

CHEMISTRY PHYSICAL CHEMISTRY & THERMODYNAMICS

Lesson 4

by

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SECOND LAW

Different Statements:

✓ **Kelvin Planck:** The heat engine or any other machine cannot produce work without releasing some amount of heat in the atmosphere. That means 100% conversion of heat to work is not possible, however hard you try. So there are no such device which can develop 100% work. Nothing is in the world which convert energy from one form to another with no such losses. There has to be some losses. And that's why, no one is 100% efficient!

✓ **Clausius:** It is impossible to transfer heat from lower temperature to higher temperature reservoir in heat pump. That means heat flow always will follow the natural direction i.e., from higher temperature (higher heat content) body to the lower temperature (lower heat content) one. If you wish to make the transfer in reverse direction, it must need some external driving force, i.e., your effort from outside.

✓ **The entropy of the universe tends to a maximum.** In other words Entropy either stays the same or gets bigger, the entropy of the universe can never go down. The entropy of an isolated system (not in equilibrium) will always tend to increase over time, approaching a maximum value at equilibrium.

MORE ON SECOND LAW

✓ **Perpetual motion machine of 2nd kind** (a machine that spontaneously converts heat into work without any heat release or loss) **is impossible**. That means a machine cannot make 100% conversion of heat to work in lieu with **Kelvin Planck** statement.

Interpretation:

- Heat to work 100% conversion is not at all possible.
- No machine can be 100% efficient or in other words, anyone's efficiency can never be 1, must be less than 1 always.
- In absence of any external influence, heat will always flow from the higher temperature body to the lower temperature one without any violation.
- In all spontaneous processes of nature, the entropy of the universe always increases and thereby tends to a maximum.
- By these natural entropy rising processes, when universe will reach its entropy maxima, what would happen actually? Later you would be introduced with the **Heat Death of Universe** problem and surely will learn to tackle that fallacy!

WHAT IS ENTROPY ?

Definition: Entropy is a thermodynamic state function that is a measure of **disorder or randomness** of a system. **An ordered system has lower entropy. A disordered system has higher entropy.** It is an **extensive** property. But the entropy of a pure substance is usually given as an intensive property.

Highlight: The **entropy of an isolated system never decreases**; such a system will **spontaneously evolve towards thermodynamic equilibrium**; the **configuration with maximum entropy**. Systems that are not isolated may decrease in entropy, provided they increase the entropy of their surrounding/environment by at least that same amount.

MORE ON ENTROPY

Since entropy is a **state function**, the change in entropy of a system is the **same for any process that goes from a given initial state to a given final state**, whether the process is **reversible or irreversible**. However, irreversible processes increase the combined entropy of the system and its environment.

According to the second law of thermodynamics, in a theoretical and fictional **reversible heat transfer**, an element of heat transferred, δQ , is the product of the temperature (T), both of the system and of the sources or destination of heat, with the increment (dS) of the system's conjugate variable; its entropy (S). [$\delta Q_{\text{rev}} = TdS$]

THIRD LAW

Different Statements:

- ✓ The entropy of a perfect crystal of any pure substance approaches zero as the temperature approaches absolute zero.
- ✓ As the temperature of a system approaches absolute zero (-273.15°C , 0 K), then the value of the entropy approaches a minimum.

Interpretation:

- ✓ There is no such device which has zero entropy. As for entropy to be zero, we must reach 0K , the absolute zero of temperature, which is next to impossible.
- ✓ The value of the entropy must be zero at 0K , however there are some cases where there is still a small amount of entropy in the system. The constant value (not necessarily zero) is called the **residual entropy** of the system.

MORE ON THIRD LAW

Summary: So actually this law emphasise on **non attainability of absolute zero temperature.**

It reminds us of the similar restriction in the field of relativity; that **we cant ever attain the velocity of light.** The velocity of light is maximum. We cant ever achieve it, similarly, absolute zero is that minimum temperature, which we cant achieve too.

These are actually **two important limits** of our physical world. **We cant go beyond these limits anyhow.** But to attain the unattainable has always been the favourite task of human being and hence a separate branch of physics named as **Low Temperature Physics or Cryogenics** originated. These section of scientists try hard to reach nearer to the absolute zero as much as possible, if not achieved.

CONCLUSION

- **0. This is the Game:** You're here, remember well, you are a part of the system.
- **1. You Can't Win:** You can't get more energy out of this system than you put into it. Remember always, "As you sow, so you reap".
- **2. You Can't Break Even:** Any transfer of energy from this system to another would definitely result in some waste of energy, unless and until a temperature of absolute zero can be achieved.
- **3. You Can't Get Out of the Game:** You must never forget that you cannot ever achieve that absolute zero, the real tragedy of life!

So to Conclude: There's no such thing in the whole universe as **A FREE LUNCH**. Its for sure, if you have one, **you must have to pay for it in some way or other!**

THANK YOU!

ANY QUESTION ?

