

► 普通高等学校双语教学规划教材 ◀

Thermodynamics and Statistical Physics



主编 朱婧晶



西安电子科技大学出版社
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内 容 简 介

本书包含热力学和统计物理学两部分内容。全书共七章,分别是热力学的基本规律、均匀物质的热力学性质、相变、化学反应平衡和热力学第三定律、近独立粒子的最概然分布、玻尔兹曼统计、系综理论。

本书可作为大学物理专业的教材和相关专业参考书,也可以作为介绍现代热力学和统计物理学的科普书,还可作为一本内容丰富的科技英语阅读参考书。

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前 言

宏观物体是由大量的微观粒子(分子或其他粒子)组成的,这些微观粒子永不停歇地进行着无规则运动,大量微观粒子的无规则运动称作物质的热运动。热运动有其自身固有的规律,它的存在必然影响到物质的宏观性质,如热学性质、力学性质、聚集状态、电磁性质、化学反应的方向和限度等。热运动也必然影响到宏观物质系统的演化。

热力学与统计物理学的任务是研究热运动规律,以及宏观物质的物理性质和演化规律。热力学是热运动的宏观理论,而统计物理学是热运动的微观理论。读者需要具备经典力学和量子力学的知识,并且应该在经典力学和量子力学课程中学习过这些知识。热力学与统计物理学是理工类大学的一门重要的基础课程,是大学物理课程的重要组成部分。由于科学知识在不断增加,学生必须学习更多的内容,但是教学课时却在持续减少;目前出版的教材虽然很厚,却不能详细地阐述每一部分。为了解决这些矛盾,编者编写了本书。

热力学与统计物理学包含了大量的定义、定理和公式,会使读者感到枯燥乏味,因此编者为了增加本书的趣味性而介绍了一些与日常生活有关的现象。这些熟悉的事物可以激发读者的学习兴趣,提高他们的学习积极性。

由于编者水平和时间有限,书中不足之处在所难免,恳请广大读者理解并提出宝贵建议。

编 者
2017 年 12 月

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Chapter 1 The Basic Law of Thermodynamics

§ 1.1 Equilibrium state and description of thermodynamic system

The research object of thermodynamics is composed of a large number of microscopic particles (molecules or other particles), which is called thermodynamic system. The other objects which interact with the system are called surroundings. The concept of a thermodynamic system requires further specification. According to the interaction of system and surroundings, the system can be categorized into three types:

1. Isolated systems

These systems do not interact with the surroundings in any way. The container has to be impermeable to any form of energy or matter. Especially, for such a system, the total energy E is a conserved quantity, and can thus be used to characterize the macrostate. The particle number N and the volume V are conserved quantities, and can also be used to characterize the macrostate. Q represents the heat, W represents the work. Use an ideal gas system for example, which is shown in Figure 1.1.1.

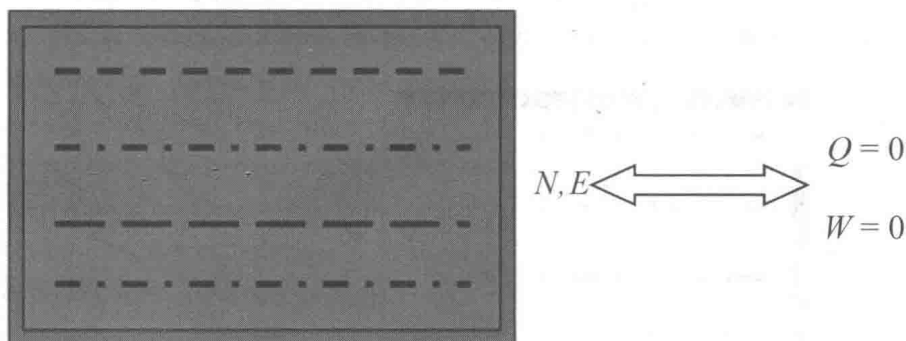


Figure 1.1.1

2. Closed systems

These systems allow only one for the exchange of energy with the surroundings, but not for the exchange of matter. Thus, the energy E is no longer a conserved quantity. Because of the energy exchange with the surroundings, the actual energy E of the system will fluctuate. However, if the closed system is in equilibrium with its surroundings, the energy will assume an average value which is related to the temperature of the system or the surroundings. The system does not exchange matter with its surroundings, so the total particle number N is a conserved quantity. We can use the temperature T , in addition to N and V , to characterize the macrostate. Use an ideal gas system for example, which is shown in Figure 1.1.2.

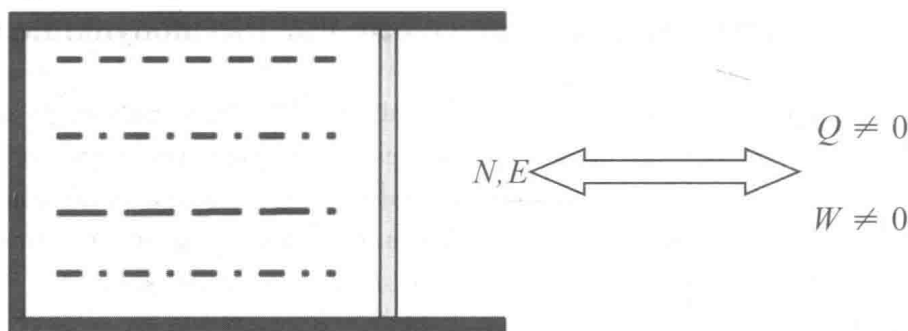


Figure 1.1.2

3. Open systems

These systems can exchange both energy and matter with their surroundings. Hence, both the energy E and the particle number N are not conserved quantities. If the open system is in equilibrium with its surroundings, the values of the energy E and the particle number of the system N are assumed to be related to the temperature and the chemical potential. We can only use the temperature T and the chemical potential μ to characterize the macrostate. Use an ideal gas system for example, which is shown in Figure 1.1.3.

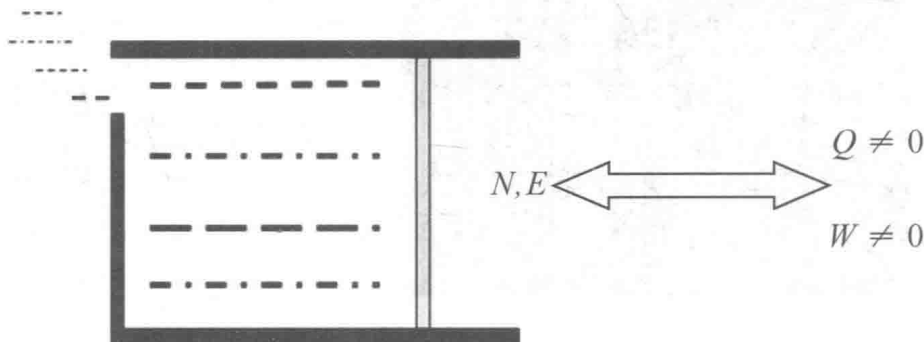


Figure 1.1.3

In fact, the isolated system is an ideal system. Because for a real system, the exchange of energy and matter with the surroundings cannot be prevented in the strict sense. However, the isolated system can be approximately realized by means of well-isolated vessels.

Thermodynamic equilibrium state is defined as follow: an isolated system will attain, after a sufficiently long period of time. And the macroscopic state quantities will no longer change with time, such as volume V , energy E and particle number N .

The time which characterizes the approach to equilibrium state is called the relaxation time. Relaxation time can be as short as a few microseconds, or as long as several millennia.

If the properties of a system are the same for any parts of the system, we call such a system homogeneous. However, the system is heterogeneous if the properties change discontinuously at certain marginal surfaces. The homogeneous parts of a heterogeneous system are called phases, and the separating surfaces are called phase boundaries. A typical example for such a system is a closed container which contains water, steam and air. In this case, the surface of the water is the phase boundary. One speaks of a gaseous phase (steam and air) and another speaks of a liquid phase (water). If the closed pot contains water, steam, ice and air, the system has three phases. One speaks of a gaseous phase (steam and air), one speaks of a liquid phase (water) and a solid phase (ice). In some cases, the macroscopic properties of a system depend on the size and shape of the phase boundaries.

The macroscopic parameters which describe a system are called state parameters. Besides 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 also include the charge, the electric field intensity, the electric polarization intensity, the magnetic induction intensity, the magnetization, the dipole momentum, the refractive index, the viscosity, the chemical composition, the size of phase boundaries, and so on.

Roughly speaking, these parameters are of two classes:

1) Extensive (additive) state parameters

These parameters are proportional to the amount of matter in a system, for example, to the particle number or mass. In other words, these parameters which are proportional to the size of the system are called extensive state parameters. Specific examples of extensive quantities are the volume and the energy. In particular, an extensive state parameter of a heterogeneous system is additively composed of the corresponding extensive properties of the single phase. For example, the volume of a container which contains water, steam and air is the sum of the volumes of the liquid and gaseous phases.

2) Intensive state parameters

These parameters are independent of the amount of matters and not additive for the particular phases of a system. The intensive state parameters are independent of the size of the system. It is not necessary to assume different values in different phases. Examples of intensive quantities are the refractive index, the density, the pressure, the temperature, and so on. Typically, intensive state parameters can be defined locally, i. e. they may be spatially. For example, the density of the atmosphere, which is the largest at the surface of the earth and continuously decreases with the increase of altitude, or the water pressure in an ocean, increases with the increasing depth.

More precisely, we can characterize those two classes of parameters by considering a homogeneous system in equilibrium and imaging the system being divided into two parts. Suppose that A macroscopic parameter x which characterizes the whole system assumes the values x_1 and x_2 for the two resulting subsystems. Then,

a. the parameter x is extensive if

$$x = x_1 + x_2 \quad (1.1.1)$$

b. the parameter x is intensive if

$$x = x_1 = x_2 \quad (1.1.2)$$

For example, the volume V and the total mass M of a system are extensive state parameters, the density ρ ($\rho = M/V$) of a system is an intensive state parameter. Indeed, it is obvious that the ratio of any two extensive state parameters is an intensive state parameter.

The last we mention the thermodynamic unit; in the international system of unit, the unit of the length is meter (m), the unit of the volume is cubic meter (m^3), the unit of the force is Newton (N). The pressure p due to gas (or in fact any fluid) is defined as the ratio of the perpendicular contact force to the area of contact. So the unit of force (N) divided by that of area (m^2) is called the Pascal (Pa). The almost equivalent atmosphere (atm) is also used to measure the pressure. The relationships are:

$$1\text{N} = 1\text{kg} \cdot \text{m} \cdot \text{s}^{-2}$$

$$1\text{Pa} = 1\text{N} \cdot \text{m}^{-2}$$

$$1\text{atm} = 1.01325 \times 10^5 \text{Pa}$$

§ 1.2 Thermal equilibrium and temperature—the zeroth law of thermodynamics

Temperature is simply a measure of “hotness” or “coldness” of object, so we can say that a cold object has a lower temperature than a hot one. Temperature is a state quantity

which is specially introduced into the thermodynamics.

Let us consider what will happen if a hot body and a cold body are placed in adiabatic contact and diathermic contact (which is also called thermal contact). Adiabatic contact means that the two bodies are unable to exchange energy, and diathermic contact means that they are able to exchange energy, which are shown in Figure 1.2.1 and Figure 1.2.2. We only discuss the bodies which are in thermal contact. Being in thermal contact after some time, the macroscopic properties of the bodies no longer change with time. Then, the bodies are said to be in thermal equilibrium. Here, the thermal equilibrium is defined as the temperatures, and the energy content of the bodies will no longer change with time. We can also say that the condition for thermal equilibrium between these bodies is the equality of temperature. As experiment has shown, if all bodies are in thermal equilibrium with each other, we could say that their temperatures are also the same. We also call it the zeroth law of thermodynamics.

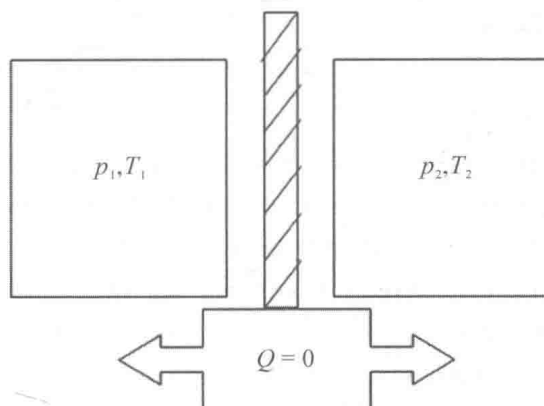


Figure 1.2.1

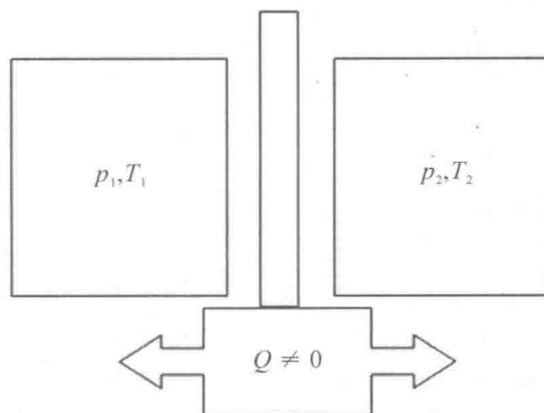


Figure 1.2.2

Two statement of the zeroth law of thermodynamics

Statement one: if each of two systems is in thermal equilibrium with a third, then they are also in thermal equilibrium with each other.

Statement two: two systems, each separately in thermal equilibrium with a third, are in equilibrium with each other.

The zeroth law of thermodynamics has been shown in Figure 1. 2. 3.

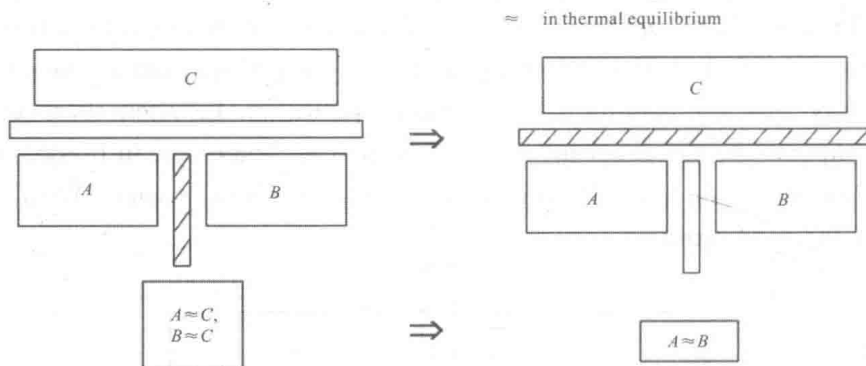


Figure 1. 2. 3

The zeroth law of thermodynamics implies that the systems which are in thermal equilibrium have a common intensive property with each other, and we shall call it temperature T . Therefore, the systems which are not in thermal equilibrium with each other have different temperatures. The zeroth law gives us some ways for how to actually measure temperature: a system whose temperature need to be measured is placed in thermal contact with a second system whose thermal equilibrium state is connected with a well-known state quantity which depends on temperature, then the two systems come into thermal equilibrium after some time. The second system is called a thermometer. The state quantity to be observed can be, for example, the volume of a fluid (fluid thermometer) or the volume of a gas (gas thermometer).

§ 1.3 Equation of state

If the macroscopic observable properties of a system have fixed, definite values, independent of “how they get there”, we say the system is in an equilibrium state. These properties are called functions of state (sometimes called variables of state). These functions of state are any physical quantities which have well-defined values for each equilibrium state of the system. Thus, these functions of state have no time dependence in

thermal equilibrium. Examples are volume, pressure, temperature and internal energy. And we will introduce a lot more in what follows. These functions of state are extensive (proportional to system size), e. g. energy, volume, magnetization and mass, or intensive (independent of system size), e. g. temperature, pressure, magnetic field, density and energy density. In general, one can find an equation of state that connects functions of state; for an easy system, this takes the form $f(p, V, T) = 0$. Before introducing the equation of state, we will introduce some additional ideas.

(1) Coefficient of volume expansion α .

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad (1.3.1)$$

(2) Pressure coefficient β .

$$\beta = \frac{1}{p} \left(\frac{\partial p}{\partial T} \right)_V \quad (1.3.2)$$

(3) Isothermal coefficient of compressibility κ_T .

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \quad (1.3.3)$$

(4) Partial derivatives.

Consider x as a function of two variables y and z . This can be written as $x = x(y, z)$, then we have that

$$dx = \left(\frac{\partial x}{\partial y} \right)_z dy + \left(\frac{\partial x}{\partial z} \right)_y dz \quad (1.3.4)$$

But rearranging $x = x(y, z)$ can lead to having z as a function of x and y , so that $z = z(x, y)$, in which case

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy \quad (1.3.5)$$

Substituting equation (1.3.5) into equation (1.3.4) gives

$$dx = \left(\frac{\partial x}{\partial z} \right)_y \left(\frac{\partial z}{\partial x} \right)_y dx + \left[\left(\frac{\partial x}{\partial y} \right)_z + \left(\frac{\partial x}{\partial z} \right)_y \left(\frac{\partial z}{\partial y} \right)_x \right] dy \quad (1.3.6)$$

The terms multiplying dx give the reciprocal theorem

$$\left(\frac{\partial x}{\partial z} \right)_y = \frac{1}{\left(\frac{\partial z}{\partial x} \right)_y} \quad (1.3.7)$$

and the terms multiplying dy give the reciprocal theorem

$$\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial x} \right)_y = -1 \quad (1.3.8)$$

For easy system, p , V and T are the function of $f(p, V, T) = 0$, so that

$$\left(\frac{\partial V}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial T}{\partial V} \right)_p = -1 \quad (1.3.9)$$

Thus, coefficient of volume expansion α , pressure coefficient β and isothermal coefficient of compressibility κ_T satisfy the following relationship

$$\alpha = \kappa_T \beta p \quad (1.3.10)$$

1. The equation of state for the ideal gas

A lot of experiments on gases show that the pressure p and the volume V of a gas system depend on its temperature T . For example, a fixed amount of gas at constant temperature T obeys

$$p \propto \frac{1}{V} \quad (1.3.11)$$

The result is known as Boyle's law (sometimes as the Boyle-Mariotte law). It was discovered experimentally by Robert Boyle (1627—1691) in 1662 and independently by Edmé Mariotte (1620—1684) in 1676.

At constant pressure p , the gas system also obeys

$$V \propto T \quad (1.3.12)$$

where the temperature T is the measure in Kelvin. This was discovered experimentally, in a crude fashion, by Jacques Charles (1746—1823) in 1787, so it is known as Charles' law. The law was more completed by Joseph Louis Gay-Lussac (1778—1850) in 1802, though their work was partly anticipated by Guillaume Amontons (1663—1705) in 1699, who also noticed that a fixed amount of gas at constant volume V obeys

$$p \propto T \quad (1.3.13)$$

The result which was found by Gay-Lussac himself independently in 1809 is often known as Gay-Lussac's law.

These three empirical laws can be combined to give

$$pV \propto T \quad (1.3.14)$$

It turns out that, if there are N molecules in the gas, we can express this founding as follows:

$$pV = NkT \quad (1.3.15)$$

This is known as the ideal gas equation. The constant k ($k = 1.3807 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$) is known as the Boltzmann constant. Another form of the ideal gas equation for a fixed system which has n ($n = \frac{N}{N_A}$) moles particles is

$$pV = nRT \quad (1.3.16)$$

Where T is the temperature in degrees Kelvin, p is the pressure in Pascal, V is the volume in cubic meters. The constant $N_A = 6.02252 \times 10^{23} \text{ mol}^{-1}$ is called Avogadro's number and the constant $R = N_A k = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ is named the gas constant. However, the ideal gas equation is valid only for dilute gases (at low pressure).

If there are m different types of particles in the gas, then the ideal gas law takes the form

$$pV = \sum_{i=1}^m n_i RT \quad (1.3.17)$$

where n_i is the number of moles of the i th constituent.

The virial expansion,

$$p = \left(\frac{nRT}{V} \right) \left[1 + \frac{n}{V} B_2(T) + \left(\frac{n}{V} \right)^2 B_3(T) + \dots \right] \quad (1.3.18)$$

expresses the equation of state of a gas as a density expansion. The quantities $B_2(T)$ and $B_3(T)$ are called the second and the third virial coefficients. They are functions of temperature T only.

2. The equation of state for a real gas

The most commonly used model of real gas behavior is the van der Waals gas. The van der Waals equation of state is the first equation of state which applies to both the gas and liquid phases and exhibits a phase transition, so it is of immense importance historically. It contains most of the important qualitative feature of the gas and liquid phases, although it becomes less accurate as density increases. The van der Waals equation takes into account the form of the interaction between real particles, which contains corrections to the ideal gas equation of state. The interaction potential between molecules in a gas system contains a strong repulsive core and a weaker attractive region surrounding the repulsive core. So the equation of state for a van der Waals gas is

$$\left(p + \frac{an^2}{V^2} \right) (V - nb) = nRT \quad (1.3.19)$$

where n is the number of moles. In this equation, the constant a parameterizes the strength of the intermolecular interactions, and the constant b accounts for the volume excluded owing to the finite size of molecules. If a and b are both set to zero, we can recover the equation of state for an ideal gas, $pV = nRT$. In Table 1.3.1, we have given values of a and b for some simple gases.

Table 1.3.1 van der Waals constants for some simple gases

Gas	$a/(\text{Pa} \cdot \text{m}^6 \cdot \text{mol}^{-1})$	$b/(10^{-3} \cdot \text{m}^3 \cdot \text{mol}^{-1})$
H ₂	0.02476	0.02661
He	0.003456	0.02370
CO ₂	0.3639	0.04267
H ₂ O	0.5535	0.03049
O ₂	0.1378	0.03183
N ₂	0.1408	0.03913

§ 1.4 Work

Quasi static process refers to the sum of all the state that the system changes from one equilibrium state to another. The process is the result of the system balance being destroyed. If the system continuously changes from an equilibrium state to another equilibrium state after innumerable middle equilibrium states, that is, the system can deviate from the equilibrium states infinitesimally and restore balance at any time in the process which has no mutation, and changes slowly and evenly, we call it quasi equilibrium or quasi static process.

The work of ideal gas during any quasi static state will be discussed in this section. When a system does work itself, or a system has work done on it, there is a flow of energy either out or into of the system. This will lead to a change in one or more of the thermodynamics parameters of the system and will cause a change in the state of the system, so will cause a change in the work (W), done on or by the system, too.

Let us consider the important case of a fluid (a substance which is either a gas or a liquid) system and derive an expression for the work done on this fluid system in a quasi static process. In Figure 1.4.1, the fluid (a substance which is either a gas or a liquid) is filled in a container with a piston, the area of the piston is A , the volume of the container is V , and the pressure on the piston is p . When the piston moves a distance dx in the quasi static process, the work done on the system is $dW = pAdx$. Considering $dV = -Adx$, the work can be written as

$$dW = -pdV \quad (1.4.1)$$

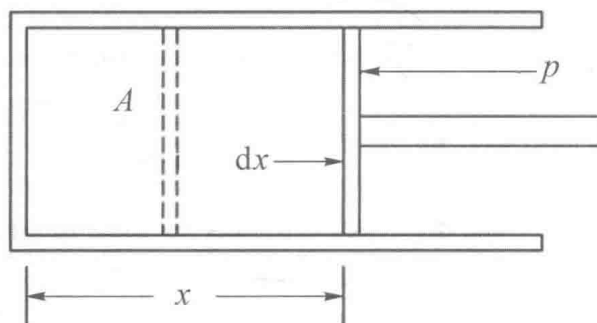


Figure 1.4.1

In equation(1.4.1), the negative sign ensures that the work dW done on the system is positive when dV is negative, for example, when the fluid is being compressed. If the volume of the fluid is changed quasi-statically from some initial volume V_A to some final

volume V_B , its pressure p at any stage of the quasi static process will be some function of its volume and temperature. The total work W done on the fluid in this process is then simply obtained by adding all the infinitesimal works. That is,

$$W = - \int_{V_A}^{V_B} p dV \quad (1.4.2)$$

The work W done on the fluid is positive if $V_B < V_A$, and is negative if $V_B > V_A$.

The magnitude of the equation (1.4.2) can be discussed in the p - V diagram, e. g. in Figure 1.4.2. By virtue of equation (1.4.1), its magnitude is equal to the shade area in Figure 1.4.2. The area under the curve of Figure 1.4.2 represents the work done on the system when its volume is changed quasi-statically from V_A to V_B .

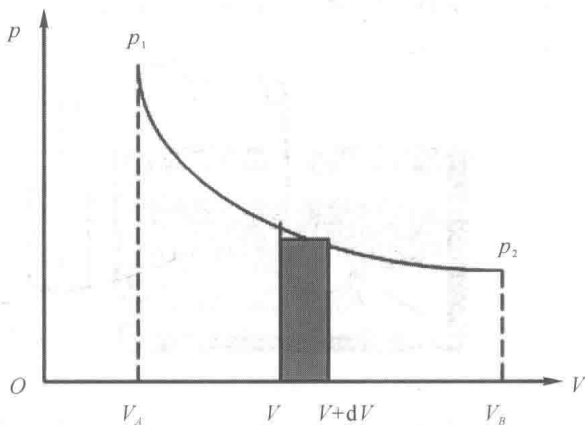


Figure 1.4.2

The work done on the system in two important special processes will be discussed, which are constant volume process and constant pressure process. In the constant volume process, the volume of the system is constant in the total process, so the work done on the system is zero, $W = 0$. In the constant pressure process, the pressure of the surroundings is constant in the total process, when the volume of the system changed from some initial volume V_A to some final volume V_B , the work done on system is

$$W = - p(V_B - V_A) = - p\Delta V \quad (1.4.3)$$

§ 1.5 The first law of thermodynamics

The expression of work is discussed in the previous section. Work is a way of transmitting energy between the system and its surroundings in the process. When the system and external energy transfer through the form of work, the external parameter system must change. In addition to work, the system and the outside can also pass through the energy exchange. In the case of heat exchange, the external parameters of the system are not changed, and the energy is transmitted by the collision of the molecules on the contact surface and the heat radiation.

First, we consider the energy transfer and transformation in the adiabatic process. Adiabatic process is the process of heat exchange between the system and the outside world. Figure 1.5.1 and Figure 1.5.2 is the schematic diagram of the two adiabatic