

Chapter 1

Heat and the First Law

1.1 The Scope of Thermodynamics

Thermodynamics, a branch of science based on the the observations and studies of many scientists over the past three hundred or so years, can be summarized in a few principles and laws (notably the three well-known thermodynamic laws). These laws govern the behavior and the relationships between the thermodynamic state variables of any macroscopic thermodynamic system. Among all the state variables, the most important one is *temperature*. Temperature is defined and derived in thermodynamics. Its nature is quite unique and rather different from other basic physical quantities, such as mass, time, length, electric charge, etc., which are defined in other branches of physics, such as mechanics, electricity and magnetism, etc. We may say that, in general, any phenomenon or theory which involves the physical quantity of temperature belongs to the subject of thermodynamics or its applications. However, the three well-known laws of thermodynamics govern only the thermodynamic behavior in equilibrium states. There are many more, and much more complex phenomena in nature which belong to the category of non-equilibrium thermodynamics. Except for a few sections, this book is confined in the study of equilibrium thermodynamics. Non-equilibrium thermodynamics is beyond its scope.

Any physical system on the earth is not only surrounded by the atmosphere, but also is constantly interacting with its surroundings. The study of the behavior of all these interacting systems belongs to the subject of thermodynamics or its applications. The reason is that the

atmosphere is actually a huge macroscopic thermodynamic system; any system in contact with it will have thermodynamic properties. All material systems are composed of atoms; therefore we begin with the simplest system, an atom, to see what thermodynamic properties we can explore. If we put *an atom* in the atmosphere, the atom will be affected by the atmosphere in the following two ways: (1) the motion of the atom as a whole, and (2) the internal structure of the atom. The atmosphere is composed of many molecules and atoms. The *added atom* will become part of the atmosphere, therefore its motion as a whole (the translational motion) will be affected by the atmosphere. This is because the behavior of the atom is influenced by the thermodynamic properties of the atmosphere. However the internal structure of the atom (the orbital electrons) will not be affected. The reason is that the energy gap between the ground state and the first excited state of the orbital electrons is at least several electron volts (eV), while the thermal energy at room temperature is just around 0.025 eV. The orbital electrons will therefore remain in the ground state, unaffected by the atmosphere. This is the reason why, in the study of the electronic structure of an atom, the temperature effect is usually not considered.

In thermodynamics, we often consider an atom, as one of the particles in the atmosphere, a particle without internal structure, but we may also consider an atom as a system (albeit a small system) which is surrounded by the atmosphere (a big system). Now we consider the case where the small system is composed of two atoms (a diatomic molecule). There is not much difference as compared with the case that the small system is a monatomic molecule. The motion of the small system as a whole (translation and rotation) will be affected by the atmosphere,¹ yet the internal structure of the small system is not affected by the atmosphere. It is known that when two atoms attract each other to become a single molecule, each original energy level will be split into two levels, thus the energy gaps will become smaller. However, the energy gap to the first excited state is still on the order of a few eV, which is much greater than the room temperature energy. The orbital electrons will therefore remain in the ground state. In addition to the energy levels of the orbital electrons, the internal structure of a diatomic molecule also includes the relative motion of the two atoms (vibration), but the energy required to

¹According to quantum mechanics, rotational energy is quantized, however the energy required to excite the rotational motion of a diatomic molecule is usually much smaller than the room temperature thermal energy. Therefore the classical concepts and methods may be used.

excite the vibrational motion is much more than the room temperature energy,² therefore we may say that vibrational motion is also not affected by the atmosphere.

However when the number of atoms in the small system is increased to several hundred or more, the situation will be changed significantly. In such a case the mass of the system is much larger than that of a single atom; the motion of the system as a whole is mainly determined by the gravitational force, and therefore its role in thermodynamic properties becomes insignificant. On the other hand, the internal structure now plays the major role in its thermodynamic properties. The energy required to excite the vibrational motion is now decreased to the order of the room temperature thermal energy. Moreover in some materials, the energy required to excite the orbital electrons is also gradually reduced to be close to the room temperature energy. Yet this is still a small system. The vibrational energy levels and the energy levels of the orbital electrons will be changed as the number of the atoms of the system increases, or the geometrical arrangement of the atoms in the system changes. Only when the system contains a very large number of atoms, which are arranged in a normal way (e.g., not in a reduced dimension), will the thermodynamic properties of the system not depend on the number of its atoms, or on the geometrical arrangement of the atoms.

In view of the fact that the thermodynamic properties of a system may depend on the number of atoms in it, we may classify thermodynamic systems, *according to the size of the system*, into the following three classes:

1. A **microscopic system**: the number of atoms in the system is small, so that its internal structure is independent of temperature.

2. A **mesoscopic system**: the number of atoms in the system is much more than that of a microscopic system, but not large enough that the thermodynamic properties of its internal structure depend on the number of the atoms and their geometrical arrangement.

3. A **macroscopic system**: the number of atoms in the system is very large, so that the thermodynamic properties of the system are

²According to quantum mechanics, vibrational energy is also quantized. The energy gap between the neighboring levels is equal to the Planck constant times the vibration frequency. The vibrational energy gap of almost of all diatomic molecules is much greater than the room temperature energy.

independent of the number of atoms or their geometrical arrangement.³

There are, however, no clear cut distinctions between these three classes of systems, and transition regimes do exist. Here we introduce a concept which is called the **thermodynamic limit**. We consider a thermodynamic system, and double both the number of its atoms and its volume (but keeping the density of the system constant). If the thermodynamic properties of the system remain unchanged, then we say that the system has reached the thermodynamic limit. It is therefore a macroscopic system. A mesoscopic system is not large enough to reach the thermodynamic limit.

According to the above analysis, we may roughly divide the study of equilibrium thermodynamics into two categories. One is to study systems consisting of a very large number of almost independent particles (atoms, molecules) which are confined in the same space (volume). Particle-particle collisions are the main mechanism with which the system maintains its thermodynamic equilibrium. During the collisions, particles exchange their translational and rotational energies, but the internal structures do not change. Between collisions, each particle may be considered as a free particle. We are familiar with this type of systems, they are known as gases. The other is to study systems consisting of a very large number of atoms (molecules) which attract one another strongly and are closely tied together, to become a type of *condensed matter*, in other words a liquid or a solid. In these systems, the main thermodynamic properties come from the relative motion between the particles (vibrations), rather than the translational and rotational motion of each particle. The behavior of the orbital electrons may also play an important role in its thermodynamic properties.

Classical thermodynamics does not look into the microscopic details of the system, and therefore has its limitations. During the latter part of the nineteenth century, scientists began to try to understand thermodynamics from the microscopic point of view. For gases, one may approximate that the only type of interaction that occurs between particles is the *hard core* collision. This theory, known as the **kinetic theory**

³If there are two systems composed of the same kind of atoms, but one is macroscopic and the other mesoscopic, then these two systems may have different thermodynamic properties, e.g., magnetic properties, non-equilibrium transport properties, etc. We are familiar with the macroscopic world, but our understanding of the mesoscopic systems is just in the beginning stages. Therefore the study of mesoscopic systems (notably nano-sized systems) is a new and important area. Research in this area may lead us to new and useful discoveries both in science and technology.

of gases, has been very successful in studying the properties of dilute classical gases. Using it, one can also calculate some of the transport coefficients in non-equilibrium thermodynamics, but this theory can not be generalized to study much more complex systems such as liquids and solids. The reason is that in condensed matter, the interactions between the particles are much more complicated than hard core collisions. The theory which successfully treats these complicated systems is called **statistical thermodynamics**, or **statistical mechanics**. In this branch of science, one does not look into the details of the motion of each particle. Instead, one uses the concepts and methods of statistics to treat the complex thermodynamic systems and to simplify the problems. Mean values of thermodynamic variables are taken to represent the thermodynamic properties of the system under consideration. If the condition of the thermodynamic limit is satisfied, the predictions of statistical mechanics (obtained using mean values) can be considered as precise, and the errors (fluctuations) are negligibly small.⁴

1.2 Some Definitions

Thermodynamics is a branch of science which studies the thermodynamic properties of thermodynamic systems. A thermodynamic *system* (for brevity, a system) together with its *surroundings* constitute the universe. There are three types of thermodynamic systems, *according to how the system interacts with its surroundings*:

1. An **open system**: the system can exchange energy and mass with its surroundings.
2. A **closed system**: the system can exchange energy with its surroundings, but not mass.
3. An **isolated system**: the system can exchange neither energy nor mass with its surroundings.

In this book we will confined ourselves, except for a few sections, to the study of equilibrium state thermodynamic properties. A system is said to be in an **equilibrium state** (for brevity, a **state**) if the thermo-

⁴In statistical mechanics, the root mean square fluctuations are usually proportional to the inverse of the square root of the number of particles of the system. The fluctuations are negligibly small if the number of particles of the system becomes very large.

dynamic properties of the system do not change with time.⁵ A physical quantity is said to be a **state variable** of the system, if the magnitude of the variable is fixed once the system reaches an equilibrium state. If two systems are identical, and they are in the same equilibrium state, then they will have the same value for every state variable. This implies that if the *state* of a system is specified, then all of the state variables of the system have definite values. Volume, pressure and temperature are known examples of state variables. There are two types of the state variables: **extensive** variables and **intensive** variables. In the same equilibrium state, the value of an extensive variable will be proportional to the size of the system,⁶ such as its volume or mass. On the other hand, the value of an intensive variable, such as temperature and pressure, is independent of the size of the system. When an extensive variable is divided by the volume (or mass, or number of kilomoles) of the system, it will become an intensive variable. In this book, if an intensive variable is derived from an extensive variable (e.g., by dividing by volume), then it will be denoted by a *lower case* letter. All the extensive variables are denoted by *upper case* letters. However, it should be noted that the two capital letters P (pressure) and T (temperature) are intensive variables. These two (because of historical reasons) are the only exceptions to the rule.

Bring two isolated systems, A and B, into contact with each other. If we now let the wall which separates A and B becomes thermally conducting (but fixed in position), then A and B can exchange energy (but not mass). A and B separately are no longer isolated, but A+B as a whole is an isolated system. In this situation, we say that A and B are in *thermal contact*. After a period of time, A and B will separately reach their own equilibrium states. When this happens, we say that A and B are in **thermal equilibrium**. If the wall between A and B can move freely (with no friction and no mass exchange) and a final equilibrium state is reached, then we say that A and B are in **thermodynamic equilibrium**. In the latter case, in addition to thermal equilibrium, there is also a mechanical (pressure) equilibrium. The individual volume of A and B may be changed, but the total volume of A+B does not change.

⁵It is also required that the system is not under the action of any external force or field.

⁶This statement is true for macroscopic systems only, but not for mesoscopic systems.

1.3 The Zeroth Law of Thermodynamics

The zeroth law of thermodynamics defines a state variable T called *temperature*. This means that when a system is in an equilibrium state then it has a definite value of T . The physical significance of T in thermodynamics can be understood from the following consideration.

Consider two *isolated* systems A and B which are in their own respective equilibrium states. Bring A and B together and let them to be in thermal contact with each other. Right after A and B make thermal contact, there are two possibilities:

1. A and B reach thermal equilibrium immediately. In this case we say that the temperature of A just before contact T_A and the temperature of B just before contact T_B are equal to each other, i.e., $T_A = T_B$. Also, after contact, both T_A and T_B remain unchanged. This means that when two isolated systems have an equal temperature, then their temperatures will remain unchanged when (and after) they are placed in thermal contact.
2. It takes a period of time for A and B to reach thermal equilibrium. This implies that before contact $T_A \neq T_B$. After thermal equilibrium is reached, the temperatures of A and B become T'_A and T'_B , respectively. Thermal equilibrium requires that $T'_A = T'_B$.

The zeroth law of thermodynamics can be stated as follows. Consider three isolated systems A, B and C, which are in their own respective equilibrium states with temperatures T_A , T_B and T_C , respectively. Place A and B in thermal contact. If A and B reach thermal equilibrium right after their contact, then $T_A = T_B$. Remove A from B, and place B and C in thermal contact. If B and C reach thermal equilibrium right after contact, then $T_B = T_C$. If the above situations occur, then one is certain that A and C have the same temperature, i.e., $T_A = T_C$. A and C will reach thermal equilibrium immediately if they are placed in thermal contact.

The above consideration and the zeroth law have the following implications. Consider two systems which are in their respective equilibrium states; place them in thermal contact. If the systems have the same temperature before contact, then after contact they will remain in their equilibrium states with the same temperature. If the systems have different temperatures before contact, then after contact, the systems will experience a period of non-equilibrium. The temperatures of the two

systems will eventually become equal to each other and the systems will reach their new respective equilibrium states. The temperature in the final equilibrium states will be different from the temperatures before contact. However if the size (such as the mass) of one of the systems is much larger than that of the other, then the temperature change of the large system will be very small, and can be neglected. The final temperature of the small system will be equal to that of the large system. An example of the above case is the use of a thermometer. The thermometer is the small system, which is used to measure the temperature of the large system.

Now we would like to introduce the concept of a heat reservoir. A **heat reservoir** is a very large system which makes thermal contact with much smaller systems. In the contact it can exchange thermal energy with the smaller systems, without changing its own temperature. A constant temperature process usually needs the help of a heat reservoir.

Finally, it may be helpful to give *temperature* a more precise physical meaning. We may say that temperature is a measure of the average energy per particle in a system due to the *random motions* of the particles. We will derive this result microscopically in Chapters 3, 9 and 11.

1.4 Equilibrium State

We have stated that if a system is in an equilibrium state then its thermodynamic properties will not change with time. The thermodynamic properties mean the behavior of the state variables of the system. The values of the state variables depend on the state of the system only, and are independent of the past history of the system. The most familiar state variables are *pressure*, *volume* (quantities defined in mechanics) and *temperature*. Temperature is a physical quantity defined in thermodynamics (not in other disciplines of physics), and therefore it may be considered as the most important state variable in thermodynamics. For magnetic systems, the main concern is the magnetic properties, therefore instead of pressure and volume, the basic state variables are the magnetic field, the magnetic moment (quantities defined in electromagnetism), and the temperature. Besides the above well-known state variables, we will introduce more state variables in the latter chapters and sections of this book. These additional state variables will be useful in studying thermodynamic properties under different situations.

For most of the thermodynamic systems we consider, if the values of *any two* of the state variables are fixed, then the values of all other state

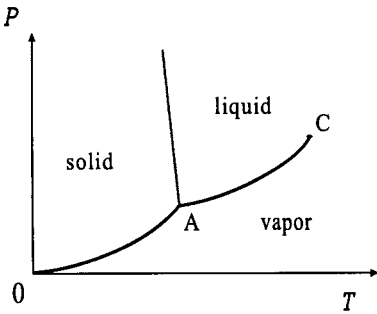


Figure 1.1: A sketched phase diagram of H_2O . A is the triple point; C is the critical point. Note that the slope of the solid-liquid coexistence curve is negative.

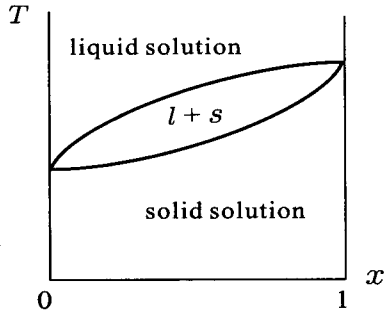


Figure 1.2: A sketched phase diagram (at a constant P) of the alloy A_{1-x}B_x , where x is the fraction of B by weight. The area labeled by $l + s$ is the liquid-solid coexistence region.

variables will also be fixed. This means that there are only two independent variables for most of the thermodynamic systems. For ordinary (non-magnetic) systems, the most frequently used variables are pressure P , volume V , and temperature T (known as PVT systems). However only two of them are independent, therefore there is a relation between P , V and T , which can be written as

$$f(P, V, T) = 0. \quad (1.1)$$

This is called the equation of state. The most well-known is the equation of state for an ideal gas $f(P, V, T) = PV - nRT$. In magnetic systems, the equation of state can be written as $f'(B, M, T) = 0$, where B and M are the magnetic field and the magnetic moment, respectively. We see that an equation of state always involves the state variable T . This is one of the reasons why we say that temperature plays quite a unique role in thermodynamics.

If we need two equations of state to describe two different states of the same system, then these two different states (denoted as states 1 and 2) belong to different *phases*. When the system changes from state 1 to state 2 (or vice versa), there will be a process of *phase transition*. For a phase transition to occur, the system must satisfy an additional phase equilibrium condition. Therefore the number of independent variables

will be reduced to one. If we plot the condition of phase equilibrium on a P - T diagram, it will take the shape of a curve which separates the two different phases. This is called a phase diagram, as shown in Fig. 1.1. If the system, however, is a mixture composed of two constituents, there will be one additional variable, which is the mole (or mass) fraction x of the second constituent. In this case, the phase diagram is usually plotted as a T - x diagram, at a constant P , as shown in Fig. 1.2. Different values of P will give different phase diagrams. The most useful and frequently used value of P is one atmospheric pressure.

1.5 The First Law of Thermodynamics

Before we state the first law of thermodynamics, we would like to introduce two important concepts: (1) the internal energy⁷ of the system U is a state variable; (2) heat is a form of energy, which is also called thermal energy.⁸

The first law can be stated as follows. When a system changes from an initial state to a final state, the change in its internal energy ΔU is equal to the heat it absorbs from the surroundings ΔQ minus the work done by the system ΔW . This can be expressed as

$$\Delta U = \Delta Q - \Delta W. \quad (1.2)$$

If the changes of both of the two independent variables are very small, then the changing process is called an *infinitesimal process*. In this case, the first law is written as

$$dU = dQ - dW, \quad (1.3)$$

where dU , dQ and dW indicate that in the process, the changes in the internal energy U , the heat absorbed Q , and the work done W are all very small quantities. From the above equations, we may say that the first law is just a statement of the conservation of energy. Here we should note that in Eq. (1.3) we use two different notations d and Δ to denote

⁷Internal energy is the sum of the kinetic and potential energy of all particles in the system, but excluding the kinetic energy for the system moving as a whole.

⁸The first scientist who expressed heat in terms of the units of energy was James Joule (1840). The latest data on the mechanical equivalent of heat is 1 cal=4.186 J. One calorie is the energy required to increase the temperature of 1 gram of water from 14.5°C to 15.5°C. James P. Joule, British physicist (1818–1889).

small quantities. The notation dU means that the internal energy U is a state variable. The function U exists if the state of the system is specified. Whereas dQ (or dW) implies that Q (or W) is not a state variable. This means that the function which represents Q (or W) does not exist. Therefore the value of ΔU in Eq. (1.2) depends only on the initial and the final states, but the value of ΔQ (or ΔW) will depend on the *process*, i.e., the path by which the system changes from the initial to the final state. In mathematics, we call dU an *exact* differential and dQ (or dW) an *inexact* differential.

1.6 Exact and Inexact Differentials

Consider a system with two independent variables x and y . An infinitesimal quantity dF can be expressed as

$$dF = a(x, y) dx + b(x, y) dy. \quad (1.4)$$

If dF is an exact differential, then the function $F = F(x, y)$ exists. From calculus we find

$$dF = \left(\frac{\partial F}{\partial x} \right)_y dx + \left(\frac{\partial F}{\partial y} \right)_x dy. \quad (1.5)$$

Therefore (by comparing Eq. (1.4) and (1.5)) we have

$$a(x, y) = \left(\frac{\partial F}{\partial x} \right)_y, \quad b(x, y) = \left(\frac{\partial F}{\partial y} \right)_x, \quad (1.6)$$

and

$$\left(\frac{\partial a}{\partial y} \right)_x = \left(\frac{\partial b}{\partial x} \right)_y. \quad (1.7)$$

Equation (1.7) is the necessary and sufficient condition for the infinitesimal quantity $dF = a(x, y)dx + b(x, y)dy$ to be an exact differential. In this case $F(x, y)$ is a well-defined function. But if the condition Eq. (1.7) is not satisfied, then the function $F(x, y)$ does not exist. In that case we rewrite dF as dF' and call it an inexact differential (for the convenience of discussion we replace F by F').

The main difference between an exact differential dF and an inexact differential dF' is the following. When the independent variables (x, y) change from the initial (x_1, y_1) to the final (x_2, y_2) , the change of F is

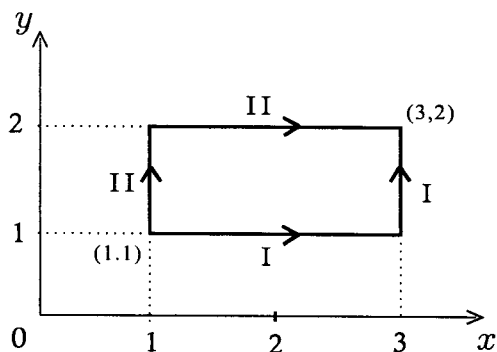


Figure 1.3: Two different integration paths.

a fixed value. It is simple to get $\Delta F = \int dF = F(x_2, y_2) - F(x_1, y_1)$, but the change of F' depends on the path, i.e., $\Delta F' = \int dF'$ depends on the path. A path is a curve that connects the initial point (x_1, y_1) and the final point (x_2, y_2) . Since $F'(x, y)$ does not exist, we can not write $\Delta F'$ as $\Delta F' = F'(x_2, y_2) - F'(x_1, y_1)$; $F'(x_1, y_1)$ and $F'(x_2, y_2)$ are not defined. We give a simple example in the following. If $dF = ydx + xdy$, then $a(x, y) = y$ and $b(x, y) = x$, therefore Eq. (1.7) is satisfied,

$$\left(\frac{\partial a}{\partial y}\right)_x = \left(\frac{\partial b}{\partial x}\right)_y = 1. \quad (1.8)$$

From calculus we easily get

$$dF = ydx + xdy = d(xy + c), \quad (1.9)$$

thus $F = xy + c$ (c is a constant). Therefore $\Delta F = \int dF = F(x_2, y_2) - F(x_1, y_1) = x_2y_2 - x_1y_1$, independent of the path. However if $dF' = ydx - xdy$, then $a(x, y) = y$ and $b(x, y) = -x$, therefore

$$\left(\frac{\partial a}{\partial y}\right)_x = 1, \quad \left(\frac{\partial b}{\partial x}\right)_y = -1, \quad (1.10)$$

Eq. (1.7) is not satisfied. The function $F'(x, y)$ does not exist and $\Delta F'$ will depend on the path. If we take $(x_1, y_1) = (1, 1)$ and $(x_2, y_2) = (3, 2)$, then $\Delta F = x_2y_2 - x_1y_1 = 5$ is a fixed value and independent of the path, but $\Delta F'$ will depend on the path. Consider path I in Fig. 1.3. We have

$\Delta F' = -1$. However if we take path II, we get $\Delta F' = 3$. Thus exact and inexact differentials have quite different properties, that should not be mixed up. An exact differential is the same as a differential in calculus, but an inexact differential is not a differential (as defined in calculus), it is just an infinitesimal quantity. In thermodynamics, both dQ and dW are inexact differentials, which mean that *heat* Q and *work* W are *not* state variables.

1.7 Work in Thermodynamics

In mechanics, work equals force times the displacement. In thermodynamics, work equals pressure times the volume change. We get this result because pressure is force divided by area, and the volume change is the displacement times the area. In an infinitesimal process, we can write

$$dW = PdV, \quad (1.11)$$

where P is the pressure and dV is the infinitesimal change of volume. The work defined by Eq. (1.11), is usually called **configuration work**. This type of work is the result due to a change of the configuration of the system (here the volume). The pressure P can be considered as a generalized force X , and the volume change dV a generalized displacement dY . The general form of a configuration work can be written as

$$dW_{\text{conf}} = XdY. \quad (1.12)$$

In thermodynamics, different systems may have different appearances for the configuration work. Some are listed in Table 1.1.

Table 1.1 Examples of configuration work

System	X (force)	Y (displacement)	dW
PVT system	P (pressure)	V (volume)	PdV
magnetic material	B (magnetic field)	M (magnetization)	$-BdM$
dielectric material	E (electric field)	\mathcal{P} (polarization)	$-Ed\mathcal{P}$
thin film	σ (surface tension)	A (area)	$-\sigma dA$
string	J (tension)	L (length)	$-JdL$

One of the main characteristics of configuration work is that it may be positive or negative. When the value of X makes an infinitesimal change (keeping the sign unchanged), it is possible that dY may change from positive to negative (or vice versa), thus dW_{conf} changes its sign. This means that the system can do work on its surroundings and the surroundings can also do work on the system. We call this *reversible work*. There is another type of work, which can do work in one direction only. We call this *irreversible work*. For example, the work done by a resistor is always on its surroundings (by producing heat). It is impossible, by an infinitesimal change (or by reversing the direction) of the current, to change the direction of the work (i.e., so that the resistor absorbs heat from the surroundings). This type of work is called *dissipative work*, because it can not be recovered. Any work produced by a frictional force is categorized as this type of work. The result of this type of work is to generate heat; it is not related to a change in the configuration of the system. It is therefore quite different from configuration work.

In the following, we use $dW = PdV$ as an example to explain the fact that work depends on the path. Consider a system which changes from state 1 (P_1, V_1) to state 2 (P_2, V_2); the work done by the system during the process is

$$\Delta W = \int_{V_1}^{V_2} PdV. \quad (1.13)$$

From calculus we know that ΔW is equal to an area in Fig. 1.4. The magnitude of the area depends on the shape of the curve connecting points 1 and 2. The connecting curve is the *path* mentioned above. In the figure, we plot two paths, I and II. It is obvious that the magnitude of $\Delta W_{\text{II}} - \Delta W_{\text{I}}$ equals the area enclosed by the paths I and II. Except for when there are two identical paths, the enclosed area will not be equal to zero. Therefore ΔW depends on the path.

1.8 Enthalpy

In a constant pressure process (*isobaric process*), if the volume changes from V_1 to V_2 , the work done by the system is $\Delta W = P(V_2 - V_1)$. In this case the first law can be written as

$$\Delta U = \Delta Q_P - P(V_2 - V_1), \quad (1.14)$$

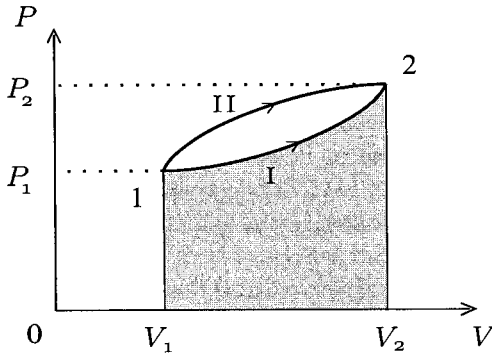


Figure 1.4: Work depends on the path. The difference between the work done along paths I and II is equal to the area (in white) enclosed by the paths I and II.

where ΔQ_P means that heat is absorbed in a constant P process. Since $\Delta U = U_2 - U_1$, Eq. (1.14) can be written as

$$\Delta H = H_2 - H_1 = \Delta Q_P, \quad (1.15)$$

where we have defined a new state variable the **enthalpy**:

$$H = U + PV. \quad (1.16)$$

From Eq. (1.15) we see that in a constant P process, the heat absorbed by the system is equal to the change of the enthalpy of the system. This is very useful in the study of phase transitions, because during a phase transition the pressure is usually kept constant. Therefore, when two phases coexist, the difference of the enthalpy between the two phases is the well-known *latent heat* in the phase transition.

1.9 Heat Capacity

When a system absorbs a certain amount of heat ΔQ , its temperature T will increase by ΔT . From this we can define a physical quantity known as the *heat capacity* C :

$$C = \lim_{\Delta T \rightarrow 0} \frac{\Delta Q}{\Delta T} = \frac{dQ}{dT}. \quad (1.17)$$

The last expression of the above equation is not a differentiation, because the function Q does not exist. This implies that the magnitude of C depends on the path. Specific examples are the well-known constant pressure heat capacity C_P and constant volume heat capacity C_V . Apparently, C will be proportional to the size of the system. It is therefore an extensive variable. We can define the corresponding intensive variable called the **specific heat** c , which is independent of the size of the system:

$$c_\alpha = \frac{C_\alpha}{n}, \text{ or } c_\alpha = \frac{C_\alpha}{m}, \quad (1.18)$$

where n is the number of kilomoles, m the mass, and α may be P or V , etc. Therefore, c_α is the heat capacity per kilomole, or the heat capacity per unit mass and is known as the specific heat.

That the heat capacity C depends on the path in PVT systems is well-known. This means that the constant volume C_V is not equal to the constant pressure C_P . In the following we derive the formula for $C_P - C_V$ for a PVT system. In an *isochoric* (i.e., constant V) process $dW = 0$, $dQ_V = dU$ (Eq. (1.3)), and in an *isobaric* (i.e., constant P) process $dQ_P = dH$ (Eq. (1.15)), thus we get from Eq. (1.17)

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \text{ and } C_P = \left(\frac{\partial H}{\partial T} \right)_P. \quad (1.19)$$

From the above equations, we have

$$\begin{aligned} C_P - C_V &= \left(\frac{\partial H}{\partial T} \right)_P - \left(\frac{\partial U}{\partial T} \right)_V \\ &= \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P - \left(\frac{\partial U}{\partial T} \right)_V \\ &= \left(\frac{\partial V}{\partial T} \right)_P \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right]. \end{aligned} \quad (1.20)$$

Here in the second equality, we have used $dH = dU + PdV + VdP$, and in the last equality we have used

$$\left(\frac{\partial U}{\partial T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_V + \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P, \quad (1.21)$$

which is obtained from the following equation divided by dT term by term, and keeping P constant:

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV. \quad (1.22)$$

1.10 $C_P - C_V$ for an Ideal Gas

We use the ideal gas as an example to evaluate $C_P - C_V$. The equation of state of an ideal gas is

$$PV = nRT, \quad (1.23)$$

where n is the number of kilomoles (or moles) and R is the **gas constant**. The temperature T in this equation is called the **ideal gas temperature**, which is also known as the absolute temperature.⁹ The unit of the absolute temperature is K (kelvin). The SI units of P and V are $\text{N/m}^2 \equiv \text{Pa}$ (pascals) and m^3 , respectively. The value of the gas constant R is then

$$R = 8.314 \times 10^3 \text{ J kilomole}^{-1} \text{ K}^{-1} = 8.314 \text{ J mole}^{-1} \text{ K}^{-1}. \quad (1.24)$$

Some people use one atmospheric pressure (atm) as the unit for pressure and liters as the unit of volume; the value of R is then¹⁰

$$R = 8.206 \times 10^{-2} \text{ liter atm mole}^{-1} \text{ K}^{-1}. \quad (1.25)$$

We will show in Chapter 2 that for an ideal gas $(\partial U/\partial V)_T = 0$, which implies that the internal energy U is a function of T only, independent of V . Therefore, Eq. (1.20) becomes

$$C_P - C_V = P \left(\frac{\partial V}{\partial T} \right)_P = nR, \quad (1.26)$$

which implies that $C_P - C_V > 0$ for an ideal gas. In Chapter 4 we will show that $C_P - C_V \geq 0$ for all systems. This means that C_P is always greater than, or at least equal to, C_V . This can easily be understood, because in an isochoric process the system does no work. The heat absorbed is entirely used to increase the temperature. In an isobaric process, however, part of the absorbed heat is used to do work, and the system needs to absorb more heat to increase the temperature by the same amount as in the isochoric case.

⁹We will introduce another temperature, the thermodynamic temperature, in Chapter 2. The origins by which the ideal gas and the thermodynamic temperatures are defined are quite different, but we will show in Chapter 2 that these two temperatures can be chosen to be identical to each other. This new temperature scale is known as the absolute temperature.

¹⁰For the units conversion: $1 \text{ atm} = 1.013 \times 10^5 \text{ Pa}$; $1 \text{ liter} = 10^{-3} \text{ m}^3$.

1.11 Reversible Adiabatic Process for an Ideal Gas

In thermodynamics, we frequently encounter both reversible and irreversible processes. These are important concepts, and we will come back to this subject and give a more detailed explanation in Chapter 2. Here we give simple criteria for a reversible process. A process is called reversible, if the following two conditions are satisfied:

1. There is no dissipative work involved (i.e., frictional force is negligible).
2. The process is a *quasi-static* process.

A process is said to be quasi-static if it proceeds very slowly, such that at any moment in the process the system can be considered as almost being in an equilibrium state. Next we shall consider an adiabatic process. A process is said to be adiabatic if, during the process, the system absorbs or rejects no heat, that is $dQ = 0$. In a reversible adiabatic process we have $dU = -PdV$.

As an example, we consider an ideal gas. The internal energy U is a function of T only, it is independent of V . Therefore

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV = C_V dT \quad (\text{ideal gas}), \quad (1.27)$$

and

$$C_V dT = -PdV = -\frac{nRT}{V} dV, \quad (1.28)$$

$$c_v \frac{dT}{T} = -R \frac{dV}{V}, \quad c_v = \frac{C_V}{n}. \quad (1.29)$$

Integrating both sides from (T_1, V_1) to (T_2, V_2) we obtain

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{R/c_v}. \quad (1.30)$$

From the equation of state and $R = c_p - c_v$, we can rewrite Eq. (1.30) as

$$P_1 V_1^\gamma = P_2 V_2^\gamma, \quad \gamma \equiv \frac{c_p}{c_v}. \quad (1.31)$$

Equation (1.31) is equivalent to

$$PV^\gamma = \text{constant}. \quad (1.32)$$

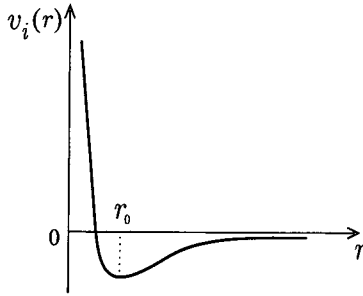


Figure 1.5: The relation between the interaction energy $v_i(r)$ and the distance between molecules r , where $v_i(r)$ is minimum at r_0 .

This is the well-known equation which an ideal gas must obey in a reversible adiabatic process. For a monatomic ideal gas, the molar specific heat $c_v = 3R/2$ and $c_p = 5R/2$ by Eq. (1.26), therefore $\gamma = 5/3 \approx 1.67$. For a diatomic ideal gas¹¹ $c_v = 5R/2$ and $c_p = 7R/2$, thus $\gamma = 7/5 = 1.40$. Note that in this process a monatomic and a diatomic ideal gas obey different equations.

1.12 Virial Expansion

In thermodynamics, the most frequently discussed system is the ideal gas, which has the equation of state $PV = nRT$. The ideal gas is an idealized system which is based on the following two assumptions:

1. There is no interaction between the molecules, except for collisions.
2. The molecular volume is approximately zero.

These two conditions can be met only when the density of the gas is very small.¹² When the density is not sufficiently low, the behavior

¹¹For a diatomic molecule, in addition to the translational energy, there is also rotational energy, which also makes a contribution to the heat capacity. We will give a more detailed discussion on this subject in Chapters 9 and 11.

¹²Here we are talking about the *classical ideal gas*. In addition to a low density, one also needs the condition of high temperature, in order that quantum effects can be neglected. The condition under which a gas can be considered as a classical ideal gas is $\lambda_{\text{th}} \ll \bar{d}$, where $\lambda_{\text{th}} = h/\sqrt{2\pi mkT}$ is the thermal wavelength (m is the particle mass, h and k are the Planck constant and the Boltzmann constant) and $\bar{d} = (V/N)^{1/3}$ is the mean distance between two particles. This condition will be derived in Chapter 10.

of the gas may deviate from the ideal gas law, and corrections may be needed. In the following, we introduce a commonly used approximate method which includes the non-ideal gas part in the equation of state. The method is called the *virial expansion*. It is an ideal method for the study of a dilute gas, where the density of the gas is still low. This approximation uses the method of series expansion to treat the problem. In Fig. 1.5 we plot the relation between the particle-particle interaction energy $v_i(r)$ and the distance between two particles r . In the figure, r_0 is the distance where $v_i(r)$ has a minimum value. For $r > r_0$, the slope $dv_i/dr > 0$, and particles attract each other. When r increases, the attraction decreases, going to zero for large r . For $r < r_0$, $dv_i/dr < 0$, and the particles repel each other. The repulsive force increases very rapidly as r decreases, which is rather similar to a hard core.

Consider a system with n kilomoles of particles moving in a container of volume V . The condition under which the density can be considered as dilute is

$$\frac{v_0}{v} \ll 1; \quad v_0 \equiv N_A r_0^3, \quad v \equiv \frac{V}{n}, \quad (1.33)$$

where $N_A = 6.02 \times 10^{26}$ molecules kilomole⁻¹ is **Avogadro's¹³ number**. The virial expansion method is to express the equation of state of a gas as a power series in v_0/v :

$$Pv = RT \left[1 + \frac{B_2(T)}{v} + \frac{B_3(T)}{v^2} + \frac{B_4(T)}{v^3} + \dots \right]. \quad (1.34)$$

In the above equation, we let the constant v_0 be included in the expansion coefficients B_i , thus v_0 does not appear in the equation. We also replace B_1 by 1, because it is equal to 1 identically. The condition for an ideal gas is that $v_0/v \rightarrow 0$, i.e., $B_i/v^{i-1} = 0$ for $i \geq 2$. The coefficients of expansion $B_2(T)$, $B_3(T)$... etc. are called the **virial coefficients**.

In addition to the ideal gas law, the *van der Waals¹⁴ equation of state* is the other most frequently studied equation of state for a gas system. The equation is

$$\left(P + \frac{a}{v^2} \right) (v - b) = RT; \quad a > 0, \quad b > 0. \quad (1.35)$$

In the equation, a and b are constants, which may have different values for different gases. In many applications, we may consider this as the

¹³Count A. Avogadro, Italian physicist (1776–1856).

¹⁴Johannes D. van der Waals, Dutch physicist (1837–1923), Nobel prize laureate in physics in 1910.

equation of state for a real gas. It can be used to study the phenomenon of gas-liquid coexistence in phase transitions. Equation (1.35) may be considered as being obtained from the virial expansion. If we take $B_2 = b - a/RT$, $B_3 = 0$, $B_4 = ab^2/RT$, and $B_i = 0$ for $i \geq 5$, and substitute them into Eq. (1.34), we have

$$\begin{aligned} Pv &= RT \left[1 + \left(b - \frac{a}{RT} \right) \frac{1}{v} + \left(\frac{ab^2}{RT} \right) \frac{1}{v^3} \right] \\ &= RT \left(1 - \frac{a}{RT} \frac{1}{v} + \frac{ab}{RT} \frac{1}{v^2} \right) \left(1 + \frac{b}{v} \right). \end{aligned} \quad (1.36)$$

This can be rewritten as

$$Pv \left(1 + \frac{b}{v} \right)^{-1} = RT - \frac{a}{v} + \frac{ab}{v^2} = RT - \frac{a}{v} \left(1 - \frac{b}{v} \right). \quad (1.37)$$

Under the condition $0 < b \ll v$, $(1 + b/v)^{-1} \approx 1 - b/v$, after a rearrangement of the terms, Eq. (1.37) becomes the van der Waals equation of state (1.35). If we define the two new variables, P' and v' , as

$$P' = P + \frac{a}{v^2}, \quad v' = v - b, \quad (1.38)$$

then Eq. (1.35) becomes

$$P'v' = RT. \quad (1.39)$$

If we interpret P' and v' as the new pressure and the new molar volume, respectively, then P' and v' satisfy the ideal gas equation of state. Therefore we may consider that P' and v' are the pressure and the volume of an ideal gas, which is derived from the *original* real gas system. We note that the *real* pressure P is smaller than P' ($a > 0$). This is understandable since attractions between the molecules make the real gas pressure smaller than the corresponding ideal gas pressure. Since $b > 0$, this implies that v' (the volume available for the ideal gas) is smaller than v (volume available for the real gas). The reason for this is that in the real gas, the *free* volume available for a molecule to move without colliding with other molecules is smaller than the volume of the container V ($V = nv$). Part of the volume V is occupied by the hard cores of the molecules. From the above analysis, we can see that the constant a in the van der Waals equation of state is related to the attractions between the molecules, and the other constant b represents the size of the hard core of a molecule.

1.13 Expansion Coefficient and Compressibility

One can rewrite the equation of state of a system $f(P, V, T) = 0$ as $V = V(T, P)$, i.e., V is a function of T and P . The temperature T and pressure P are controllable variables in the laboratory. Therefore, in principle, the function $V(T, P)$ can be determined experimentally. However in practice, it is more useful to measure experimentally the *expansion coefficient* (also called *expansivity*) and the *compressibility*. These two quantities determine the rate of change of the volume V as the temperature T or the pressure P changes.

From $V = V(T, P)$ we have

$$dV = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP. \quad (1.40)$$

The **expansion coefficient** (or **expansivity**) β determines, when P is kept constant ($dP = 0$), the rate of change of V as T changes,

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P. \quad (1.41)$$

On the other hand, the **compressibility** κ determines, when T is kept constant ($dT = 0$), the rate of change of V as P changes,

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T. \quad (1.42)$$

Therefore, Eq. (1.40) can be written as

$$dV = \beta V dT - \kappa V dP. \quad (1.43)$$

There are two points in Eq. (1.42) which are worthwhile mentioning. (1) There is a *minus* sign in front of the partial differentiation, which makes κ a positive quantity. The reason is that for a thermodynamic system to be stable, the volume of the system should decrease as the pressure increases.¹⁵ (2) The compressibility defined in Eq. (1.42) under the condition of constant temperature is called the *isothermal compressibility*. However, the compressibility may also be measured adiabatically; this is called *adiabatic compressibility*, which is denoted as κ_S . This means that

$$\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S, \quad (1.44)$$

¹⁵We will prove this statement in Chapter 5.

where S denotes the entropy, which will be defined in Chapter 2. The subscript S of the partial differentiation means that during the differentiation S is kept constant, which is the condition for an adiabatic process. There is a relation between the isothermal compressibility κ and the adiabatic compressibility κ_S , which will be discussed in Chapter 4.

When the equation of state for a system is known, for example the ideal gas, we can use Eqs. (1.41)–(1.42) to calculate the theoretical expansion coefficient and the isothermal compressibility. From the ideal gas equation of state $V = nRT/P$, we obtain the expansion coefficient

$$\beta = \frac{1}{V} \left(\frac{nR}{P} \right) = \frac{1}{T}, \quad (1.45)$$

and the isothermal compressibility

$$\kappa = -\frac{1}{V} \left(\frac{-nRT}{P^2} \right) = \frac{1}{P}. \quad (1.46)$$

However for systems for which the equation of state is unknown, we can use the experimental values of β and κ to determine the equation of state. For example, for some dilute real gases, the equation of state can be expressed as the form of a virial expansion. Usually only a small number of the expansion terms are non-negligible, and higher order terms may be neglected. The lower order virial coefficients may be determined by the experimental values of β and κ and some other properties of the system. The equation of state may then be determined.

For liquids and solids, it is not easy to obtain the complete form of $V = V(T, P)$. In general both β and κ are functions of T and P , thus if one wants to obtain the complete form of $V = V(T, P)$ by integrating Eq. (1.43), one needs a very large amount of experimental data for β and κ . It is not practical to do this. In practice, one usually only needs to know the equation of state for the small range of T and P of interest. If the range is small enough, then we may consider that both β and κ are constants, independent of T and P . If one is interested in the properties of the system near $T = T_0$ and $P = P_0$, then by integrating Eq. (1.43), one obtains

$$V = \int dV = V_0[1 + \beta(T - T_0) - \kappa(P - P_0)], \quad (1.47)$$

where $V_0 = V(T_0, P_0)$, and β and κ are considered as constants. This may be considered as an approximate equation of state for a liquid or

a solid for temperatures T that do not deviate too much from T_0 , and pressures P that do not deviate too much from P_0 .

1.14 Problems

- 1.1. A cylindrical container is divided into two parts A and B by a wall between them. Both A and B contain gas molecules. Describe what kind of the dividing wall can make the gases in A and B maintain the following situations: (a) in mechanical but not thermal equilibrium; (b) in thermal but not mechanical equilibrium; (c) in thermodynamic equilibrium.
- 1.2. The initial state of n kilomoles of an ideal gas is at temperature T_1 and pressure P_1 . The gas is then compressed reversibly against a piston to a volume equal to one-half of its original volume. The temperature of the gas is varied during the compression so that at each instant the relation $P = AV$ is satisfied; A is a constant.
 - (a) Express A in terms of P_1 , T_1 , n and the gas constant R .
 - (b) Draw a diagram of the process in the P - V plane.
 - (c) Find the final temperature T_2 in terms of T_1 .
 - (d) Find the work done on the gas in terms of n , R , and T_1 .
- 1.3. The temperature of an ideal gas at an initial pressure P_1 and volume V_1 is increased at constant volume until the pressure is doubled. The gas is then expanded isothermally until the pressure drops to its original value, where it is compressed at constant pressure until the volume returns to its initial value.
 - (a) Sketch these processes in the P - V plane and the P - T plane.
 - (b) Compute the work in each process and the net work done in the cycle if $n = 2$ moles, $P_1 = 1$ atm and $V_1 = 0.04$ m³.
- 1.4. An ideal gas is contained in a cylindrical container with a movable piston. Initially, the volume of the gas is 0.1 m³, the pressure is 2×10^6 N m⁻², and the temperature is 300 K.
 - (a) The gas is expanded isothermally until the final pressure is reduced to 1×10^6 N m⁻². Find the final volume of the gas.

- (b) The piston is held fixed at its initial position and the pressure is reduced to $1 \times 10^6 \text{ N m}^{-2}$. Find the final temperature.
- (c) The system starts from its initial conditions, expands isothermally until the pressure is $1.5 \times 10^6 \text{ N m}^{-2}$, and then it is cooled at a constant volume until the pressure is $1 \times 10^6 \text{ N m}^{-2}$. Find the final temperature and volume of the gas.
- (d) The system starts from its initial conditions, is cooled at a constant volume until the pressure is $1.5 \times 10^6 \text{ N m}^{-2}$, and this is followed by an isothermal expansion until the pressure is $1 \times 10^6 \text{ N m}^{-2}$. Find the final temperature and volume of the gas.
- (e) Plot each of the above processes on a T - V diagram.
- 1.5. The initial state of a monatomic ideal gas is $P_0 = 1 \text{ atm}$, $T_0 = 273 \text{ K}$, and $V_0 = 10^{-3} \text{ m}^3$. The gas is isothermally expanded to $V_1 = 2V_0$ and is then cooled at constant pressure to a volume V . The volume V is such that a reversible adiabatic compression to the pressure P_0 returns the system to its initial state. All of the changes are conducted reversibly. Calculate the value of V and the total work done on or by the gas.
- 1.6. One mole of N_2 gas is contained at $T = 273 \text{ K}$ and $P = 1 \text{ atm}$. The addition of 3000 J of heat to the gas at constant pressure causes 832 J of work to be done during the expansion. Calculate
- the final state of the gas;
 - the values of ΔU and ΔH for the change of state; and
 - the values of c_v and c_p for N_2 .

Assume that nitrogen behaves as an ideal gas, and that the above changes of state is conducted reversibly.

- 1.7. For a diatomic ideal gas near room temperature, what fraction of the heat absorbed is available for doing external work if the gas expands at a constant pressure? What is the result if the gas expands at a constant temperature?
- 1.8. Show that the work done by a gas in an arbitrary process can be expressed as

$$dW = PV\beta dT - PV\kappa dP.$$

What is this expression for an ideal gas?

- 1.9. The equation of state of a certain gas is $(P + b)v = RT$, its specific internal energy is given by $u = aT + bv + u_0$. (a) Find c_v . (b) Show that $c_p - c_v = R$.
- 1.10. Suppose the molar internal energy of a van der Waals gas is given by $u = cT - a/v + u_0$, where a is one of the constants in the equation of state, and c and u_0 are constants. Calculate the molar specific heat capacities c_v and c_p .
- 1.11. The constant pressure molar specific heat of most substances (except at very low temperatures) can be satisfactorily expressed by the empirical formula

$$c_p = a + 2bT - cT^{-2},$$

where a , b and c are constants and T is measured in kelvin.

- (a) Find the heat required to raise the temperature of n moles of the substance at constant pressure from T_1 to T_2 . Express your answer in terms of a , b , c , T_1 , and T_2 .
- (b) Find the mean heat capacity per mole between T_1 and T_2 .
- 1.12. Show that $\left(\frac{\partial h}{\partial P}\right)_T = -c_p \left(\frac{\partial T}{\partial P}\right)_h$.
- 1.13. Show that $\left(\frac{\partial u}{\partial T}\right)_P = c_p - P\beta v$.
- 1.14. Show that $\left(\frac{\partial u}{\partial P}\right)_T = P\kappa v - (c_p - c_v)\frac{\kappa}{\beta}$.
- 1.15. Show that the following relations hold for a reversible adiabatic expansion of an ideal gas:
 (a) $TV^{\gamma-1} = \text{constant}$, (b) $TP^{(1/\gamma)-1} = \text{constant}$.
- 1.16. One liter of air at a pressure of 1 atm is pumped into a bicycle tire. The final pressure of the tire is 7 atm. Consider this process as a reversible adiabatic process and the air molecules as diatomic.
- (a) What is the final volume of the air in the tire?
 (b) How much work is done in compressing the air?
 (c) If the temperature of the air is initially 300 K, what is the temperature after compression?

- 1.17. Two identical bubbles of gas, A and B, are formed at the bottom of a lake and then rise to the surface. Suppose the pressure at the bottom of the lake is twice that of the surface, and the temperature of the water in the lake is a constant independent of the depth. Consider the situation where bubble A rises so rapidly that no heat is exchanged between it and the water, while bubble B rises so slowly that it always remains in thermodynamic equilibrium with the water. Find the ratio of the final volume (just beneath the surface) of A and B, assuming that A undergoes a reversible adiabatic process and B undergoes a reversible isothermal process. The gas molecules are assumed to be diatomic.

- 1.18. (a) Show that the expansion coefficient β can be expressed as

$$\beta = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P,$$

where $\rho = 1/v$ is the density (v is the molar volume).

- (b) Show that the isothermal compressibility κ can be written as

$$\kappa = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T.$$

- 1.19. Show that the expansion coefficient of a van der Waals gas is

$$\beta = \frac{Rv^2(v-b)}{RTv^3 - 2a(v-b)^2}.$$

Show that this reduces to the ideal gas result when $a = b = 0$.

- 1.20. Show that the isothermal compressibility of a van der Waals gas is

$$\kappa = \frac{v^2(v-b)^2}{RTv^3 - 2a(v-b)^2}.$$

Show that this reduces to the ideal gas result when $a = b = 0$.

- 1.21. A hypothetical substance has an expansivity of $\beta = 2bT/v$ and an isothermal compressibility of $\kappa = a/v$, where a and b are constants. Show that the equation of state is $v - bT^2 + aP = \text{constant}$.
- 1.22. A hypothetical substance has an expansivity of $\beta = bT^2/P$ and an isothermal compressibility of $\kappa = aT^3/P^2$, where a and b are constants. Find the equation of state of the substance and the ratio a/b .

1.23. Show that, in general,

$$\left(\frac{\partial\beta}{\partial P}\right)_T + \left(\frac{\partial\kappa}{\partial T}\right)_P = 0,$$

where β and κ are the expansivity and the isothermal compressibility, respectively.

1.24. If the equation of state is given in the form $P = P(T, V)$, show that the following relation holds:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{\kappa},$$

where β and κ are the expansion coefficient and the isothermal compressibility, respectively. From this, show that

$$dP = \frac{1}{\kappa} \left(\beta dT - \frac{dV}{V} \right).$$