Journal of Sustainable Energy & Environment
12 (2021) 107-109

A non-mathematical outline of thermodynamics

Robert H.B. Exell[1,2,*]

[1]The Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi, Thailand
[2]Center of Excellence on Energy Technology and Environment, Ministry of Higher Education, Science, Research and Innovation, Bangkok, Thailand
*corresponding author: robert.har@kmutt.ac.th

Abstract: A simple qualitative presentation of the laws of thermodynamics is given for non-specialists without using mathematics. Descriptions of the properties of a thermodynamic system are given in terms of the random motion of the particles in the system. It is shown how the Principle of Conservation of Energy and the First Law lead to the concept of internal energy and the State Principle. The Second Law is divided into two parts. The first part is concerned with entropy and thermodynamic temperature. Entropy is an indicator for the possibility of adiabatic changes between equilibrium states. Thermodynamic temperature is an indicator for the internal energy of equilibrium states. The second part of the Second Law is the Principle of Increase of Entropy, which states that when coupled systems move spontaneously from disequilibrium to equilibrium with each other, the total entropy of the systems increases. The Third Law states that no finite process can cool a system to the absolute zero of temperature.

Keywords: Thermodynamics, non-technical presentation, First Law, internal energy, State Principle, adiabatic reversibility, Second Law, entropy, thermodynamic temperature, Principle of Increase of Entropy, Third Law, absolute zero.

1. Introduction

The traditional presentation of thermodynamics is difficult for students to understand, and a good knowledge of logic and calculus is needed to follow the usual arguments developing the subject. I have sometimes been asked by interested non-specialists who do not have this background to explain the concepts of thermodynamics without mathematics. Here I give a new outline of thermodynamics in terms of the qualitative behavior of thermodynamic systems viewed as an assembly of particles in random motion. The following sections follow the pattern of an earlier paper in this Journal [1] giving the mathematical details, and another paper [2] written for specialists.

2. Thermodynamic Systems

A simple closed thermodynamic system is a quantity of matter separated from its **environment** by the walls of a container.

An example is a gas consisting of particles moving freely at random in a container with rigid walls. The walls of the container also consist of particles, which can vibrate randomly about their fixed mean positions.

The thermodynamic system has a set of stable **equilibrium states**. Each state has a pair of measurable non-thermal properties: **volume** and **pressure**. The volume of the system is determined simply by the size of the container. The pressure of the system is caused by the impacts of the gas particles on the walls of the container.

The environment of the system may be **hot**, such as a bath of boiling water, or **cold**, such as a bath of melting ice. The particles in a hot environment are moving rapidly. The particles in a cold environment are moving slowly.

If the walls of the container are **thermally conducting**, like walls of thin metal, then the impacts of the particles in the environment on the walls cause the particles in the walls to vibrate. These vibrations influence the random motion of the particles in the system until they are in equilibrium with the random motions of the particles in the environment. In this way a change in the environment from cold to hot, or from hot to cold, will cause a corresponding change in the random motion of the particles in the system making the system hot or cold.

If, however, the walls are **thermally insulating**, like the double walls of a vacuum flask, then a change in the environment from cold to hot or from hot to cold will not cause a change in the equilibrium state of the system. In the case of a vacuum flask, there are no particles in the vacuum between the walls through which the motion of the particles in the environment can influence the motion of the particles in the system.

Although it is not possible to make the thermal insulation of the walls of a real container perfect, the insulation can be made good enough for practical purposes, and it is possible to use the concept of perfectly insulating walls for discussing thermodynamics.

When the state of the system is caused to change and the walls of the container are thermally insulating, the change of state is called adiabatic.

3. The First Law and Internal Energy

Energy can be transferred between the system and its environment by methods such as those shown in Fig. 1, where the walls of the container are thermally insulating and the change of state is adiabatic. In these cases the amount of energy transferred to or from the system can measured by work done in the environment.

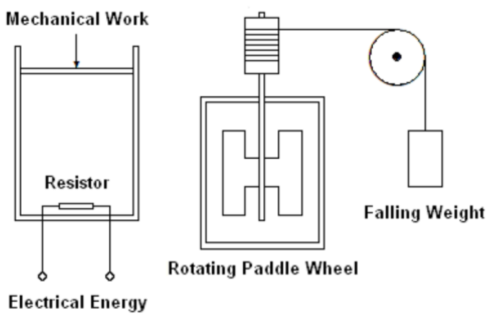

Figure 1. Adiabatic energy transfers between a system and its environment.

The **First Law of Thermodynamics** can now be stated as follows:

The amount of energy transferred to or from a thermodynamic system in an adiabatic change of state, measured by work in the environment, depends only on the initial and final states of the system.

It follows from this First Law of Thermodynamics and the **Principle of Conservation of Energy** (which is a general principle independent of thermodynamics) that we may assign an **internal energy** to each equilibrium state of the system. The amount of energy transferred to or from the system causes a corresponding increase or decrease in the internal energy. This internal energy is the energy of motion of the particles in the system.

Example: The internal energy of a given volume of air determines the air's pressure. If this air is in thermal contact with a hot environment (for example, boiling water) it will have a higher internal energy, and a higher pressure, than the same air in thermal contact with a cold environment (for example, melting ice). This is because the random motions of the particles in the hot air have a higher energy than the random motions of the same particles when the air is cold, and the impacts of the particles with the higher energy on the walls of the container cause the pressure of the gas to be higher.

The State Principle: The pressure and volume of a simple closed thermodynamic system do not always specify the state of the system uniquely. For example, liquid water at a pressure of one atmosphere has a minimum volume per unit mass when it is slightly warmer than melting ice. In the neighborhood of this minimum there are different states that have the same pressure and volume but different internal energies. These are states that are slightly warmer than and slightly cooler than the state with a minimum volume. Indeterminacies such as this are resolved by the **State Principle** as follows:

The stable equilibrium state of a simple closed thermodynamic system is specified uniquely by its volume and its internal energy.

4. Adiabatically Reversible and Irreversible Processes

Work done by a movement of the wall (as shown on the left in Figure 1) is reversible because the volume may be reduced or increased, and energy can be transferred mechanically to or from the system. We call this process **reversible adiabatic work**.

If, however, an electrical current is passed through the resistor (as shown on the left in Figure 1), or the weight falls (as shown on the right in Figure 1), energy is transferred to the system, but these processes are irreversible. We call them **irreversible adiabatic heating** of the system. It is impossible for the energy in the system to make an electrical current flow in the resistor, or to lift the weight.

5. The First Part of the Second Law: Entropy and Temperature

The **Second Law of Thermodynamics** may be divided into two parts. The first part is concerned with **entropy** and **thermodynamic temperature**, which are the basic thermal properties of thermodynamic systems. They are analogous to the non-thermal properties volume and pressure. Volume and entropy are **extensive** properties because they are proportional to the size of the system. Pressure and thermodynamic temperature are **intensive** properties; they have well defined values which are the same everywhere inside the system. Measurements of energy transfers to and from the system are used to establish quantitative measures of the entropy and the thermodynamic temperature.

Entropy has the following properties:

- *When an adiabatic change of state has been produced by reversible work, the final state has the same entropy as the initial state.*
- *Adiabatic changes of state are possible between any pair of states that have the same entropy.*
- *When a change of state has been produced by irreversible heating, the final state has a higher entropy than the initial state.*
- *It is not possible for any adiabatic process to change the state of the system to a state having a lower entropy than the initial state.*
- *It is possible, by the adiabatic processes of reversible work and irreversible heating, to change the state of the system to any state having a higher entropy than the initial state.*

Entropy can therefore be viewed as the property of thermodynamic systems that indicates whether or not it is possible to make a specified change of state of the system by an adiabatic process.

It is commonly said that entropy is a measure of "disorder" in thermodynamic systems. However, the word "disorder" is misleading here because the properties of a thermodynamic system, including entropy, are well defined only when the system is in a stable equilibrium state in which the total internal energy is distributed in a proper orderly manner over the random motions of the particles. This distribution is called the Boltzmann distribution.

The correct qualitative view is to see that entropy is an indicator for "adiabatic accessibility". This can be understood by the following examples:

- In two states of a gas with the same internal energy but different volumes, the entropy of the state with the larger volume is higher than the entropy of the state with the smaller volume. Here, *the state with the higher entropy is adiabatically accessible from the state with lower entropy* by allowing the gas to expand into an evacuated space to make the required increase in volume without doing work, and therefore without changing the internal energy. But *the initial state with lower entropy is not adiabatically accessible from the final state* by an adiabatic compression because the work of compression would increase the internal energy.
- In two states with the same volume but different internal energies, the state with the higher internal energy has a higher entropy than the state with the lower internal energy. *Here, the state with the higher entropy is adiabatically accessible from the state with lower entropy* by adiabatic heating. But *the initial state with lower entropy is not adiabatically accessible from the final state* because the adiabatic heating is irreversible.

The scale for thermodynamic temperature is defined so that hot states, in which the particles are moving rapidly, have a higher temperature than cold states, in which the particles are moving slowly. Thermodynamic temperature is therefore an indicator for the internal energy of thermodynamic systems.

6. The Second Part of the Second Law: The Principle of Increase of Entropy

The second part of the Second Law is concerned with the spontaneous changes of state that occur when a system is put in contact with an environment with which it is not initially in equilibrium.

The **environment** is assumed to have the two constant intensive properties: **Pressure** and **temperature**. There are four possible ways in which the walls of the container determine how the system behaves when it is put in contact with the environment.

Fixed thermally insulating walls: In this case, there is no mechanical or thermal contact with the environment and no change of state occurs. **Movable thermally insulating walls:** In this case, a spontaneous change in the volume of the system occurs until the pressure in the system is equal to the pressure in the environment.

Fixed thermally conducting walls: In this case, a spontaneous change in the temperature of the system occurs until the temperature in the system is the same as the temperature in the environment.

Movable thermally conducting walls: In this case, spontaneous changes in both the volume and the temperature of the system occur until the system is in equilibrium with the environment.

It can be shown that in the last three spontaneous changes of state listed above the sum of the changes in the entropies of the system and the environment is positive. These results lead to the following statement:

When a closed thermodynamic system, which is not initially in equilibrium with its environment, is put in mechanical or thermal contact with the environment, a spontaneous change of state occurs in the system to a final state in equilibrium with the environment, and the sum of the changes in the entropies of the system and the environment is positive.

The **Principle of Increase of Entropy** is a generalization of this result for all natural processes where coupled systems move spontaneously from states of disequilibrium towards states of mutual equilibrium and the total entropy of the coupled systems increases.

7. The Third Law: The Absolute Zero of Temperature

A thermodynamic system can lose internal energy by thermal contact with a colder environment through thermally conducting walls. The loss of internal energy makes the random motion of the particles in the system slower, and the temperature of the system falls. The system can then be made colder than its environment by doing work in an adiabatic expansion against the pressure of the environment. This expansion causes the random motion of the particles in the system to lose energy.

If a thermodynamic system were to have zero internal energy, it would be at its lowest possible temperature. This lowest possible temperature is called **absolute zero**.

However, it is not possible to remove *all* the internal energy of the system by any finite process. To remove all the internal energy of a system by reversible adiabatic work, the system would have to be expanded to an infinite volume. If we try to construct a sequence of thermodynamic systems, each system being made colder than the previous one by an adiabatic expansion in order to reach the absolute zero of temperature step by step, the sequence would have to contain an infinite number of systems.

The Third Law of Thermodynamics can therefore be stated as follows:

No finite process can reduce the temperature of a thermodynamic system to absolute zero.

References

[1] Exell, R.H.B. 2018. A Personal View of Macroscopic Equilibrium Thermodynamics, *Journal of Sustainable Energy & Environment*, 9, 21-24.

[2] Exell, R.H.B. A Simple Macroscopic Reformulation of Equilibrium Thermodynamics, *The Journal of the Royal Institute of Thailand*, VI, 99-115.