1   Thermodynamic System and First Law

James Prescott Joule, 1818–1889

J. P. Joule was the owner of a brewery in England and worked as a self-educated scientist making major contributions to the development of thermodynamics. In 1840, he stated the law that bears his name on power dissipated by a current passing through a resistance. In 1843, there began a series of observations on the heat equivalent pertaining to mechanical work.

1.1 Historical Introduction

At the beginning of the nineteenth century, steam engines had been converting heat into work for about 150 years. Scientific investigations were under way to establish a quantitative equivalence of heat and work. With time, this concept became the law of energy conservation, which we will discuss in this chapter.

In 1839, Marc Séguin, nephew of the famous Mongolfier, published his 'Study on the influence of railways' [1]. It was clear for him that the condenser of a heat engine played a role that was equally important as that of the furnace [2]. Séguin assumed that the steam that caused the volume of the cylinder to increase performed work that was equal in
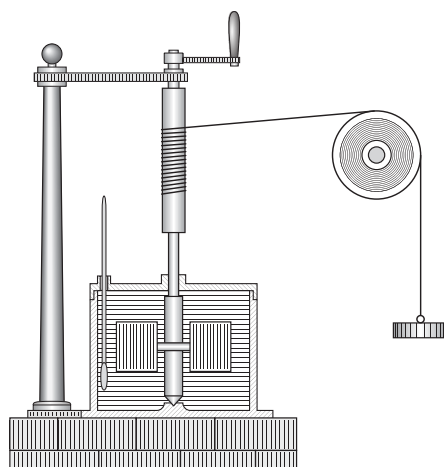
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Figure 1.1 Joule's calorimeter: the fall of the weight at nearly constant velocity (because of the fluid viscosity) drives a stirring mechanism in the calorimeter. The change in potential energy of the weight determines the work performed on the liquid. The increase in energy of the liquid is deduced from its temperature rise.

magnitude to the heat lost by the steam in the process. He sought to estimate this heat loss by measuring the heat taken from the furnace and returned to the condenser.

A year later, Julius Robert von Mayer travelled to the tropics as a medical doctor. He observed that the colour difference between veinous and arterial blood was more pronounced there than at latitudes where the climate is colder. He attributed this difference to the heat released by the body. His thoughts on the human body as a heat engine led him to the idea of an equivalence between heat and work, which he later tested on inert matter.

In his 1842 treatise [3], he asked the following question: what is the change in temperature of a stone when it hits the ground after falling from a given height? James Prescott Joule succeeded in doing this measurement, thanks to his development of highly sensitive thermometers. Joule also observed that an electrical current dissipates heat, an effect that bears his name. In 1845, he published his fundamental work on energy conservation [4]. With a calorimeter (Fig. 1.1), he determined the equivalence between work (defined by masses going down in the gravitational potential) and heat (corresponding to the warming of the liquid stirred by the device). Before Joule established this link, it was customary to measure heat in *calories*. Joule established the conversion to the unit that bears his name, the *joule* [J]: 1 [cal] = 4.1855 [J] .

These are units of energy. Joule and others observed in various circumstances that the heat provided to a system and the work performed on it are equal and opposite to each other for every process that brings the system back to its initial state [5]. Von Mayer, in his treatise of 1842, expressed the idea that every system is characterised by a quantity, energy, that can only be modified by an external action in the form of work or heat [6]. Hermann von Helmholtz, in 1847, gives energy conservation the status of a physical law [7].

1.2 Thermodynamic System

A ***thermodynamic system*** consists of matter contained in a region of space delineated by a closed surface, called an ***enclosure***, that separates the system from its ***environment*** or ***surroundings***. The system is assumed to be large, in the sense that the amount of substance it contains is typically counted in moles. A mole corresponds to the Avogadro number $6.02 \cdot 10^{23}$ that is used to count the number of elementary constituents of matter. This definition can be extended to a thermodynamic system that includes radiation and any other kind of physical field. In the first two parts of this book, we will discuss systems consisting of matter only. We will introduce electromagnetic fields in the third part.

We use the following terms to characterise how a system interacts with its environment. A system is said to be:

- ***open***, if its enclosure allows convective matter exchange with the environment
- ***closed***, if its enclosure does not allow convective matter exchange with the environment
- ***diathermal***, if its enclosure allows conductive heat exchange with the environment
- ***adiabatic***, if its enclosure does not allow conductive heat exchange with the environment
- ***isolated***, if its enclosure does not allow any interaction with the environment

A thermodynamic system can be decomposed in ***subsystems*** that can be considered as thermodynamic systems themselves. The separation between two subsystems is called a ***wall***. The enclosure between a system and its environment consists of one or several walls. We use the following terms to characterise a wall. A wall is said to be:

- ***fixed***, if it cannot move
- ***movable***, if it can move
- ***permeable***, if it allows convective matter exchange with the environment
- ***impermeable***, if it does not allow convective matter exchange with the environment
- ***diathermal***, if it allows conductive heat exchange with the environment
- ***adiabatic***, if it does not allow conductive heat exchange with the environment

1.3 State, Variables and State Functions

The ***state*** of a system is characterised by physical properties that are described by a set of ***state variables***. The state is entirely specified by the values of these state variables and it does not depend on the history of the system. The set of these state variables is written as,

$$\{X_1, X_2, X_3, X_4, X_5, \ldots\}$$

A ***state function*** is a physical property that depends only on the state of the system. Thus, a state function is expressed as,

$$F(X_1, X_2, X_3, X_4, X_5, \ldots)$$

1.3.1 Partial Derivatives of a Function

Let $f(x, y)$ be a function of two variables x and y. The **partial derivatives** with respect to the variables x and y are defined by,

$$\frac{\partial f(x, y)}{\partial x} \equiv \lim_{\Delta x \to 0} \frac{f(x + \Delta x, y) - f(x, y)}{\Delta x}$$
$$\frac{\partial f(x, y)}{\partial y} \equiv \lim_{\Delta y \to 0} \frac{f(x, y + \Delta y) - f(x, y)}{\Delta y} \tag{1.1}$$

Thus, in the calculation of a partial derivative with respect to one variable, the other variables are kept constant. As an example, let us consider the function $f(x, y) = x^2 + 3xy$. The partial derivatives of this function are,

$$\frac{\partial f(x, y)}{\partial x} = 2x + 3y \qquad \text{and} \qquad \frac{\partial f(x, y)}{\partial y} = 3x$$

1.3.2 Differential of a Function

Let $f(x, y)$ be a function of two variables x and y [8]. The variation of the function $f(x, y)$ from point (x, y) to point $(x + \Delta x, y + \Delta y)$ is written as,

$$\Delta f(x, y) = f(x + \Delta x, y + \Delta y) - f(x, y) \tag{1.2}$$

It can be recast as,

$$\Delta f(x, y) = f(x + \Delta x, y + \Delta y) - f(x, y + \Delta y) + f(x, y + \Delta y) - f(x, y)$$
$$= \frac{f(x + \Delta x, y + \Delta y) - f(x, y + \Delta y)}{\Delta x} \Delta x$$
$$+ \frac{f(x, y + \Delta y) - f(x, y)}{\Delta y} \Delta y \tag{1.3}$$

The **differential** $df(x, y)$ is defined as the infinitesimal limit of the variation $\Delta f(x, y)$,

$$df(x, y) \equiv \lim_{\Delta x \to 0} \lim_{\Delta y \to 0} \Delta f(x, y) \tag{1.4}$$

Taking into account the limit

$$\lim_{\Delta y \to 0} \Big(f(x + \Delta x, y + \Delta y) - f(x, y + \Delta y) \Big) = f(x + \Delta x, y) - f(x, y) \tag{1.5}$$

in equation (1.3), the differential (1.4) can be written as,

$$df(x, y) = \lim_{\Delta x \to 0} \frac{f(x + \Delta x, y) - f(x, y)}{\Delta x} \Delta x$$
$$+ \lim_{\Delta y \to 0} \frac{f(x, y + \Delta y) - f(x, y)}{\Delta y} \Delta y \tag{1.6}$$

Using the definition (1.1) of the partial derivatives of a function, the differential (1.6) is reduced to,

$$df(x, y) = \frac{\partial f(x, y)}{\partial x} dx + \frac{\partial f(x, y)}{\partial y} dy \tag{1.7}$$

1.3.3 Time Derivative of a Function

Let $f(x, y)$ be a function of two time-dependent variables x and y. The time derivative of the function is obtained using the chain rule,

$$\dot{f}(x, y) = \frac{\partial f(x, y)}{\partial x}\, \dot{x} + \frac{\partial f(x, y)}{\partial y}\, \dot{y} \tag{1.8}$$

where

$$\dot{f}(x, y) \equiv \frac{df(x, y)}{dt} \qquad \dot{x} \equiv \frac{dx}{dt} \qquad \dot{y} \equiv \frac{dy}{dt}$$

1.4 Processes and Change of State

A thermodynamic system can interact with its environment through *processes* that change the state of the system. We distinguish three types of physical processes:

- mechanical processes
- thermal processes
- chemical processes

As we will see, thermodynamics allows us to provide a quantitative characterisation of the effects that processes have on the state of a system. Mechanical processes can lead to mechanical or thermal changes of the state. In the experiment of Joule's calorimeter (Fig. 1.1), work is performed on the system and its temperature changes. Thus, a mechanical process can lead to a thermal change of state. Likewise, thermal processes can lead to thermal or mechanical changes of the system state. In the experiment illustrated in Fig. 1.2, heat is provided to the system by hand contact. The pressure of the gas rises, causing a shift of the water levels in the U-shaped tube. Thus, a thermal process can lead to a mechanical change of state.
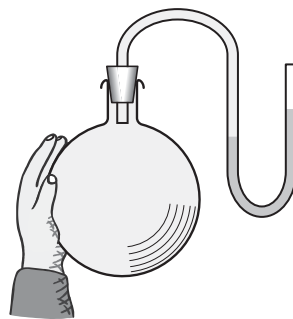
Figure 1.2 A vessel contains a fixed amount of gas. The liquid in the tube measures the changes of pressure when the gas is heated by the hand.

In the context of describing the types of processes that take place between a system and its environment, the term "chemical process" refers specifically to matter being exchanged between a system and its environment. This is not to be confused with chemical reactions among different substances. Such reactions occurring within the system will be explored in Chapter 8. The enclosure of the system should be defined so as to encompass the regions of space where chemical reactions take place.

1.5 Extensive and Intensive Quantities

A quantity is called *extensive* when it has the following property: its value for the whole system is equal to the sum of its values for every subsystem. The following are extensive quantities:

- mass
- momentum
- angular momentum
- energy
- volume

Sometimes we refer to extensive quantities divided by the volume, the mass or the number of moles of the system. They are called a volume density, a mass density or a molar density. In that case we speak of a *specific quantity* or a *reduced extensive quantity*. The following are densities:

- mass density
- momentum density
- angular momentum density
- energy density

A quantity is called *intensive* when it is conjugated to an extensive quantity, which means that it is defined as the partial derivative of the energy with respect to this extensive quantity. The following are intensive quantities:

- velocity
- pressure
- temperature

To determine if a quantity is extensive or intensive, it is useful to imagine what happens to this quantity when the size of the system doubles. If the quantity is extensive, its value doubles, but if it is intensive, its value does not change. It is also useful to clarify that *certain quantities are neither extensive nor intensive*. This is the case of the entropy production rate, which we will introduce in Chapter 2.

A system is called *homogeneous* when all the intensive scalar functions conjugated to the extensive scalar state variables do not depend on position. This means that they have the same value for every subsystem. A system is called *uniform* when the intensive vectorial

functions conjugated to the extensive vectorial state variables do not depend on position. This means that they have the same norm and orientation in every subsystem.

1.6 First Law of Thermodynamics

Thermodynamics is based on two fundamental laws. Their justification is based on the empirical validity of their implications. In this chapter, we discuss the first law. We will present the second law in Chapter 2.

The *first law of thermodynamics* states that:

For every system, there is a scalar extensive state function called *energy* (E). When the system is isolated, the energy is conserved.

The energy conservation law is mathematically written as,

$$\dot{E} = 0 \quad \text{(isolated system)} \tag{1.9}$$

where $\dot{E} \equiv dE/dt$. This conservation is related to time homogeneity [9]. It implies that energy is defined up to a constant.

When the system interacts with its environment, the energy evolution results from the power of the processes exerted on the system. We distinguish four types of external processes and write [10]:

$$\dot{E} = P^{\text{ext}} + P_W + P_Q + P_C \quad \text{(open system)} \tag{1.10}$$

- P^{ext} represents the *power* associated with the *external forces* and *torques* that modify the *translational kinetic energy* of the centre of mass and the *rotational kinetic energy* around the centre of mass. These forces and torques do not modify the shape of the system.
- P_W represents the *mechanical power* associated with the work performed by the environment on the system that results in a deformation of the system without any change in its state of motion, in particular its kinetic energy.
- P_Q represents the *thermal power* associated with heat exchange with the environment through conduction.
- P_C represents the *chemical power* associated with matter exchange with the environment through convection.

Any physical process performing work is called a *mechanical action*. Any physical process in which heat is exchanged is called a *heat transfer*. A physical process in which matter is exchanged is called a *matter transfer* or *mass transfer*. When a heat transfer takes place through a matter transfer, it is called a heat transfer by *convection*. When a heat transfer occurs without matter transfer, it is called a heat transfer by *conduction*. In general, a matter transfer leads simultaneously to a mechanical action and to a heat transfer.

We have characterised systems according to ways in which they interact with their environment. We can now specify such characteristics in terms of the powers of the various processes considered here. Hence, a system is called:

- **rigid** if no work by deformation is possible, i.e. $P_W = 0$.
- **closed** if there is no matter transfer, i.e. $P_C = 0$, and **open** otherwise.
- **adiabatic** if there is no heat transfer, i.e. $P_Q = 0$ and **diathermal** in the opposite case.
- **isolated** if it is rigid, adiabatic and closed in the absence of external forces and torques, i.e. $P^{\text{ext}} = P_W = P_Q = P_C = 0$.

When a system is closed, the energy evolution equation (1.10) reduces to,

$$\dot{E} = P^{\text{ext}} + P_W + P_Q \quad \text{(closed system)} \tag{1.11}$$

The first law can be expanded on to include two other conservation laws that impose additional constraints on the possible states of the system. The first is related to the translational state of motion and the second to the rotational state of motion.

Concerning translations, we have the following conservation law:

For every system, there is a vectorial extensive state function called *momentum* (P). When the system is isolated, the momentum is conserved.

The momentum conservation law is mathematically written as,

$$\dot{P} = 0 \quad \text{(isolated system)} \tag{1.12}$$

where $\dot{P} \equiv dP/dt$. This conservation law is related to the homogeneity of space [9]. It implies that the momentum is defined up to a constant.

In the case of a system interacting with the environment, the evolution of the momentum with respect to an inertial frame of reference is given by the centre-of-mass theorem [11],

$$\dot{P} = F^{\text{ext}} \tag{1.13}$$

where F^{ext} is the net external force exerted on the system. If the system undergoes a uniform translational motion, the momentum is constant. A net external force causes a departure from the state of uniform translation.

Concerning rotations, we have the following conservation law:

For every system, there is a vectorial extensive state function called *angular momentum* (L). When the system is isolated, the angular momentum is conserved.

The angular momentum conservation law is mathematically written as,

$$\dot{L} = 0 \quad \text{(isolated system)} \tag{1.14}$$

where $\dot{L} \equiv dL/dt$. This conservation law is related to the isotropy of space. It implies that the angular momentum is defined up to a constant.

In the case of a system interacting with the environment, the evolution of the angular momentum with respect to an inertial frame of reference is given by the angular momentum theorem [11],

$$\dot{L} = M^{\text{ext}} \tag{1.15}$$

where M^{ext} is the net external torque exerted on the system. If the system undergoes a uniform rotational motion, the angular momentum is constant. A net external torque causes a departure from the state of uniform rotation.

1.7 Thermodynamics and Mechanics

The first law, expanded with the two mechanical conservation laws, links thermodynamics and mechanics. We will now illustrate this link by considering a particular system that is homogeneous, deformable, closed, diathermal, electrically neutral and cylindrical in shape. The centre of mass of the system is moving with a velocity v that is small compared to the speed of light in vacuum. The system rotates with an angular velocity ω around its axis of symmetry, which is a principal axis of inertia [12]. The motion of the system is such that the velocity v is collinear to the angular velocity ω.

We assume further that the deformation of the system is symmetric in the direction of the rotational axis and leaves the radius of the cylinder constant. It is a contraction or dilatation of the system that does not modify its translational kinetic energy. The deformation does not modify the rotational kinetic energy either since the moment of inertia with respect to the rotation axis is constant (Fig. 1.3). It modifies the total kinetic energy of the system since there is a symmetric motion of matter relative to the centre of mass. However, we consider here a deformation that is sufficiently slow for this kinetic energy variation to be negligible.

The translational motion of the system is characterised by its momentum P and the rotational motion by its angular momentum L. According to the first law, these quantities are extensive state functions that can be chosen as extensive state variables. A state variable is a trivial state function for which all other variables are kept constant. The state of the system at time t is determined by a set of $n + 3$ extensive state variables $\{P, L, X_0, X_1, \ldots, X_n\}$.

According to the first law, energy is a state function. Thus, it is a function of all the state variables of the system, i.e. $E = E(P, L, X_0, X_1, \ldots, X_n)$. The **momentum** is proportional to the velocity v,
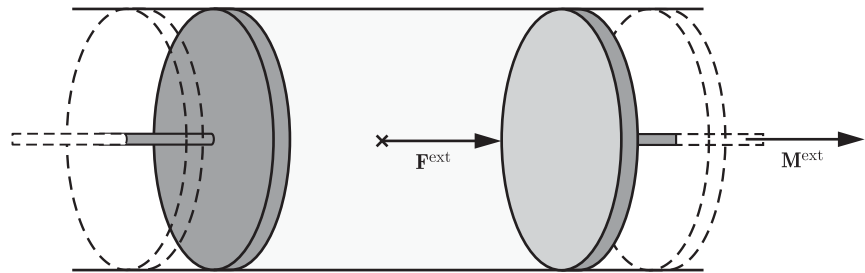
$$P = Mv \tag{1.16}$$

Figure 1.3 A net external force F^{ext} and a net external torque M^{ext} are exerted on a homogeneous system that is symmetrically deformed.

where the mass M is constant, i.e. $\dot{M} = 0$. Substituting the expression (1.16) into the centre of mass theorem (1.13), we obtain,

$$F^{\text{ext}} = M\dot{v} \qquad (1.17)$$

The **velocity v** is the **intensive quantity conjugated** to the momentum P,

$$v = \frac{\partial E\left(P, L, X_0, X_1, \ldots, X_n\right)}{\partial P} \qquad (1.18)$$

The **angular momentum L** is proportional to the angular velocity ω,

$$L = I\omega \qquad (1.19)$$

where I is the moment of inertia with respect to the rotational axis. Since the system is cylindrical in shape with a constant radius R_0, the moment of inertia $I = \frac{1}{2} MR_0^2$ is constant, i.e. $\dot{I} = 0$. Substituting the expression (1.19) into the angular momentum theorem (1.15), we obtain,

$$M^{\text{ext}} = I\dot{\omega} \qquad (1.20)$$

The **angular velocity ω** is the **intensive quantity conjugated** to the angular momentum L,

$$\omega = \frac{\partial E\left(P, L, X_0, X_1, \ldots, X_n\right)}{\partial L} \qquad (1.21)$$

In order to satisfy the definitions, (1.18) and (1.21), taking into account relations (1.16) and (1.19), the energy of the system $E\left(P, L, X_0, X_1, \ldots, X_n\right)$ is given by [13],

$$E\left(P, L, X_0, X_1, \ldots, X_n\right) = \frac{1}{2} v \cdot P + \frac{1}{2} \omega \cdot L + U(X_0, X_1, \ldots, X_n) \qquad (1.22)$$

The first term is the translational kinetic energy of the centre of mass and the second term the rotational kinetic energy around a principal axis of inertia. The state function $U \equiv U(X_0, X_1, \ldots, X_n)$ is called the **internal energy** of the system, because it is independent of its state of motion. If we wanted to identify the internal energy of a system which is more complex than the one examined here, we would have to split it into homogeneous subsystems (as in Chapter 3) and apply the present approach to each of the subsystems. If the system is too complex, then it has to be described by the continuum approach that will be developed in Chapter 10.

For the simple system treated here, we can determine the time derivative of its energy by taking the time derivative of expression (1.22). Applying the mathematical rule (1.8) for the time derivative of a function of several variables, and taking into account the definitions (1.18) and (1.21), we obtain:

$$\dot{E}\left(P, L, X_0, X_1, \ldots, X_n\right) = v \cdot \dot{P} + \omega \cdot \dot{L} + \dot{U}(X_0, X_1, \ldots, X_n) \qquad (1.23)$$

Taking into account relations (1.16) and (1.19), the expression (1.23) of the time derivative of the energy becomes,

$$\dot{E} = M v \cdot \dot{v} + I \omega \cdot \dot{\omega} + \dot{U} \qquad (1.24)$$