

Conceptual Introduction

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Abstract

To be Defined

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1 Introduction

Thermodynamics is a branch of physics that deals with heat, work, and temperature, and their relation to energy, radiation, and physical properties of matter. The behavior of these quantities is governed by the four laws of thermodynamics which convey a quantitative

description using measurable macroscopic physical quantities, but may be explained in terms of microscopic constituents by statistical mechanics.

Thermodynamics is principally based on a set of four laws which are universally valid when applied to systems that fall within the constraints implied by each. In the various theoretical descriptions of thermodynamics these laws may be expressed in seemingly differing forms, but the most prominent formulations are the following.

Bellow we state the four law of thermodynamics.

Zeroth law of thermodynamics states that If two systems are each in thermal equilibrium with a third, they are also in thermal equilibrium with each other.

First law specifies that energy can be exchanged between physical systems as heat and work and can be denoted by $dU = dQ - dW$.

Second law defines the existence of a quantity called entropy, that describes the direction, thermodynamically, that a system can evolve and quantifies the state of order of a system and that can be used to quantify the useful work that can be extracted from the system.

Third law states that as the temperature of a system approaches absolute zero, all processes cease and the entropy of the system approaches a minimum value.

2 Definitions

Thermodynamic system is a body of matter and/or radiation, confined in space by walls, with defined permeability, which separate it from its surroundings. The surroundings may include other thermodynamic systems, or physical systems that are not thermodynamic systems.

Thermodynamic equilibrium is an axiomatic concept of thermodynamics. It is an internal state of a single thermodynamic system, or a relation between several thermodynamic systems connected by more or less permeable or impermeable walls. In thermodynamic equilibrium there are no net macroscopic flows of matter or of energy, either within a system or between systems. In a system that is in its own state of internal thermodynamic equilibrium, no macroscopic change occurs.

Walls enclose thermodynamic systems bounding it and connecting it to its surroundings. Often a wall restricts passage across it by some form of matter or energy, making the connection indirect. A wall can be fixed (constant volume reactor) or moveable (piston). Ideally, a wall may be declared adiabatic, diathermal, impermeable, permeable, or semi-permeable.

Surroundings is the remainder of the universe that lies outside the boundaries of the system. It is also known as the environment, and the reservoir. Depending on the type of system, it may interact with the system by exchanging mass, energy (including heat and work), momentum, electric charge, or other conserved properties.

Thermodynamic State Function is a function defined for a system relating several state variables or state quantities that depends only on the current equilibrium thermodynamic state of the system not the path which the system took to reach its present state. A state function describes the equilibrium state of a system, thus also describing the type of system. Internal energy, enthalpy, and entropy are examples of state quantities because they quantitatively describe an equilibrium state of a thermodynamic system, regardless of how the system arrived in that state.

State variable is one of the set of variables that are used to describe the mathematical state of a dynamical system and determine its future behavior in the absence of any external forces affecting the system. In thermodynamics, a state variable is an independent variable of a state function like internal energy, enthalpy, and entropy. Examples include temperature, pressure, and volume. Heat and work are not state functions, but process functions.

Process Function is a quantity that is well defined so as to describe the path of a process through the equilibrium state space of a thermodynamic system it can also be called a path function. As an example, mechanical work and heat are process functions because they describe quantitatively the transition between equilibrium states of a thermodynamic system. Infinitesimal changes in a process function X are often indicated by δX to distinguish them from infinitesimal changes in a state function Y which is written dY . The quantity dY is an exact differential, while δX is not, it is an inexact differential. Infinitesimal changes in a process function may be integrated, but the integral between two states depends on the particular path taken between the two states, whereas the integral of a state function is simply the difference of the state functions at the two points, independent of the path taken.

State Variables are the macroscopic quantities which describe a thermodynamic system. Examples of state quantities are the energy E , the volume V , the particle number N , the entropy S , the temperature T , the pressure P and the chemical potential μ , such quantities include also the charge, the dipole momentum, the refractive index, the viscosity, the chemical composition and the size of phase boundaries. The number of state quantities which are necessary for a unique determination of a thermodynamic state is closely related to the number of phases of a system. It is sufficient to choose a few state variables, such that all other state quantities assume values which depend on the chosen state variables.

Extensive (additive) state quantities are proportional to the amount of matter in a system, the particle number or mass for instance. Characteristic examples of extensive properties are the volume and the energy. An extensive state quantity of a heterogeneous system is additively composed of the corresponding extensive properties of the single phases, so the volume of a pot containing water, steam and air is the sum of the volumes of the fluid and gaseous phases. The most characteristic extensive state quantity for

thermodynamics and statistical mechanics is the entropy, which is closely related to the microscopic probability of a state.

Intensive State Quantities are independent of the amount of matter and are not additive for the particular phases of a system. They might assume different values in different phases, but this is not necessarily the case. Examples are refractive index, density, pressure, temperature. Intensive state quantities can be defined locally so they may vary spatially. For example the density of the atmosphere, which is largest at the surface of the earth and continuously decreases with height, or the water pressure in an ocean, which increases with increasing depth.

3 Thermodynamic Systems

A thermodynamic system is an arbitrary amount of matter, energy or radiation and can be uniquely and completely described by specifying macroscopic parameters. Thermodynamic systems may be isolated, closed, and open.

Isolated system has walls that are non-conductive of heat and perfectly reflective of all radiation, that are rigid and immovable, and that are impermeable to all forms of matter and all forces. These systems do not interact in any way with the surroundings. The container has to be impermeable to any form of energy or matter. Especially, the total energy E (mechanic, electric, etc.) is a conserved quantity for such a system and can thus be used to characterize the macrostate. The same holds for the particle number N and the volume V .

Closed thermodynamic system is confined by walls that are impermeable to matter, but can be made permeable (diathermal) or impermeable (adiabatic) to heat, and that can be allowed or not allowed to move, also the energy can be dissipated by internal friction in the system thus the energy is no longer a conserved quantity. If this system is in equilibrium with its surroundings the energy will assume an average value that is related to the temperature of the system or of the surroundings. The macrostate is characterized by the temperature T , the volume V and the number of particles N .

Open thermodynamic system has walls that separate them from other thermodynamic systems but the walls can be permeable to energy, matter and radiation. The energy and the particle number of this system assumes average values when the system is in equilibrium with its surroundings and both energy and particle number are related to the temperature and the chemical potential, which can be used to describe the macrostate.

4 Postulates of Thermodynamics

Bellow we state the four postulates of thermodynamics (taken from Callen's book on thermodynamics).

Postulate I: There exist particular states, called equilibrium states, of simple systems that, macroscopically, are characterized completely by the internal energy U , the volume V , and the mole numbers N_1, N_2, \dots, N_r .

Postulate II: There exists a function, called the entropy, of the extensive parameters of any composite system, defined for all equilibrium and having the following property, the values assumed by the extensive parameters in the absense of an internal constraint are those that maximise the entropy over the manifold of constrained equilibrium states.

Postulate III:

Postulate IV:

5 Zeroth Law of Thermodynamics

6 First Law of Thermodynamics

The first law of thermodynamics is a version of the law of conservation of energy, adapted for thermodynamic processes, distinguishing two kinds of transfer of energy, as heat and as thermodynamic work, and relating them to a function of a body's state, called Internal energy.

The law of conservation of energy states that the total energy of an isolated system is constant; energy can be transformed from one form to another, but can be neither created nor destroyed. For a thermodynamic process without transfer of matter, the first law is often formulated as

$$dU = dQ - dW , \tag{6.1}$$

where dU denotes the change in the internal energy of a closed system, dQ denotes the quantity of energy supplied to the system as heat, and dW denotes the amount of thermodynamic work done by the system on its surroundings. An equivalent statement is that perpetual motion machines of the first kind are impossible. It is worth noting that the differentials dQ and dW are not exact.

The internal energy U of a system is a state function. This means that the total energy content of a system is always the same for a given macroscopic state. The change of the internal energy for an arbitrary infinitesimal change of state is a total differential.

Work is a process of transferring energy to or from a system in ways that can be described by macroscopic mechanical forces acting between the system and its surroundings. The work done by the system can come from its overall kinetic energy, from its overall potential

energy, or from its internal energy. For example, when a machine (not a part of the system) lifts a system upwards, some energy is transferred from the machine to the system. The system's energy increases as work is done on the system and in this particular case, the energy increase of the system is manifested as an increase in the system's gravitational potential energy.

Heat is energy in transfer to or from a thermodynamic system, by mechanisms other than thermodynamic work or transfer of matter. The quantity of energy transferred as heat in a process is the amount of transferred energy excluding any thermodynamic work that was done and any energy contained in matter transferred. Heat can be conducted by radiation, conduction or friction.

Internal energy is all the energy available of a system that is associated with its microscopic components like atoms and molecules when measured by an observer in a laboratory, that is a reference frame at rest. This rest condition ensures that any kinetic energy from the motion of the system in space is not accounted for the internal energy.

7 Changes of State

The change of state of a thermodynamic system is defined by a passage from an initial state to a final state of thermodynamic equilibrium for which the changes may occur. The states and the thermodynamic equilibrium of a phase are unchanged unless a thermodynamic process is initiated upon the system. The equilibrium state is completely specified by a set of state variables that depend upon on the specific equilibrium state. The changes on the system may be reversible or irreversible.

7.1 Irreversible process

Irreversible process in an isolated system occur in only one direction since they can not be reversed without a thermodynamic process acting upon the system. Example of an irreversible process is the expansion of a gas from a smaller into a larger volume. Other example is a pendulum swinging without a driving external force, it will eventually stop swinging since its mechanical energy will be transformed into heat to the surroundings due to friction with the air, but that does not mean you can make a pendulum at rest starts swinging spontaneously by just cooling the surroundings. Most of the real process are irreversible in nature.

7.2 Reversible process

Reversible process are an idealization since if a system is in equilibrium state the variables of state are time independent and nothing happens to the system. Reversible

processes can be simulated by infinitesimal changes of the state variables making the equilibrium state to suffer small disturbances. The time spent for this small changes is really slow compared to the relaxation time of the system.

Changes of state may occur as **cyclic processes**. Such processes undergoes changes from one state to another with state variables describing each equilibrium state for each phase and the process ends in the same state where it started. Those changes depend on the transfer of heat and work into and out of the system, thus we called heat and work **process quantities**.

The changes of phase of a system occur when the state variables that describes the equilibrium state suffer changes while other variables remain unchanged. We may group such types of processes as adiabatic, isothermal, isentropic, isobaric, isochoric, and isenthalpic.

7.3 Isobaric process

Isobaric process occurs at constant pressure $\delta P = 0$. An example would be a movable piston in a cylinder with the pressure inside always at atmospheric pressure, although it is separated from the atmosphere. The system is dynamically connected by a movable boundary to a constant pressure reservoir.

7.4 Isochoric process

Isochoric process is one in which the volume is held constant, with the result that the mechanical work done by the system will be zero. Any heat energy transferred to the system externally will be absorbed as internal energy. An isochoric process is also known as an isometric process or an isovolumetric process.

7.5 Isothermal process

Isothermal process occurs at a constant temperature. An example would be a closed system immersed in and thermally connected with a large constant-temperature bath. Energy is gained by the system through work done on it and is lost to the bath so that its temperature remains constant.

7.6 Adiabatic process

Adiabatic process is a process in which there is no matter or heat transfer, because a thermally insulating wall separates the system from its surroundings. For the process to be natural, either work must be done on the system at a finite rate, so that the internal energy of the system increases and the entropy of the system increases even though it is

thermally insulated or the system must do work on the surroundings, which then suffer increase of entropy, as well as gaining energy from the system.

7.7 Isentropic process

Isentropic process is customarily defined as an idealized quasi-static reversible adiabatic process of transfer of energy as work. For a constant-entropy process, if work is done irreversibly, heat transfer is necessary, so that the process is not adiabatic, and an accurate artificial control mechanism is necessary. This is not an ordinary natural thermodynamic process.

8 Mathematical Definitions

The ideal gas law which is valid only for diluted gases in a low pressure approximation is given by the following equation

$$PV = NRT, \quad (8.1)$$

where P is the pressure, V is the volume, N is the particle number and T is the temperature of the gas at a particular equilibrium state. The particle number is usually on the order of the Avogadro number constant given by

$$N_A = 6.0221367 \times 10^{23} \quad (8.2)$$

which is defined as the ratio between one gram and one unit of atomic mass and it is also called Mole number. R is the ideal gas constant and it is the same for all gases and is defined as

$$R = N_A k_B = 8.31451 \text{ J K}^{-1} \text{ mol}^{-1}, \quad (8.3)$$

where k_B is the Boltzmann constant. The work W is defined as

$$W = \oint P dV \quad (8.4)$$

where the integration \oint is taken over a complete cycle. The heat Q can be calculated via the heat capacity C and the following equation

$$C = \frac{dQ}{dT}, \quad (8.5)$$

and the heat capacity can be calculated for constant volume and for constant pressure.

9 Internal Energy and Heat Capacity

Considering an ideal gas in a system with rigid walls, so there is no change in volume. We know that the ideal gas law is given by

$$PV = NkT = \frac{2}{3}N\langle\epsilon_{kin}\rangle, \quad (9.1)$$

where $\langle \epsilon_{kin} \rangle$ is the mean kinetic energy per particle. In the case of an ideal gas the particles possess only kinetic energy and no potential energy, hence $\langle \epsilon_{kin} \rangle$ is the total mean energy. In this case the internal energy in the statistical framework is the total mean energy available for the system (ideal gas)

$$U = N\langle \epsilon_{kin} \rangle = N\langle E_{kin} \rangle = \frac{3}{2}NkT. \quad (9.2)$$

Now we proceed to calculate the specific heat for the ideal gas. Again considering the ideal gas in a container with rigid walls so no volume change and in contact with a heat bath with temperature T . If the temperature suffers a small change dT , by the first law of thermodynamics

$$dU = \delta W + \delta Q, \quad (9.3)$$

but since there is no change in volume the total work is zero

$$\delta W = -p dV = 0, \quad (9.4)$$

so the system suffers a isochoric change and from the definition of heat and remembering that we are dealing with constant volume

$$dU = C_V(T)dT, \quad (9.5)$$

where C_V is the heat capacity at constant volume. For the ideal gas the heat capacity is constant so the integration is straightforward.

$$U(T) - U(T_0) = C_V(T - T_0), \quad (9.6)$$

and we can relate the heat capacity with the total particle number and the Boltzmann constant as

$$C_V = \frac{3}{2}Nk, \quad (9.7)$$

remembering that $C_V = Nc_V$, where c_v is the specific heat per particle for the ideal gas. With the help of the specific heat one can determine the internal energy for ideal gases, for constant volume the definition for the specific heat at constant volume is given by

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V. \quad (9.8)$$

10 Second Law of Thermodynamics

References

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