

Thermodynamics for Introductory Physics or Chemistry in 14 Pages

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To the beginners, the most confusing aspect of thermodynamics is the number of variables describing a thermodynamic system. Sometimes the variables seem to be dependent on each other but sometimes they seem to be independent of each other. This very short exposition aims to help college freshmen to clear up the confusion on thermodynamics that they often encounter in their introductory physics or chemistry courses.

Introduction

If all objects fall to the ground by gravity, why don't all the air molecules fall to the surface of earth? Why does water vaporize in high temperature and freeze in low temperature? Why does a rubber band shrink instead of expand when heated? The branch of physics answering this type of questions is called thermodynamics. We would like to learn thermodynamics in the fashion we learn mechanics. For mechanics problems, we always start from Newton's laws. Thermodynamics is for the most part based on two laws; they are called the first and the second laws of thermodynamics. (There is a third law that concerns the thermodynamic properties in the limit of the lowest temperature. Historically there were many other laws discovered by the pioneers in this field, but most of them are now understood to be the consequences of the two laws.) We shall try to discuss all thermodynamic questions starting from the first and second laws.

When we observe the behavior of a system consisting of a large number of particles (say, water in a cup that contains $\sim 10^{25}$ H₂O), we are not concerned with the mechanics of individual particles. Rather, we are interested in the macroscopic properties, i.e., the properties on a spatial scale much larger than molecular sizes and on a time scale much longer than that of the molecular processes. Take water in a cup as an example. We would like to know, for instance, how water changes to ice or vapor, rather than how individual molecules move in water. It turns out there are physical laws governing the macroscopic behavior and properties, to a large extent independent of the mechanics of individual constituent particles. These laws that were derived from experimental evidence are called thermodynamics. Thermodynamic describes the average properties of the individual particles.

Thermodynamics describes a macroscopic system in equilibrium and how a macroscopic system approaches its equilibrium state. For the beginners, it is important to remember that a thermodynamic statement is always qualified by conditions. For example, one might have seen a statement like "according to the second law of thermodynamics, the entropy of a system always increases to a maximum." This is an unphysical statement, because the entropy of a system increases to a maximum only under a certain condition, not always. Without stating the qualifying condition, it is meaningless to say what will happen.

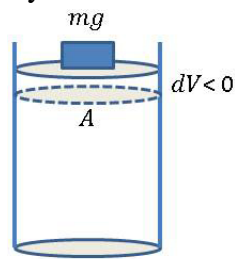
Therefore the first thing we need to learn is how to specify a macroscopic state. Macroscopic systems can be arbitrarily complicated. Think about a biological system. However in most cases, a complicated macroscopic system can be viewed as a collection of smaller, but still macroscopic,

simple systems. If we understand the thermodynamics of simple systems, we can also understand the complicated systems. A macroscopic state describable with a small number of physical quantities is necessarily in equilibrium; that means the state does not change within the time of measurement. A state in equilibrium is independent of its prior history. Only a state in thermal equilibrium is determined by thermodynamics. For instance, if you want to know how the thermodynamic state of a system changes with temperature, you have to change the temperature gradually and keep the whole system in uniform temperature that at any moment during the transition the system is practically in equilibrium. Such a transition is called quasi-static.

1. Macroscopic state and laws of thermodynamics

In classical mechanics, the physical state of a particle is specified by its position and velocity. This is because, given the position and velocity of a particle at a time, Newton's second law tells us the physical state (i.e., the position and velocity) of the particle at all other times. (There is a corresponding description in quantum mechanics.) Thus the first question in thermodynamics is what defines the physical state of a macroscopic system? The answer depends on the system. The simpler the system, the smaller the number of physical quantities is needed to specify its macroscopic state. The proper approach is to start with the simplest system, such as a box of an inert gas which has no chemical reactions. Once the thermodynamics of a simple system is established, it is straightforward to add additional features such as chemical reactions into the system.

A simple system: Consider an inert gas in a container, or a gas in which chemical reactions are negligible, like air. The fundamental assumption of thermodynamics for such a system is that its macroscopic state is defined by two, and only two, quantities: its volume V and its energy content E . (Later we will show that V and E can be replaced by other two quantities.) Remember that energy is a relative quantity. E is the difference of energy relative to a reference state taken as having energy equal to zero (or any constant). The pioneers of thermodynamics in the 19th century worked very hard to prove that if a system can be transformed from state A to state B quasi-statically, the energy difference between the two states is always measurable.



Suppose that the container of the gas is a cylinder closed on the top by a movable piston whose weight is mg (as in the figure). The pressure the gas exerts on its wall is P . In equilibrium, the weight of the piston is balanced by the pressure the gas exerting on the piston and the weight: $PA = mg$, where A is the cross sectional area of the cylinder. (In reality we should include the atmospheric pressure--for illustration this is ignored.) If the piston is displaced downward by an infinitesimal distance ℓ , the gravity would have done an amount of work $PA\ell$ (i.e., force PA times displacement ℓ) on the gas. In this case, the gas has a change of volume $dV = -A\ell$ which is negative. By

convention, we define a work exerted on the system (the gas) as a positive quantity W , so we write an amount of work $\Delta W = -PdV$. If the piston is displaced upward, dV would be positive and the work would have been done by the system against the gravity: then $\Delta W = -PdV$ is negative. (Physical laws require certain sign conventions which are arbitrarily defined. But once you adopt a sign convention, you have to stick to it consistently.). In our case, the work done on the system is defined as positive; work done by the system is negative. In both cases, this is expressed by $\Delta W = -PdV$. The work will increase the energy content of the system if it is done on the system (i.e., when ΔW is positive). On the other hand, the energy change of the system would be negative if a work is done by the system. Importantly the pioneers of thermodynamics discovered that when a gas changes its macroscopic state with a change of its energy content denoted by dE , dE is not always equal to the work $-PdV$. They discovered a form of energy called heat that completes the energy conservation:

$$dE = \text{work} + \text{heat} = -PdV + \text{heat} \quad (1)$$

This statement is called *the first law of thermodynamics*, which recognizes heat as a form of energy that can be used to do work. Like work, heat is considered positive if added to the system, negative if extracted from the system. We now understand that heat is the kinetic energy of disordered motions of atoms and molecules. However, the thermodynamics laws are used without entering the kinetic mechanism.

One of the most significant developments in the history of science is the discovery of the concept called entropy. Entropy is a property of a macroscopic system, which will be expressed as a physical quantity S . Before we discuss its meaning, we can formally state that S is a function of E and V , or $S(E, V)$ since we have assumed that E and V define the macroscopic state of a gas—this mathematical statement is very important (see Exercise 1). We emphasize again that E and V completely define the macroscopic state of a gas only in equilibrium. A system of a large number of gas molecules has a huge number of degrees of freedom. The degrees of freedom include, for example, the molecules not homogeneously distributed in the container even when their total energy remains at the constant value E . Such degrees of freedom are called (unconstrained) internal degrees of freedom. The implicit assumption of thermodynamics is that each of all internal degrees of freedom assumes a definitive value when the system is in equilibrium.

An example in which the internal degrees of freedom deviate from equilibrium is that in a small volume V_1 , the gas density is different from the average. Assuming that the gas in volume V_1 and the gas in the rest of volume $V - V_1$ are each momentarily in equilibrium. Then the total entropy of the entire gas consists of two part: $S_{non-eq}(E, V) = S_1(E_1, V_1) + S_2(E - E_1, V - V_1)$.

The essence of *the second law of thermodynamics* is the axiom that if the values of total energy E and total volume V are held constant, the value of entropy decreases from its equilibrium value if the internal degrees of freedom deviate from equilibrium, i.e., $S_{non-eq}(E, V) < S(E, V)$. In this way the second law of thermodynamics gives us the direction of naturally occurring evolution for the macroscopic state of a system not in equilibrium. The spontaneous process of evolution in a system of constant E and V is in the direction of increasing its entropy toward the maximum value

$S(E, V)$ when the entire system reaches the equilibrium state. That is why the second law of thermodynamics is also called *the principle of maximum entropy*.

Note that $S_{non-eq}(E, V)$ is not a function of E and V (see Exercise 1 for explanation). We mentally partition a gas not in equilibrium into small regions, such that the gas in each region can be regarded as momentarily in equilibrium with energy E_i and volume V_i which then has a well defined entropy $S_i(E_i, V_i)$. $S_{non-eq}(E, V)$ is the sum $\sum_i S_i(E_i, V_i)$ with $\sum_i E_i = E$ and $\sum_i V_i = V$. That is how a value of entropy is assigned to a non-equilibrium state, and that makes it possible to say that the entropy of a system in non-equilibrium spontaneously increases to the maximum value when the system evolves to equilibrium.

In thermodynamics, we rarely know the mathematical expression of the function $S(E, V)$ (except for very simple systems such as dilute gases). It is only important to know the derivatives of the function. (See Exercise 1 on partial differentiation of multiple-variable functions). The rate of change of entropy with respect to change of energy, while volume is held constant, is defined as the inverse of temperature:

$$\left(\frac{\partial S}{\partial E}\right)_V \equiv \frac{1}{T} \quad (2)$$

Eq. (2) means that, at constant V , we have $dE = TdS$. Comparing with eq. (1) at constant V , we thus identify TdS as heat. So we have in general,

$$\boxed{dE = TdS - PdV}, \quad (3)$$

which is often called the first law of thermodynamics. Experiments have shown that temperature T is always positive. Its theoretical minimum value is zero, also called the absolute zero. The entropy S is introduced as a dimensionless quantity. Therefore temperature has the same dimension as energy. As a convention, the unit of temperature is degrees Kelvin (K). The ice point is $273.15^\circ K$. (The conventional degree Celsius defines the ice point as $0^\circ C$. $T^\circ K = T^\circ C + 273.15^\circ$) The conversion factor between energy and temperature is called the Boltzmann constant k ,

$$k = 1.38 \times 10^{-23} \text{ Joule}/K \quad (4)$$

Entropy is measurable

If a small amount of heat TdS added to a system at constant volume raises its temperature by an interval dT . Then the ratio, TdS divided by dT , $T \left(\frac{\partial S}{\partial T}\right)_V$ is called the heat capacity of the system. If this is for a unit mass of the system, it is called the specific heat at constant volume, C_V , which has been measured for all kinds of materials. A specific heat measured as a function of T is denoted by $C_V(T)$. From the relation $T \left(\frac{\partial S}{\partial T}\right)_V = C_V(T)$, we can integrate $\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V(T)}{T}$ to obtain the value of entropy $S(T, V)$:

$$S(T, V) - S(0, V) = \int_0^T \frac{C_V(T')}{T'} dT' \quad (5)$$

Note that in the original form, all quantities are functions of E and V . From $S(E, V)$ and the derivative $\left(\frac{\partial S}{\partial E}\right)_V = \frac{1}{T}$, T is also a function of E and V , $T(E, V)$. We can then convert the function $T(E, V)$ to express E as a function of T and V , and substitute it into $S(E, V)$. That is why one can express S as a function of T and V , $S(T, V)$.

Entropy was originally introduced into thermodynamics as an abstract quantity. But the research by Maxwell, Boltzmann and Gibbs had clarified its physical meaning. Take a gas of hydrogen atoms, as an example. In quantum mechanics, we understand the microscopic states of a hydrogen. The entropy $S(E, V)$ is found to be the logarithm of the total number of possible microscopic states for the hydrogens consistent with total energy E in a volume V . (The logarithm is necessary to make the entropy S an additive quantity, i.e., the entropy of a system consisting of subsystems is the sum of the entropy functions of the subsystems.) A non-equilibrium state (consider, for example, the gas molecules occupying only one half of the volume) has a smaller number of possible microscopic states associated with it, compared with the number of possible microscopic states in equilibrium. We assume that all possible microscopic states are equally likely to occur. Then given a gas in a box, statistically we are more likely to observe the equilibrium state than a non-equilibrium state. This is the statistical interpretation of the second law of thermodynamics.

Classical ideal gas

A gas in which the molecular interactions are negligible is called an ideal gas. (However, we must remember that some molecular interactions are necessary for a gas to reach equilibrium.) A gas of low density and not at extremely low temperature (e.g., the air in the room) is a classical ideal gas (because the quantum effect is negligible). Even before the laws of thermodynamics were established, the relations among pressure, volume and temperature of classical ideal gases were known from experiments. In modern form such a relation is called the equation of state.

$$PV = NkT = nRT \quad (6)$$

where N is the number of molecules. n is the number of moles. $n = N/N_{av}$ where N_{av} is the Avogadro's number. $R = k \cdot N_{av}$ is called the gas constant. Because of the simple, exact relation among four basic physical quantities P , V , T and N , the classical ideal gas played an important role in the development of thermodynamic and statistical physics.

The gas molecules in a classical ideal gas are free particles, each moving with its own kinetic energy $\epsilon = \frac{1}{2}mv^2$ (v is the speed) in arbitrary directions. The probability of finding a molecule per unit volume with a speed v in the range between v to $v + dv$ is given by the Maxwell distribution function

$$P(v)dv = 4\pi n \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}} dv \quad (7)$$

It is straightforward to show that the average energy of the particles in a gas, according to the Maxwell distribution, is

$$\boxed{\langle \epsilon \rangle = \langle \frac{1}{2}mv^2 \rangle = \frac{3}{2}kT}. \quad (8)$$

In fact the average kinetic energy (Eq. 8) is valid for molecules in liquid and solid as well. Therefore the temperature of a system is a measure of the average kinetic energy of the molecules in the system.

Ideal gases are simple enough that their thermodynamic functions can be completely derived from the statistical mechanics developed by Boltzmann and Gibbs. For example, the entropy for a classical ideal gas (called the Sackur-Tetrode equation) is

$$S = kN \left(\ln \frac{V}{N\Lambda^3} + \frac{5}{2} \right) = k \left(\ln \left(\frac{V}{N\Lambda^3} \right)^N + \frac{5}{2} N \right) \quad (9)$$

where $\Lambda = h/\sqrt{2\pi mkT}$ (with Planck's constant h) is called the thermal wavelength. Λ^3 is a quantum mechanical measure of the size of space occupied by a molecule. The quantity $(V/N)/\Lambda^3$ in Eq. (9) is a measure of how many microscopic states are available to one molecule within the volume (V/N) , and $[(V/N)/\Lambda^3]^N$ is a measure of the total number of microscopic states available to N molecules. S/k is the logarithm of the total number of different combinations of N microscopic states available in a volume V . (The term $\frac{5}{2}N$ is not important.)

2. Free energies: the 2nd law of thermodynamics under various conditions

Mathematically Eq. (3) states that a change of E can be calculated from the changes of S and V . That means E is a function of S and V , expressed as $E(S, V)$. This means that even though we initially define a macroscopic state by its E and V , one can replace variables E and V by variables S and V , so that now we regard S and V as the independent variables. It can be shown rigorously that, if $S(E, V)$ has the property specified by the second law (i.e., the principle of maximum entropy), then $E(S, V)$ satisfies a minimum energy principle as follows: if the values of S and V are held constant, the value of energy E increases if the internal degrees of freedom deviate from equilibrium. Then the second law of thermodynamics states that, at constant S and V , the direction of spontaneous evolution for a non-equilibrium system is for its energy E to decrease to reach a minimum value when the system reaches equilibrium. The energy minimum principle in a condition we hold the values of S and V constant, is equivalent to the principle of maximum entropy in a condition we hold the values of E and V constant.

What if we hold the values of T and V constant? Do we know how will the macroscopic state of the system evolve from non-equilibrium toward equilibrium? For this, we will construct a new quantity F called Helmholtz free energy which is defined as

$$F = E(S, V) - TS \quad (10)$$

Then taking differentials of eq. (10):

$$dF = dE - SdT - TdS \quad (11)$$

and by eq. (3), we have

$$\boxed{dF = -SdT - PdV} \quad (12)$$

Therefore F is a function of T and V , written as $F(T, V)$. Again, it can be rigorously shown that if the values of T and V are held constant, the value of Helmholtz free energy F increases if the internal degrees of freedom deviate from equilibrium. Therefore, if a system is not in equilibrium, the value of Helmholtz free energy F spontaneously decreases to a minimum as the system reaches equilibrium. This is called the Helmholtz free energy minimum principle.

Another commonly used thermodynamic function is the Gibbs free energy, defined by

$$G = E(S, V) - TS + PV \quad (13)$$

Using eq. (3), we have

$$\boxed{dG = -SdT + VdP} \quad (14)$$

Again, it can be shown that if the values of T and P are held constant, the value of Gibbs free energy G increases from its equilibrium value if the internal degrees of freedom deviate from equilibrium. And the spontaneous evolution of a non-equilibrium system at constant T and P is to have its value of Gibbs free energy decrease to a minimum value when the system reaches equilibrium. This is called the Gibbs free energy minimum principle.

Thus the second law of thermodynamics dictates the direction of evolution for a macroscopic state of a system toward equilibrium under any condition the macroscopic state is specified. Under the condition E and V are held constant, it is dictated by the entropy maximum principle. Under other conditions, it is dictated by the minimum principle of the associated energy or free energy.

Why are the air molecules in a room not found all lying on the floor?

Firstly, at temperature T the mean translational energy of a molecule is $3kT/2$ (see Eq. (8)). At room temperature ($T \sim 300 \text{ K}$), kT amounts to $4 \times 10^{-21} \text{ J}$. On the other hand, the change in the gravitational potential energy for an air molecule of mass $3 \times 10^{-26} \text{ kg}$ in dropping 10 meters is about $3 \times 10^{-24} \text{ J}$, that is about $10^{-3} kT$. In other words, the kinetic energy that keeps the molecules above ground is hardly affected by gravitation.

However, there is another way of asking the same question. If the air molecules drop to the floor, the system has lowered both the kinetic and potential energies, just like an apple falls to the ground. Don't all systems evolve to the lowest energy state? To answer this question, we have to use the thermodynamic law governing the state of matter at the relevant condition. For the problem in question, the relevant condition is that the system is specified by temperature and volume. Therefore we must use the Helmholtz free energy minimum principle, i.e., the equilibrium state of a system at (T, V) is determined by the minimization its Helmholtz free energy $F = E - TS$. A system would spontaneously change to a new state only if the new state has a lower F value, or by a process of $\Delta F < 0$. At constant (T, V) , this is equivalent to $\Delta F = \Delta E - T\Delta S < 0$. In the air example, all molecules falling to the ground would indeed lower the energy ($\Delta E < 0$) that decreases F , but it also decreases the entropy ($\Delta S < 0$) that produces a positive $-T\Delta S$, that increases F . Let's do an estimate. Let's assume $V \sim 10 \text{ m}^3$, $N \sim 10^{23}$. The molecular volume is $\delta V \sim 10^{-30} \text{ m}^3 (= 1 \text{ \AA}^3)$. As mentioned

above, the loss of potential energy per molecule is $\sim -10^{-3}kT$. But the average kinetic energy is the same whether the molecules are moving in air or vibrating on the ground because it is determined by the temperature. Hence $\Delta E \sim -10^{-3}kTN$. On the other hand, from Eq. (9) entropy is a function of the volume occupied by the molecules, $\Delta S = S(\text{on ground}) - S(\text{in air}) = kN \left(\ln \frac{N \cdot \delta V}{NA^3} + \frac{5}{2} \right) - kN \left(\ln \frac{V}{NA^3} + \frac{5}{2} \right) = kN \left(\ln \frac{N \cdot \delta V}{V} \right) \sim -16kN$. Therefore if all molecules fall to the ground from air, its Helmholtz free energy would increase by $\Delta F \sim \Delta E - T\Delta S \sim +16kTN$. Hence it will not happen.

That is why air molecules would not all drop to the floor. On the other hand, at about $T \sim 79^\circ \text{K}$, air would condense to a liquid, because in this case the molecular interactions between air molecules produce a negative ΔE exceeding the positive term $-T\Delta S$.

How about apples, why do they fall? Let's assume that an apple has a mass $m \sim 0.1 \text{ kg}$, and a volume $\delta V \sim 10^{-3} \text{ m}^3$. Then one finds that, by the loss of potential energy alone, $\Delta E \sim -10^{22}kTN$, $T\Delta S \sim (-9 + \ln N)kTN$; the Helmholtz free energy is dominated by the energy term. In this case $\Delta F \sim \Delta E$ is negative, falling apples are in agreement with the Helmholtz free energy minimum principle.

Exercise 1. Partial differentiation of multi-variable functions

If f is a function of x, y and z , $df = \left(\frac{\partial f}{\partial x} \right)_{y,z} dx + \left(\frac{\partial f}{\partial y} \right)_{x,z} dy + \left(\frac{\partial f}{\partial z} \right)_{x,y} dz$. Clearly the subscript for each differentiation includes all the variables other than the differentiating variable. So for convenience, the subscripts are often omitted as understood, particularly for the higher order differentiations.

If f is a function of x and y and $df = Adx + Bdy$, then since $df = \left(\frac{\partial f}{\partial x} \right)_y dx + \left(\frac{\partial f}{\partial y} \right)_x dy$, we have $A = \left(\frac{\partial f}{\partial x} \right)_y$, $B = \left(\frac{\partial f}{\partial y} \right)_x$, and very importantly $\frac{\partial B}{\partial x} = \frac{\partial^2 f}{\partial x \partial y} = \frac{\partial A}{\partial y}$. However, an arbitrary relation written as $df = A_1 dx + A_2 dy$. It does not necessarily imply that f is a function $f(x, y)$, unless the condition $\frac{\partial A_2}{\partial x} = \frac{\partial A_1}{\partial y}$ is satisfied.

It is very important to note that all thermodynamic quantities are well defined functions of their variables. For example, the expression in Eq. (19) below implies that G is a function of T, P , and N_i 's.

3. Simple but important applications of thermodynamics

Equilibrium conditions (for example, why do two bodies in contact have the same temperature?)

The maximum and minimum principles can be used to derive equilibrium conditions. Consider a system in a container. An imaginary plane divides the container into two parts, 1 and 2. $E = E_1 + E_2$. Taking the differential of the equation gives $dE = dE_1 + dE_2$. Under the condition that total E is held constant, we have $dE = 0$, $dE_1 = -dE_2$. dE_1 (or dE_2), a transfer of a small amount of energy between part 1 to part 2, is an internal degree of freedom whose equilibrium value is zero. Thus a

non-zero value of dE_1 will decrease the entropy $S(E, V)$ from its equilibrium value (at constant E and V). Since S is maximum with respect to the change of dE_1 at equilibrium, $\frac{\partial S}{\partial E_1} = 0$ as $dE_1 \rightarrow 0$. From

$$\frac{\partial S}{\partial E_1} = \frac{\partial S_1(E_1)}{\partial E_1} + \frac{\partial S_2(E_2)}{\partial E_1} = \frac{\partial S_1(E_1)}{\partial E_1} + \frac{\partial S_2(E_2)}{\partial E_2} \frac{\partial E_2}{\partial E_1} = 0 \quad (15)$$

(V, V_1, V_2 are held constant in this operation.) Since $\left(\frac{\partial S}{\partial E}\right)_V = \frac{1}{T}$ (eq. 2), Eq. (15) becomes $T_1 = T_2$, the temperatures of part 1 and part 2 are the same in equilibrium. The above analysis is applicable to any two parts of a system or two systems in contact. As long as energy is transferrable between two parts, the temperatures of these two parts must be the same in equilibrium. In short, energy exchangeability makes the temperatures in different regions the same in equilibrium.

The same analysis can be applied to pressure using the energy minimum principle. If two parts of a system can exchange volume, imaging a movable piston between two parts of a cylinder,

$$\frac{\partial E}{\partial V_1} = \frac{\partial E_1(S_1)}{\partial V_1} + \frac{\partial E_2(S_2)}{\partial V_1} = \frac{\partial E_1(S_1)}{\partial V_1} - \frac{\partial E_2(S_2)}{\partial V_2} = 0 \quad (16)$$

(S, S_1, S_2 held constant in this operation is called an adiabatic process.) Since $\left(\frac{\partial E}{\partial V}\right)_S = -P$, the pressure in part 1 and part 2 must be the same in equilibrium. Volume exchangeability makes pressures in different regions equal in equilibrium.

Up to this point, we have considered systems of fixed composition. How does the macroscopic state change if we change the composition? We introduce a quantity μ called the chemical potential for the increase of energy E if the number of gas molecule N is increased by one, while holding S and V constant:

$$dE = TdS - PdV + \mu dN \quad (16)$$

By the same argument, if two parts of a system can exchange molecules, the chemical potential μ in the two parts must be equal in equilibrium. Molecular exchangeability makes the chemical potentials in different regions equal in equilibrium.

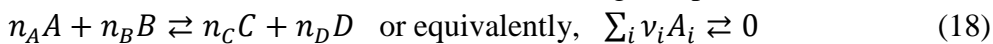
We now generalize to a system consisting of multiple species of molecules, denoted by different subscripts. Eq. (16) then generalize to

$$\boxed{dE = TdS - PdV + \sum_i \mu_i dN_i} \quad (17)$$

In this case, the thermodynamic state of the system is completely specified by S, V , and N_i ($i=1, 2, 3, \dots$) and it obeys the energy minimum principle.

Chemical reactions

Consider a chemical reaction that occur among components A, B, C and D:



with $\nu_1 = n_A, \nu_2 = n_B, \nu_3 = -n_C, \nu_4 = -n_D$, and $A_1 = A, A_2 = B$, etc. If the reaction occurs at constant T and P , such a process leads the Gibbs free energy of the system to a minimum. Use

$$\boxed{dG = -SdT + VdP + \sum_i \mu_i dN_i} \quad (19)$$

Since $dT = 0$, $dP = 0$, G is minimum with respect to a change of any N_i due to the chemical reaction. Since dN_i 's are related, only one of them is independent:

$$\frac{dG}{dN_1} = \frac{\partial G}{\partial N_1} + \frac{\partial G}{\partial N_2} \frac{\partial N_2}{\partial N_1} + \frac{\partial G}{\partial N_3} \frac{\partial N_3}{\partial N_1} + \dots = 0, \quad \frac{\partial N_i}{\partial N_1} = \frac{\nu_i}{\nu_1} \quad (20)$$

which leads to the equilibrium condition (for the reaction (18))

$$\sum_i \nu_i \mu_i = 0 \quad (21)$$

In an uncharged dilute solution, the dilute solute molecules behave similarly to an ideal gas. As a result, the chemical potential μ_i for each type of solute has a simple dependence on its concentration denoted by $[i]$:

$$\mu_i = \mu_i^o(T, P) + kT \ln[i], \quad [i] = N_i / \sum_j N_j \quad (22)$$

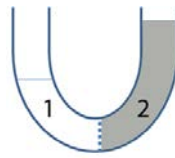
where μ_i^o is independent of molecular concentrations. Substituting the expression eq. (22) for each species of molecule into eq. (21), it is straightforward to show that when the reaction (18) reaches equilibrium, the concentrations of the four reactants satisfy the relation

$$\frac{[A]^{n_A} [B]^{n_B}}{[C]^{n_C} [D]^{n_D}} = K(T, P), \quad K(T, P) = \exp(-\sum_i \nu_i \mu_i^o / kT) \quad (23)$$

where $K(T, P)$ is independent of the solute concentrations and is called the equilibrium constant. Eq. (23) is called the law of mass action in chemistry.

Osmotic pressure

Let us consider a U shaped container with a semi-permeable membrane in the middle.



A solution containing one solute X is in side 2 of the partition through which only the solvent molecules can pass but the solute molecules cannot. Side 1 contains only the solvent. Since the solvent is free to be exchanged between side 1 and side 2, its chemical potentials on the two sides must be equal in equilibrium $\mu_1(T, P_1) = \mu_2(T, P_2)$. From Eq. (22), the concentration of pure solvent is 1. The concentration of the solvent in solution 2 is $N_o / (N_o + N_X) \sim 1 - N_X / N_o$ ($N_X / N_o \ll 1$ for dilute solution). Therefore the equality of the chemical potential gives

$$\mu_1(T, P_1) = \mu_2(T, P_2) \Rightarrow \mu^o(T, P_1) = \mu^o(T, P_2) - (N_X / N_o) kT \quad (24)$$

where we have used $\ln(1 - N_X / N_o) \sim -N_X / N_o$. The pressure difference $P_2 - P_1 = \Delta P$ is relatively small, so we can expand $\mu^o(T, P_2)$ as $\mu^o(T, P_1) + \Delta P \cdot \partial \mu^o / \partial P$, where $\partial \mu^o / \partial P$ is the molecular

volume v of the solvent (see Exercise 2). Thus we obtain the osmotic pressure proportional to the solute concentration.

$$\Delta P = (N_X/N_o)kT/v \quad (25)$$

Exercise 2. The Maxwell relations

Show $\frac{\partial \mu^o}{\partial P} = v$.

Starting from Eq. (19) for a solution of two chemical components, and from Exercise 1, we have

$$\left(\frac{\partial G}{\partial P}\right)_{T,N_1,N_2} = V, \left(\frac{\partial G}{\partial N_1}\right)_{T,P,N_2} = \mu_1 \quad (26)$$

Therefore

$$\frac{\partial V}{\partial N_1} = \frac{\partial^2 G}{\partial N_1 \partial P} = \frac{\partial \mu_1}{\partial P} \quad (27)$$

This is one example of Maxwell's relations. If the component 1 of a dilute solution is the solvent, $\frac{\partial \mu_1}{\partial P} = \frac{\partial \mu^o}{\partial P} \cdot \frac{\partial V}{\partial N_1} = v_1$ is the volume per molecule for the solvent.

4. Thermodynamics of dynamic phenomena

So far we have considered thermodynamics of equilibrium states. In nature, most of the phenomena we encountered are not in equilibrium. There are no general thermodynamic theories for an arbitrary non-equilibrium macroscopic system. However, often we can assume a system composed of small regions. Each region is small enough but still large on the microscopic scale, such that it can be described by a macroscopic state. This is the concept of local equilibrium. The entire system is not in equilibrium, but we can apply the thermodynamic principles to each local region regarded as in temporary equilibrium. A local region must contain a macroscopic number of molecules and the rate of change of the macroscopic state of the region must be on a time scale much longer than the molecular collision time which is of order 10^{-13} s. The idea is that within the local region the molecules have collided with each other sufficiently that they have come to a stationary state unchanging within the measurement time. In local equilibrium, the thermodynamic variables are each a function of position (on a scale much larger than the molecular sizes) and time (on a scale much longer than the molecular collision time). For example, hydrodynamics, the theory describes fluid flow, is based on such a concept.

Using the concept of local equilibrium, the principles of thermodynamics have been applied to study the dynamics of macroscopic states. So thermodynamics is not only applicable to equilibrium states, it has been applied to dynamic states.

Biology: cell membrane potential

The thermodynamic principles described here is not applicable to a living state of a biological system. For example, a living cell is necessarily an open system that has both influx and efflux of materials and energy. The state of a living cell cannot be defined by E and V . But the concept of local equilibrium can be applied to the fluid within a cell. Here is an example.

Ions play important roles in biological systems. Their chemical potentials include the charge effect, hence called electrochemical potentials. In the presence of an electrical potential Φ ,

$$\boxed{\mu_i = \mu_i^o + kT \ln C_i + z_i e \Phi} \quad (28)$$

where C_i is the concentration of ion species i , and z_i is its valency.

A living cell typically maintains an electrical potential difference across the cell membrane. One might think that it is due to the fact that the cell membrane has water channels that are permeable to small ions, but there are non-permeant large anions, such as DNA and proteins inside the cell. This would cause an equilibrium potential difference between the inside and outside of the cell, called the Donnan potential. Let's see how this comes about.

Consider only one permeant monovalent anion and one permeant monovalent cation. The anion's extracellular concentration is $C_-(1)$ and intracellular concentration $C_-(2)$. The corresponding cation concentration is $C_+(1)$ and $C_+(2)$. We assume they are capable of permeating through the membrane. In addition, there are intracellular non-permeant anions of concentration Z_- . Because of the extremely high energy cost for charge separation, the electro-neutrality is in general held in nature:

$$C_+(1) = C_-(1) \quad (29)$$

$$C_+(2) = C_-(2) + Z_- \quad (30)$$

Because of the permeability, the chemical potential of intracellular and extracellular permeant anion must be the same in equilibrium:

$$kT \ln C_-(1) = kT \ln C_-(2) - e \Phi \quad (31)$$

where Φ is the intracellular potential relative to the extracellular solution. Similarly for the permeant cation, we have

$$kT \ln C_+(1) = kT \ln C_+(2) + e \Phi \quad (32)$$

For a given membrane potential Φ , there are four equations, Eq. 29-32, for four unknowns. Thus $C_+(1)$, $C_-(1)$, $C_+(2)$, $C_-(2)$ can be determined from the membrane potential. Reversely, if the intracellular and extracellular ion concentrations are known, one can calculate the Donnan potential Φ . The major cellular ions are sodium Na^+ , potassium K^+ and chlorine Cl^- . Their measured concentrations strongly deviate from the prediction of a Donnan equilibrium. Historically the search for the cause of this deviation led to the discovery of sodium pump that actively (meaning requiring metabolic energy) moves Na ions out of the cell.

Expanding universe

One indisputable fact about our universe is that it is expanding, every galaxy is moving away from other galaxies. The expansion is accompanied by a uniform blackbody radiation. Blackbody radiation is emitted and absorbed by any matter. When the radiation and the matter come to equilibrium, the property of the radiation depends only on the temperature, totally independent of the nature of the matter.

Since the observable region of the universe is limited to the speed of light times the age of the universe (this edge is called the horizon), it is impossible to know what's beyond this horizon. We also don't know if the universe is finite or infinite. One possibility is that it will go on expanding forever. Another possibility is that the expansion will end and then recontracts. An exceptionally lucid description of the early universe has been given by Steven Weinberg in a book titled *The First Three Minutes*. Thermodynamics is the foundation for this description.

The theory of blackbody radiation is described by its spectral energy intensity

$$du = \frac{8\pi h}{c^3} \frac{v^3 dv}{e^{hv/kT}-1} = \frac{8\pi ch}{\lambda^5} \frac{d\lambda}{e^{hc/kT\lambda}-1} \quad (33)$$

where u is the radiation energy per unit volume at frequency ν or wavelength λ . $\lambda = c/\nu$. c is the speed of light. This formula was first determined by Planck in 1900 based on experimental evidence. It contained two revolutionary features. First, in order to derive this formula, Planck had to assume that the radiation energy consists of discrete photons (each with energy $h\nu$); previously radiation energy was always thought to be wave energy. Second, the formula required the introduction of a new physical quantity h , the Planck constant. These revolutionary features began the quantum physics. Once the spectral energy density is known, all the thermodynamic quantities of blackbody radiation can be calculated, just like the case of classical ideal gas. For example, the radiation energy in volume V is $E = V \frac{8\pi^5 (kT)^4}{15 (ch)^3}$, the entropy in volume V is $S = Vk \frac{32\pi^5 (kT)^3}{45 (ch)^3}$, the radiation pressure is $P = \frac{8\pi^5 (kT)^4}{45 (ch)^3}$, and the number of photons in volume V is $N = V16\pi\zeta(3) \frac{(kT)^3}{(ch)^3}$. (the symbol $\zeta(3) = 1.202 \dots$.)

The big bang created a primordial plasma at an extremely high temperature in which blackbody radiation was strongly interacting with the matter. As the universe expanded, both matter and radiation cooled. When the universe was approximately 0.7 million years old, the temperature dropped to about $3000^\circ K$, the dominant matter including electrons and nuclei combined to make stable neutral atoms, mostly hydrogen and helium, which do not interact strongly with radiation. Thus the blackbody photons, at that time $T \sim 3000^\circ K$, became free and have been traveling without interacting with matter or with each other ever since. By now, its temperature has dropped to $2.7^\circ K$. Its spectrum still described by Eq. (33) is mainly in the microwave region, hence called the cosmic microwave background (CMB).

Since the CMB is free of interaction, the total number of photons is conserved during the expansion. Note that in all the thermodynamic functions, only T and V are variables. The number of

photons N has a VT^3 dependence. Therefore during the expansion, VT^3 is constant. S also has a VT^3 dependence, so the expansion of the universe is called an adiabatic expansion.

Suppose the size of the universe increases by a factor $f (>1)$. The volume of the universe increases by a factor f^3 , i.e., $V \rightarrow Vf^3$, then temperature must decrease by a factor $1/f$, $T \rightarrow T/f$. Since the E has a VT^4 dependence, it decreases with temperature by a factor $1/f$, $E \rightarrow E/f$ during the expansion. One might wonder where did the energy go? Like a gas in adiabatic expansion, the radiation performs work (hence loses energy) in adiabatic expansion. Keeping VT^3 as a constant, we let

$$E = aT, \quad T = \frac{b}{V^{1/3}}, \quad P = \frac{E}{3V} = \frac{aT}{3V} = \frac{ab}{3} \frac{1}{V^{4/3}} \quad \text{where } a \text{ and } b \text{ are constants.}$$

Then $E_{final} - E_{initial} = \Delta E = - \int_V^{f^3V} P dV = ab \frac{1}{V^{1/3}} \left(\frac{1}{f} - 1 \right) = aT \left(\frac{1}{f} - 1 \right) = E \left(\frac{1}{f} - 1 \right)$. The work accounts for the energy lost.