Fifth Law of Thermodynamics – A Review

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Abstract— Thermodynamics is the branch of natural science which deals with heat and its relation to energy and work. The laws of thermodynamics govern the relationships between them. Each law either states some biblical fact with scientific proof or introduces some new terminology so that its violation can be avoided. With the recent development in technology, it has been become possible to create "negative absolute temperatures". This causes several odd consequences and also violates the already established laws of thermodynamics. This paper summarizes some of the information about the negative absolute temperature and its possibilities. A fifth law of thermodynamics which would be able to stop the violations of the other laws is also looked into.

Keywords: Fifth law, Negative absolute temperature, Lars Onsager

I. INTRODUCTION

Thermodynamics is the branch of physics that deals with the inter-conversion of heat and work based on the four laws of thermodynamics. The word 'thermodynamic' is derived from two Greek words *thermes*, meaning heat, and *dynamikos*, meaning powerful. Thermodynamics has its beginnings in the study of engines in the 17^{th} century during the Industrial Revolution in Europe.

The founding fathers of thermodynamics laid the concepts of internal energy, enthalpy, entropy, etc. and gave the four laws. Some of the best contributors in this field were Sadi Carnot, Rudolf Clausius, James Maxwell, Ludwig Boltzmann, Willard Gibbs, etc. Sadi Carnot is generally known as the 'father of thermodynamics'.

Fig. 1 shows the timeline during which they made contributions in the field.

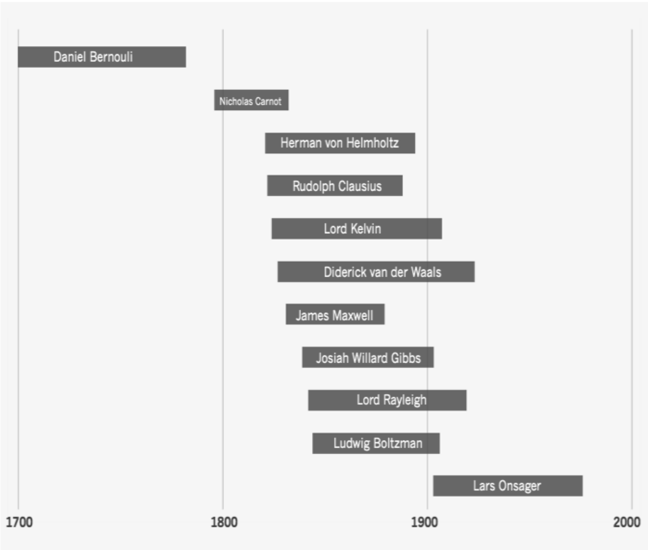

Fig. 1: Founders of thermodynamics

II. LAWS OF THERMODYNAMICS

A. *Zeroth law of thermodynamics*

The zeroth law of thermodynamics states that if two bodies are in thermal equilibrium with a third body, they are also in thermal equilibrium with each other. It may seem silly that such an obvious fact is called one of the basic laws of thermodynamics. However, it cannot be concluded from the other laws of thermodynamics, and it serves as a basis for the validity of temperature measurement. By replacing the third body with a thermometer, the zeroth law can be stated as "two bodies are in thermal equilibrium if both have the same temperature reading even if they are not in contact."

The zeroth law was first formulated and labelled by R. H. Fowler in 1931. As the name suggests, its value as a fundamental physical principle was recognized more than half a century after the formulation of the first and the second laws of thermodynamics. It was named the zeroth law since it should have preceded the first and the second laws of thermodynamics [1].

B. *First law of thermodynamics*

The first law of thermodynamics, also known as the conservation of energy principle, provides a sound basis for studying the relationships among the various forms of energy and energy interaction. Based on experimental observation of Joule in the first half of nineteenth century, the first law of thermodynamics states that, "energy can neither be created nor destroyed during a process; it can only change forms." The major consequence of the first law is the existence and definition of the property 'total energy E' [1].

C. *Second law of thermodynamics*

Kelvin-Planck Statement: It states that, "no system whose working fluid undergoes a cycle can receive heat from a single source and produce work without rejecting heat to a lower temperature sink" OR "it is impossible to construct an engine working in a cyclic process whose sole effect is the conversion of all the heat energy supplied to it by a source into an equivalent amount of work"

Clausius Statement: It states that, "it is impossible to construct a device working in a cyclic process whose sole effect is the transfer of energy in the form of heat from a body at a lower temperature to a body at a higher temperature" OR "it is impossible for energy in the form of heat to flow from a body at lower temperature to a body at higher temperature without the aid of external work" [2].

D. *Third law of thermodynamics*

The third law states that, "it is impossible to attain absolute zero within finite number of reversible engines in series developing work receiving energy from the source at a particular temperature" OR "it is impossible by any procedure, no matter how idealized, to reduce any system to the absolute zero temperature in a finite number of operations" [2].

The third law was first formulated by German chemist Walther Nernst in 1912 and therefore it is often referred to as the Nernst's theorem or Nernst's postulate. An alternate version of the third law was stated by Gilbert N. Lewis and Merle Randall in 1923.

III. NEGATIVE ABSOLUTE TEMPERATURES

The absolute temperature scales (Kelvin and Rankine) are related to Celsius and Fahrenheit scales by the following relations.

$$K = {}^{o}C + 273.15$$

$$^{o}R = {}^{o}F + 459.67$$

$$^{o}F = 1.8 * {}^{o}C + 32$$

The Kelvin temperature scale was the brainchild of British inventor and scientist William Thomson (Lord Kelvin). In 1848, Kelvin defined 'absolute' as the temperature at which molecules would stop moving, or 'infinite cold'. Absolute temperature cannot be achieved. However, scientists have been able to lower the temperature of matter to just a fraction of a Kelvin above absolute zero [3]. In 1994, the NIST achieved a record cold temperature of 700 nK (billionths of a kelvin). In 2003, researchers at MIT eclipsed this with a new record of 0.45 nK [4].

Though the third law of thermodynamics defines absolute zero temperature, it doesn't rule out the possibility of negative absolute temperatures.

Temperature is commonly interpreted as a measure of the average energy of the particles in a sample. Each of the molecules buzzing around in a pot of boiling water, for example, has more energy on average than a sluggish water molecule within an ice cube. But for scientists who study matter at quantum scales, temperature is better defined as the energy distribution of the particles in a sample. Just above absolute zero (0 K or -273° C), almost all of the particles within a sample have energies very close to zero, with little variation. But as temperatures rise, the variation in energies widens — some particles still have very small energies, but others have more [5].

Physicist Ulrich Schneider at the Ludwig Maximilians University of Munich and his team wanted to cajole the particles within a substance to be confined to a very high amount of energy. In other words, instead of having the particles start at a minimum energy (corresponding to absolute zero) and spreading out toward higher energies, they wanted to start at a maximum energy and spread toward lower energies. By definition, such a substance would have a negative kelvin temperature.

The team achieved that with potassium atoms chilled to a few billionths kelvin above absolute zero. Through the use of lasers and magnets, the team managed to get the atoms to jump to a high-energy state. By creating a cluster of particles exclusively at high energies, Schneider and his colleagues had a gas at a few billionths negative kelvin.

This temperature is technically not below absolute zero, because negative on the Kelvin scale (unlike that on the Fahrenheit or Celsius scale) is a construct (hypothesis) that simply indicates something about the energy state of the particles involved. In fact, the new creation is extremely hot because of the high energies of the particles. Heat travels from hot to cold, Schneider says, and heat will always flow away from this gas. "It's actually hotter than everything we know," he says [5].

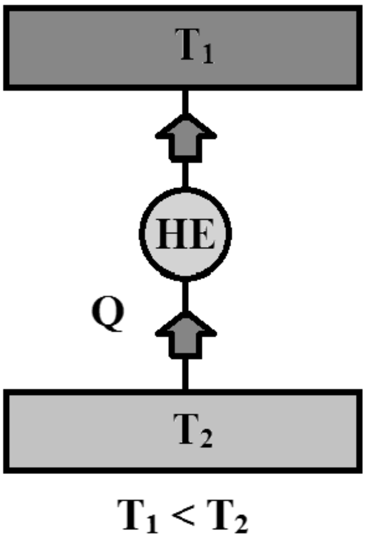

Fig. 2: Hypothetical engine working between source at T_1 (T_1 is positive absolute temperature) and sink at T_2 (T_2 is positive absolute temperature)

IV. FOURTH LAW OF THERMODYNAMICS

A. Need

If a hypothetical Carnot Engine is assumed working between a heat source at positive absolute temperature (T_1) and a heat sink at negative absolute temperature (T_2), then its Carnot efficiency will be more than 1, thus violating the first law of thermodynamics [6].

$$\eta_{carnot} = \left(1 - \frac{T_2}{T_1}\right) > 1 > 1$$

Another odd consequence of negative temperatures is with entropy. When objects with positive temperature release energy, they increase the entropy of things around them, making them behave more chaotically. However, when objects with negative temperatures release energy, they can actually absorb entropy [7]. This thus violates the second law of thermodynamics.

Hence, a fourth law is required to rule out the possibility of such a heat engine.

B. Literature review

The earliest mention if a new, fourth law of thermodynamics was in 1920s. More than 15 variations of fifth law can be found in the public domain [8]. Of these the Reciprocal relations by theoretical physicist Lars Onsager is considered by many as the fourth law. Some researchers have even tried to set an upper limit on the temperature scale.

V. CONCLUSION

The fourth law of thermodynamics is not a well-established concept. Also with the development of "negative absolute temperatures" it has become essential to accommodate that as well. Since the laws of thermodynamics occupy the status of fundamental laws of physics on which entire universe works, it is of utmost importance that they be stated keeping all possible cases in mind.

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