direction are called isotropic. For isotropic materials, the area and volumetric thermal expansion coefficient are, respectively, approximately twice and three times larger than the linear thermal expansion coefficient. Mathematical definitions of these coefficients are defined below for solids, liquids, and gases.

General volumetric thermal expansion coefficient

In the general case of a gas, liquid, or solid, the volumetric coefficient of thermal expansion is given by

Volume Thermal Expansion Coefficient Formula

$$\alpha_v = \frac{1}{V}\,\frac{\Delta V}{\Delta T}$$

α_v – *volume thermal expansion coefficient*
V – *area of the object in* m^3
ΔV – *change in volume in* m^3
ΔT – *change in temperature in kelvin*

2 Gives support to the implications of the first two laws.

The 3rd Law basically affirms the first two laws. The Third Law of Thermodynamics demonstrates another detectable, absolute, all-encompassing, important natural law. The Laws of Thermodynamics demonstrate very ordered rules of energy interactions, which the entire universe must obey. Why is the Third Law of Thermodynamics true? Why are there no exceptions in the entire universe? This law cannot be an accident, since none of the thermodynamic laws are random.

SUMMARY

The **third law of thermodynamics** is sometimes stated as follows, regarding the properties of systems in equilibrium at absolute zero temperature: The entropy of a perfect crystal at absolute zero is exactly equal to zero.At absolute zero (zero Kelvin), the system must be in a state with the minimum possible energy, and the above statement of the third law holds true provided that the perfect crystal has only one minimumu energy state. The relation between Kelvin and Celsius temperature scale is: K= degree Celsius + 273.

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Applications Of Third Law :

1 Response of materials to Temperature changes and it explains the behavior of solids at very low temperature

2 Specific heat, Thermal expansion Coefficient

3 Gives support to the implications of the first two laws

4 It helps in calculating the thermodynamic properties.

5) It is helpful in measuring chemical affinity. Because of this it is known as Nernst theorem.

6) It helps in analyzing chemical and phase equilibrium.