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Cambridge University Press
0521580560 - Methods of Statistical Physics
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The laws of thermodynamics

1.1 The thermodynamic system and processes

A physical system containing a large number of atoms or molecules is called the *thermodynamic system* if macroscopic properties, such as the temperature, pressure, mass density, heat capacity, etc., are the properties of main interest. The number of atoms or molecules contained, and hence the volume of the system, must be sufficiently large so that the conditions on the surfaces of the system do not affect the macroscopic properties significantly. From the theoretical point of view, the size of the system must be infinitely large, and the mathematical limit in which the volume, and proportionately the number of atoms or molecules, of the system are taken to infinity is often called the *thermodynamic limit*.

The *thermodynamic process* is a process in which some of the macroscopic properties of the system change in the course of time, such as the flow of matter or heat and/or the change in the volume of the system. It is stated that the system is in *thermal equilibrium* if there is no thermodynamic process going on in the system, even though there would always be microscopic molecular motions taking place. The system in thermal equilibrium must be uniform in density, temperature, and other macroscopic properties.

1.2 The zeroth law of thermodynamics

If two thermodynamic systems, A and B, each of which is in thermal equilibrium independently, are brought into thermal contact, one of two things will take place: either (1) a flow of heat from one system to the other or (2) no thermodynamic process will result. In the latter case the two systems are said to be in thermal equilibrium with respect to each other.

The zeroth law of thermodynamics *If two systems are in thermal equilibrium with each other, there is a physical property which is common to the two systems. This common property is called the temperature.*

Let the condition of thermodynamic equilibrium between two physical systems A and B be symbolically represented by

$$A \Leftrightarrow B. \tag{1.1}$$

Then, experimental observations confirm the statement

$$\text{if} \quad A \Leftrightarrow C \quad \text{and} \quad B \Leftrightarrow C, \quad \text{then} \quad A \Leftrightarrow B. \tag{1.2}$$

Based on preceding observations, some of the physical properties of the system C can be used as a measure of the temperature, such as the volume of a fixed amount of the chemical element mercury under some standard atmospheric pressure. The zeroth law of thermodynamics is the assurance of the existence of a property called the *temperature*.

1.3 The thermal equation of state

Let us consider a situation in which two systems A and B are in thermal equilibrium. In particular, we identify A as the thermometer and B as a system which is homogeneous and isotropic. In order to maintain equilibrium between the two, the volume V of B does not have to have a fixed value. The volume can be changed by altering the hydrostatic pressure p of B, yet maintaining the equilibrium condition in thermal contact with the system A. This situation may be expressed by the following equality:

$$f_B(p, V) = \theta_A, \tag{1.3}$$

where θ_A is an *empirical temperature* determined by the thermometer A.

The thermometer A itself does not have to be homogeneous and isotropic; however, let A also be such a system. Then,

$$f_B(p, V) = f_A(p_A, V_A). \tag{1.4}$$

For the sake of simplicity, let p_A be a constant. Usually p_A is chosen to be one atmospheric pressure. Then f_A becomes a function only of the volume V. Let us take this function to be

$$f_A(p_A, V_A) = 100 \left[\frac{V_A - V_0}{V_{100} - V_0} \right]_A, \tag{1.5}$$

where V_0 and V_{100} are the volumes of A at the freezing and boiling temperatures of water, respectively, under one atmospheric pressure. This means

$$\theta = 100\frac{V_A - V_0}{V_{100} - V_0}. \tag{1.6}$$

If B is an arbitrary substance, (1.3) may be written as

$$f(p, V) = \theta. \tag{1.7}$$

In the above, the volume of the system A is used as the thermometer; however, the pressure p could have been used instead of the volume. In this case the volume of system A must be kept constant. Other choices for the thermometer include the resistivity of a metal. The temperature θ introduced in this way is still an empirical temperature. An equation of the form (1.7) describes the relationship between the pressure, volume, and temperature θ and is called the *thermal equation of state*. In order to determine the functional form of $f(p, V)$, some elaborate measurements are needed. To find a relationship between small changes in p, V and θ, however, is somewhat easier. When (1.7) is solved for p, we can write

$$p = p(\theta, V). \tag{1.8}$$

Differentiating this equation, we find

$$\mathrm{d}p = \left(\frac{\partial p}{\partial \theta}\right)_V \mathrm{d}\theta + \left(\frac{\partial p}{\partial V}\right)_\theta \mathrm{d}V. \tag{1.9}$$

If the pressure p is kept constant, i.e., $\mathrm{d}p = 0$, the so-called *isobaric process*,

$$\left(\frac{\partial p}{\partial \theta}\right)_V \mathrm{d}\theta + \left(\frac{\partial p}{\partial V}\right)_\theta \mathrm{d}V = 0. \tag{1.10}$$

In this relation, one of the two changes, either $\mathrm{d}\theta$ or $\mathrm{d}V$, can have an arbitrary value; however, the ratio $\mathrm{d}V/\mathrm{d}\theta$ is determined under the condition $\mathrm{d}p = 0$. Hence the notation $(\partial V/\partial \theta)_p$ is appropriate. Then,

$$\left(\frac{\partial p}{\partial \theta}\right)_V + \left(\frac{\partial p}{\partial V}\right)_\theta \left(\frac{\partial V}{\partial \theta}\right)_p = 0. \tag{1.11}$$

$(\partial p/\partial \theta)_V$ is the rate of change of p with θ under the condition of constant volume, the so-called *isochoric process*. Since V is kept constant, p is a function only of θ. Therefore

$$\left(\frac{\partial p}{\partial \theta}\right)_V = \frac{1}{\left(\frac{\partial \theta}{\partial p}\right)_V}. \tag{1.12}$$

Hence (1.11) is rewritten as

$$\left(\frac{\partial p}{\partial V}\right)_\theta \left(\frac{\partial V}{\partial \theta}\right)_p \left(\frac{\partial \theta}{\partial p}\right)_V = -1. \tag{1.13}$$

This form of equation appears very often in the formulation of thermodynamics. In general, if a relation $f(x, y, z) = 0$ exists, then the following relations hold:

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}, \qquad \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1. \tag{1.14}$$

The quantity

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial \theta}\right)_p \tag{1.15}$$

is called the *volume expansivity*. In general, β is almost constant over some range of temperature as long as the range is not large. Another quantity

$$K = -V\left(\frac{\partial p}{\partial V}\right)_\theta \tag{1.16}$$

is called the *isothermal bulk modulus*. The reciprocal of this quantity,

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_\theta, \tag{1.17}$$

is called the *isothermal compressibility*. Equation (1.9) is expressed in terms of these quantities as

$$\mathrm{d}p = \beta K \,\mathrm{d}\theta - \frac{K}{V}\mathrm{d}V. \tag{1.18}$$

1.4 The classical ideal gas

According to laboratory experiments, many gases have the common feature that the pressure, p, is inversely proportional to the volume, V; i.e., the product pV is constant when the temperature of the gas is kept constant. This property is called the *Boyle–Marriot law*,

$$pV = F(\theta), \tag{1.19}$$

where $F(\theta)$ is a function only of the temperature θ. Many real gases, such as oxygen, nitrogen, hydrogen, argon, and neon, show small deviations from this behavior; however, the law is obeyed increasingly more closely as the density of the gas is lowered.

Thermodynamics is a branch of physics in which thermal properties of physical systems are studied from a macroscopic point of view. The formulation of the theories does not rely upon the existence of a system which has idealized properties. It is, nevertheless, convenient to utilize an idealized system for the sake of theoretical formulation. The *classical ideal gas* is an example of such a system.

Definition *The ideal gas obeys the Boyle–Marriot law at any density and temperature.*

Let us now construct a thermometer by using the ideal gas. For this purpose, we take a fixed amount of the gas and measure the volume change due to a change of temperature, θ_p, while the pressure of the gas is kept constant. So,

$$\theta_p = 100\frac{V - V_0}{V_{100} - V_0}, \tag{1.20}$$

where V_0 and V_{100} are the volumes of the gas at the freezing and boiling temperatures, respectively, of water under the standard pressure. This scale is called the *constant-pressure gas thermometer*.

It is also possible to define a temperature scale by measuring the pressure of the gas while the volume of the gas is kept constant. This temperature scale is defined by

$$\theta_V = 100\frac{p - p_0}{p_{100} - p_0}, \tag{1.21}$$

where p_0 and p_{100} are the pressures of the gas at the freezing and boiling temperatures, respectively, of water under the standard pressure. This scale is called the *constant-volume gas thermometer*.

These two temperature scales have the same values at the two fixed points of water by definition; however, they also have the same values in between the two fixed temperature points.

From (1.20) and (1.21),

$$\theta_p = 100\frac{pV - pV_0}{pV_{100} - pV_0}, \qquad \theta_V = 100\frac{pV - p_0V}{p_{100}V - p_0V}, \tag{1.22}$$

and, since $pV_0 = p_0V$ and $pV_{100} = p_{100}V$,

$$\theta_p = \theta_V, \tag{1.23}$$

and hence we may set $\theta_p = \theta_V = \theta$ and simply define

$$pV_0 = p_0V = (pV)_0, \qquad pV_{100} = p_{100}V = (pV)_{100}, \tag{1.24}$$

and

$$\theta = 100\frac{pV - (pV)_0}{(pV)_{100} - (pV)_0}. \tag{1.25}$$

When this equation is solved for pV, we find that

$$pV = \frac{(pV)_{100} - (pV)_0}{100}\left[\theta + \frac{100(pV)_0}{(pV)_{100} - (pV)_0}\right]. \tag{1.26}$$

If we define

$$\begin{aligned}\frac{(pV)_{100} - (pV)_0}{100} &= R',\\ \theta + \frac{100(pV)_0}{(pV)_{100} - (pV)_0} &= \Theta,\end{aligned} \tag{1.27}$$

(1.26) can then be written in the following form:

$$pV = R'\Theta. \tag{1.28}$$

Θ is called the *ideal gas temperature*. It will be shown later in this chapter that this temperature becomes identical with the *thermodynamic temperature scale*.

The difference between θ and Θ is given by

$$\Theta_0 = 100\frac{(pV)_0}{(pV)_{100} - (pV)_0}. \tag{1.29}$$

According to laboratory experiments, the value of this quantity depends only weakly upon the type of gas, whether oxygen, nitrogen, or hydrogen, and in particular it approaches a common value, Θ_0, in the limit as the density of the gas becomes very small:

$$\Theta_0 = 273.15. \tag{1.30}$$

We can calculate the volume expansivity β for the ideal gas at the freezing point of water $\theta = 0$:

$$\beta = \frac{1}{V_0}\left(\frac{\partial V}{\partial \Theta}\right)_p = \frac{1}{V_0}\frac{R'}{p} = \frac{R'}{R'\Theta_0} = \frac{1}{\Theta_0}. \tag{1.31}$$

When the value $\Theta_0 = 273.15$ is introduced, we find

$$\beta = 0.0036610. \tag{1.32}$$

This value may be favorably compared with experimental measurements.

1.5 The quasistatic and reversible processes

The *quasistatic process* is defined as a thermodynamic process which takes place unlimitedly slowly. In the theoretical formulation of thermodynamics it is customary to consider a sample of gas contained in a cylinder with a frictionless piston. The walls of the cylinder are made up of a diathermal, i.e., a perfectly heat conducting metal, and the cylinder is immersed in a heat bath at some temperature. In order to cause any heat transfer between the heat bath and the gas in the cylinder there must be a temperature difference; and similarly there must be a pressure difference between the gas inside the cylinder and the applied pressure to the piston in order to cause any motion of the piston in and out of the cylinder. We may consider an ideal situation in which the temperature difference and the pressure difference are adjusted to be infinitesimally small and the motion of the piston is controlled to be unlimitedly slow. In this ideal situation any change or process of heat transfer along with any mechanical work upon the gas by the piston can be regarded as reversible, i.e., the direction of the process can be changed in either direction, by compression or expansion. Any gadgets which might be employed during the course of the process are assumed to be brought back to the original condition at the end of the process. Any process designed in this way is called a quasistatic process or a *reversible process* in which the system maintains an equilibrium condition at any stage of the process.

In this way the thermodynamic system, a sample of gas in this case, can make some finite change from an initial state P_1 to a final state P_2 by a succession of quasistatic processes. In the following we often state that a thermodynamic system undergoes a finite change from the initial state P_1 to the final state P_2 by reversible processes.

1.6 The first law of thermodynamics

Let us consider a situation in which a macroscopic system has changed state from one equilibrium state P_1 to another equilibrium state P_2, after undergoing a succession of reversible processes. Here the processes mean that a quantity of heat energy Q has cumulatively been absorbed by the system and an amount of mechanical work W has cumulatively been performed upon the system during these changes.

The first law of thermodynamics *There would be many different ways or routes to bring the system from state P_1 to the state P_2; however, it turns out that the sum*

$$W + Q \tag{1.33}$$

is independent of the ways or the routes as long as the two states P_1 and P_2 are fixed, even though the quantities W and Q may vary individually depending upon the different routes.

This is the fact which has been experimentally confirmed and constitutes the first law of thermodynamics. In (1.33) the quantities W and Q must be measured in the same units.

Consider, now, the case in which P_1 and P_2 are very close to each other and both W and Q are very small. Let these values be $\mathrm{d}'W$ and $\mathrm{d}'Q$. According to the first law of thermodynamics, the sum, $\mathrm{d}'W + \mathrm{d}'Q$, is independent of the path and depends only on the initial and final states, and hence is expressed as the difference of the values of a quantity called the *internal energy*, denoted by U, determined by the physical, or thermodynamic, state of the system, i.e.,

$$\mathrm{d}U = U_2 - U_1 = \mathrm{d}'W + \mathrm{d}'Q. \tag{1.34}$$

Mathematically speaking, $\mathrm{d}'W$ and $\mathrm{d}'Q$ are not *exact differentials* of state functions since both $\mathrm{d}'W$ and $\mathrm{d}'Q$ depend upon the path; however, the sum, $\mathrm{d}'W + \mathrm{d}'Q$, is an exact differential of the state function U. This is the reason for using primes on those quantities. More discussions on the exact differential follow later in this chapter.

1.7 The heat capacity

We will consider one of the thermodynamical properties of a physical system, the *heat capacity*. The heat capacity is defined as the amount of heat which must be given to the system in order to raise its temperature by one degree. The *specific heat* is the heat capacity per unit mass or per mole of the substance.

From the first law of thermodynamics, the amount of heat $\mathrm{d}'Q$ is given by

$$\mathrm{d}'Q = \mathrm{d}U - \mathrm{d}'W = \mathrm{d}U + p\mathrm{d}V, \qquad \mathrm{d}'W = -p\mathrm{d}V. \tag{1.35}$$

These equations are not yet sufficient to find the heat capacity, unless $\mathrm{d}U$ and $\mathrm{d}V$ are given in terms of $\mathrm{d}\Theta$, the change in ideal gas temperature. In order to find these relations, it should be noted that the thermodynamic state of a single-phase system is defined only when two variables are fixed. The relationship between U and Θ is provided by the *caloric equation of state*

$$U = U(\Theta, V), \tag{1.36}$$

and there is a thermal equation of state determining the relationship between p, V, and Θ:

$$p = p(\Theta, V). \tag{1.37}$$

In the above relations, we have chosen Θ and V as the independent variables to specify the thermodynamic state of the system. We could have equally chosen other sets, such as (Θ, p) or (p, V). Which of the sets is chosen depends upon the situation, and discussions of the most convenient set will be given in Chapter 2.

Let us choose the set (Θ, V) for the moment; then, one finds that

$$\mathrm{d}U = \left(\frac{\partial U}{\partial \Theta}\right)_V \mathrm{d}\Theta + \left(\frac{\partial U}{\partial V}\right)_\Theta \mathrm{d}V, \tag{1.38}$$

$$\mathrm{d}'Q = \left(\frac{\partial U}{\partial \Theta}\right)_V \mathrm{d}\Theta + \left[\left(\frac{\partial U}{\partial V}\right)_\Theta + p\right] \mathrm{d}V, \tag{1.39}$$

and the heat capacity, C, is given by

$$C = \left(\frac{\partial U}{\partial \Theta}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_\Theta + p\right]\left(\frac{\mathrm{d}V}{\mathrm{d}\Theta}\right)_{\text{process}}. \tag{1.40}$$

The notation $(\mathrm{d}V/\mathrm{d}\Theta)_{\text{process}}$ means that the quantity is not just a function only of Θ, and the process must be specified.

The *heat capacity at constant volume* (*isochoric*), C_V, is found by setting $\mathrm{d}V = 0$, i.e.,

$$C_V = \left(\frac{\partial U}{\partial \Theta}\right)_V. \tag{1.41}$$

The heat capacity for an arbitrary process is expressed as

$$C = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_\Theta + p\right]\left(\frac{\mathrm{d}V}{\mathrm{d}\Theta}\right)_{\text{process}}. \tag{1.42}$$

The *heat capacity at constant pressure* (*isobaric*), C_p, is given by

$$C_p = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_\Theta + p\right]\left(\frac{\partial V}{\partial \Theta}\right)_p, \tag{1.43}$$

where $(\partial V/\partial \Theta)_p$ is found from the thermal equation of state, and $(\partial U/\partial V)_\Theta$ is from the caloric equation of state. This quantity may be rewritten as

$$\left(\frac{\partial U}{\partial V}\right)_\Theta = \frac{C_p - C_V}{\left(\frac{\partial V}{\partial \Theta}\right)_p} - p. \tag{1.44}$$

The denominator is expressed in terms of the volume expansivity, β, i.e.,

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial \Theta}\right)_p, \tag{1.45}$$

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and then

$$\left(\frac{\partial U}{\partial V}\right)_\Theta = \frac{C_p - C_V}{\beta V} - p. \tag{1.46}$$

This equation expresses the volume dependence of the internal energy in terms of C_p, C_V, and β.

For many real gases, if the experimentally measured values of C_p, C_V, and β are introduced into the above equation, the right hand side becomes vanishingly small, especially if the state of the gas is sufficiently removed from the saturation point; an experimental fact which led to the definition of a classical ideal gas.

Definition *The thermal and caloric equations of state for the classical ideal gas are defined, respectively, by*

$$p = p(\Theta, V) = \frac{nR\Theta}{V}, \qquad U = U(\Theta), \tag{1.47}$$

where n is the quantity of the gas measured in the number of moles of the gas and R is a constant.

It is worthwhile noting the fact that the definition of a mole can be given within the framework of thermodynamics, i.e., the amount of the gas is adjusted in such a way that the quantity pV/Θ becomes equal for all gases. Thermodynamics is a macroscopic physics, and hence the formulation of thermodynamics can be developed without taking any atomic structure of the working system into consideration.

One important property of the classical ideal gas follows immediately from the above definition of the equations of state and (1.46):

$$\left(\frac{\partial U}{\partial V}\right)_\Theta = 0, \quad C_p = C_V + \beta p V = C_V + nR. \tag{1.48}$$

1.8 The isothermal and adiabatic processes

Let us now discuss some other properties of the ideal gas. There are two commonly employed processes in the formulation of thermodynamics.

One is the *isothermal process*. In this process, the physical system, such as an ideal gas, is brought into thermal contact with a heat reservoir of temperature Θ, and all the processes are performed at constant temperature. For an ideal gas,

$$pV = \text{constant}, \quad \mathrm{d}\Theta = 0. \tag{1.49}$$

The lines drawn in the $p - V$ plane are called the *isotherms*.