

4 Thermodynamics and Statistical mechanics

4.1 System and environment

The system is some portion of matter that we separate using real walls or only in our mind, from the other part of the universe. Everything outside the system that has a direct effect on its behaviour we call the environment. For example: the gas in a container can be the system and the moveable piston and the Bunsen burner can be the environment.

We must choose suitable and observable quantities to describe the behaviour of the system. The bulk properties of the system as macroscopic are called thermodynamic variables. There are two classes of these variables

The so called extensive state variables are additive quantities as:

V volume, m mass, E energy

The mass of a combined or united system is the sum of the individual masses they are characteristic for a portion of the system.

The so called intensive state variables are equalizing quantities as:

p pressure, T temperature

The intensive state variables can be ordered to any point of a system

4.2 Basic concepts of thermodynamics

4.2.1 Thermal equilibrium

When the distribution of the intensive parameters inside a system is homogeneous, then, the system is in thermal equilibrium. When all the intensive parameters of two systems – which are in equilibrium – are the same; then these systems are in thermal equilibrium with each other.

The zeroth law of thermodynamics states:

If A and B are each in thermal equilibrium with a third body C , then A and B are in thermal equilibrium with each other.

4.2.2 Concept of internal energy

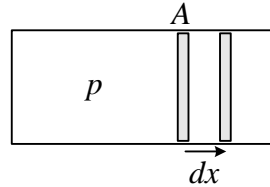
The internal energy of a many-particle system include the kinetic energy of the so called disordered molecular motion and the potential energy of the molecular interactions (Van der Waals) but doesn't contain the motion of matter in bulk appears to be "ordered" and the potential energy belongs to the interaction with external fields.

The next question arises, how can we change the internal energy of a many-particle system?

4.2.3 Work

Consider a gas inside a cylinder, one wall of which is a movable piston. Denote the pressure of the gas by p , it is the force per unit area:

$$p = \frac{F}{A}$$



If one wall of the container is moveable the force exerted by the gas may produce a displacement dx of the wall. Therefore the elementary work done by the gas:

$$dW' = Fdx = pA dx = pdV ,$$

where $dV = A dx$ is the change in volume of the gas. Since the work done by the gas (system) and the work done by the environment correspond to the same displacements and the two forces equal and opposite, the two works are equal in magnitude but have opposite signs.

The elementary work done by the environment on the system is:

$$\delta W = -pdV$$

The elementary work done by system:

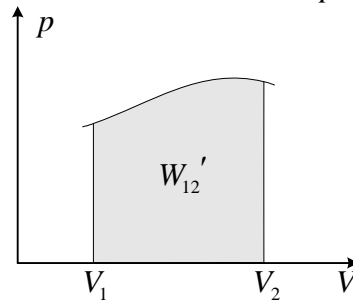
$$\delta W' = pdV$$

$$\delta W = -\delta W'$$

If the volume changes from V_1 to V_2 the finite work done by environment is:

$$W = -\int_{V_1}^{V_2} pdV$$

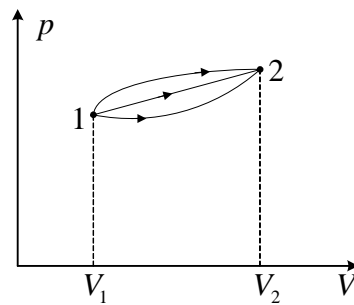
To compute the integral we must know the relation between p and V (that is the equation of state). If this relation is known we can draw the so called p - V diagram.



The geometrical meaning of the integral is the area under the curve. So the work done by the system in going from V_1 to V_2 :

$$W'_{12} = \int_{V_1}^{V_2} pdV$$

This figure indicates several processes between all of which take a system from state 1 to state 2. Since the area under each curve is different, the work done in each process is also different.



We can state, that the work depends on the process. It is often called process characteristic, or process variable.

If the gas expands $dV > 0$, and

$$\delta W' = pdV > 0, \text{ but } \delta W = -pdV < 0.$$

If the environment compress the gas $dV < 0$, and

$$\delta W' = pdV < 0, \text{ but } \delta W = -pdV > 0.$$

If work is done on the system we can say that its internal energy changes. So this is the so called “ordered” way to change the internal energy of a system.

4.2.4 Heat

Consider a gas inside a rigid container. If we bring a hot body, such as a flame, close to the container we observe an increase in temperature and pressure of the gas. This suggests that the energy of the molecules has also increased. This type of energy transfer is called heat and denoted by Q . This energy transfer is due to the large number of energy exchanged between the molecules of the system and the molecules of the surrounding.

The heat is considered $Q > 0$ positive if the system gains energy (so it is absorbed) the heat is $Q < 0$ negative if the system loses energy (so it is given off by the system). If there is no net exchange of energy between two systems, we say that they are in thermal equilibrium. In such case there is no net heat transfer.

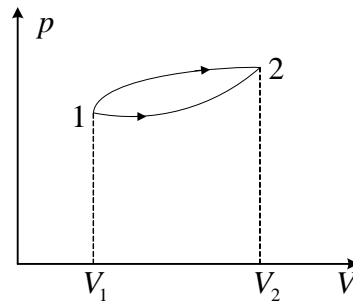
4.3 Conservation of energy, *The first law of thermodynamics*

The conservation of the energy for a many-particle system states that the change of internal energy of a system is equal to the heat absorbed plus the external work done on the system.

$$\Delta E = Q + W$$

The statement above is called the first law of thermodynamics.

It is important to recognize that the internal energy of a system depends only on the state of the system because it is determined by the energy distribution of the molecules in the state considered. We can say that the internal energy is a state variable. The change of the internal energy is independent of the process taken.



ΔE is the same for both processes shown on the figure.

Consider the first law of thermodynamics:

$$Q = \Delta E - W$$

The heat Q must also depend on the path since W depends but ΔE doesn't depend.

The first law for a finite process:

$$\Delta E = Q + W ,$$

and for an elementary small process:

$$dE = \delta Q + \delta W$$

or

$$dE = \delta Q - p dV .$$

4.4 Temperature

An important concept related to the sensations of hot and cold is that of temperature.

When we feel a “hot” body we say it has high temperature. When we feel a “cold” body we say its temperature is low.

We learned to define and measure the temperature of a body long before we understand its physical meaning. The instrument used to make the measurement is called thermometer.

Temperature is measured by observing the changes in some physical property (for example: the length of a liquid column in a capillary tube).

In the Celsius scale the unit of temperature is a degree, denoted by $^{\circ}\text{C}$. With the value of 0°C assigned to the temperature of melting ice, and 100°C to the temperature of boiling water both at standard atmospheric pressure.

4.4.1 The ideal Gas Temperature

Some properties of a gas are so sensitive to temperature changes that they may be used to measure the temperature of the gas. Let us consider a mass of gas that at a certain temperature occupies a volume V . The pressure of the gas designated as p . Boyle recognised that if the temperature does not vary the product of the pressure times volume remains constant:

$$pV = \text{constant}$$

This result is known as Boyle's law. A process during which the temperature does not vary is called an isothermal transformation. It is also an experimental result that, for a given mass of gas the constant depends on the temperature. Therefore, the value of the product pV for a given mass of gas in an indicator of the temperature of the gas. We shall define the gas temperature as a quantity proportional to the product pV , so we may write:

$$pV = CT$$

When the gas is at the freezing point of water the pressure is p_0 and volume is V_0 , at the boiling point p_1 , V_1 and T_{100} are the corresponding temperature.

$$p_0V_0 = CT_0, \text{ and } p_1V_1 = CT_{100}$$

Next we decide that between T_0 and T_{100} we measure 100 units:

$$p_1V_1 - p_0V_0 = C(T_{100} - T_0)$$

$$p_1V_1 - p_0V_0 = 100C$$

Taking the ratio of the two equations:

$$\frac{p_0V_0}{p_1V_1 - p_0V_0} = \frac{T_0}{100},$$

we can obtain:

$$T_0 = 100 \frac{p_0V_0}{p_1V_1 - p_0V_0}$$

It has been observed that the value of T_0 is:

$$T_0 = 273,15 \text{ K} .$$

The unit of the gas temperature scale is called Kelvin scale and designated by K. On this scale the freezing point of water is $T_0 = 273,15 \text{ K}$, and the boiling point is $T_{100} = 373,15 \text{ K}$. The general rule is:

$$K = ^\circ C + 273,15$$

If we have n moles of a gas we may write in the form:

$$pV = nRT$$

Where R is a new constant, essentially the same for all gases and is called the gas constant, its experimentally determined value is:

$$R = 8,31 \frac{\text{J}}{\text{molK}} .$$

If the mass of the gas is m and the molar mass is M then: $n = \frac{m}{M}$, and the state equation is:

$$pV = \frac{m}{M} RT ,$$

$$pV = nRT$$

The equation relates the pressure, volume and the temperature is called the equation of state of the gas. Gases follow this equation only at high temperatures and low densities.

A gas that follows this equation at all temperatures and densities is called an ideal gas, and T is called absolute temperature.

If N is the number of molecules of the gas, and N_A is Avogadro's number, the number of moles of the gas is:

$$n = \frac{N}{N_A}, \text{ and}$$

$$pV = N \frac{R}{N_A} T$$

Introducing the Boltzmann's constant as:

$$k = \frac{R}{N_A} = 1,38 \cdot 10^{-23} \frac{J}{K},$$

The state equation can be written:

$$pV = NkT$$

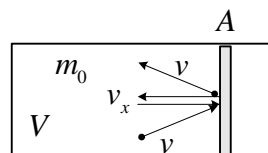
4.5 Ideal Gas. Microscopic Description

From the microscopic point of view we define an ideal gas by making the following assumptions:

1. A gas consists of particles called molecules.
2. The molecules are in random motion and obey Newton's laws of motion. They move in all directions and with various speeds.
3. The total number of molecules is large.
4. The volume of the molecules is a negligibly small fraction of the volume occupied by the gas.
5. No appreciable forces act on the molecules except during a collision. (Between two collisions molecules move uniformly.)
6. Collisions are perfectly elastic and are of negligible duration.
7. Consider now mono-atomic gas.

4.5.1 Kinetic calculation of pressure

Let us now calculate the pressure of an ideal gas from kinetic theory. Consider ideal gas in a container. Determine the force exerted by the molecules collide with the wall A.



Let m_0 be the mass of a molecule and v its speed. Denote the x component of velocity which is perpendicular to the wall by v_x . After the elastic collision with the wall, the change of the linear momentum:

$$\Delta p_x = 2m_0v_x.$$

If n is the number of molecules in unit volume:

$$n = \frac{N}{V}.$$

During a given time Δt only those molecules can reach the wall and collide, whose distance from the wall is less than $v_x \Delta t$. During Δt time $nv_x \Delta t A$ molecules collide. The total change of linear momentum is:

$$\Delta p_x nv_x A \Delta t.$$

The force exerted by the gas molecules, when they collide with the wall:

$$F = \frac{\Delta p}{\Delta t} = \frac{\Delta p_x n v_x A \Delta t}{\Delta t} = 2m_0 v_x n v_x A.$$

The pressure is the force over the area:

$$p = \frac{F}{A} = 2m_0 v_x^2 n.$$

It is better to suppose that only the half of molecules move in one direction, and the other half away from the wall, so we can reduce by 2:

$$p = m_0 v_x^2 n.$$

Actually, since the molecules move with different velocities we must use the average value

$$p = m_0 \overline{v_x^2} n.$$

We may assume that if the gas homogeneous the average molecular velocity is the same in any direction:

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2},$$

and

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}.$$

$$\overline{v^2} = 3\overline{v_x^2}.$$

Apply that $n = \frac{N}{V}$, and $\overline{v_x^2} = \frac{\overline{v^2}}{3}$:

$$p = m_0 \frac{\overline{v^2}}{3} \frac{N}{V}$$

$$pV = \frac{1}{3} m_0 \overline{v^2} N,$$

$$pV = \frac{2}{3} \frac{1}{2} m_0 \overline{v^2} N.$$

Introduce the average kinetic energy $\overline{\varepsilon}$ of a molecule, so:

$$\frac{3}{2} pV = N\overline{\varepsilon}.$$

In case of ideal gas the internal energy is kinetic energy of the disordered molecular motion, and the Van der Waals potential energy is negligible. So $N\overline{\varepsilon} = E$ is just the total internal energy of the ideal gas:

$$E = \frac{3}{2} pV$$

Comparing this result with the ideal gas equation:

$$pV = NkT,$$

$$E = \frac{3}{2} NkT.$$

The average kinetic energy, and so the internal energy of a gas directly proportional to the absolute temperature:

$$pV = \frac{2}{3} \overline{\varepsilon} N,$$

$$pV = NkT, \text{ and so:}$$

$$\frac{2}{3} \overline{\varepsilon} = kT$$

$$\bar{\varepsilon} = \frac{3}{2} kT .$$

The average kinetic energy of a gas molecule is related to the absolute temperature. Since by definition an ideal gas has no potential energy the total internal energy of an ideal gas of N particles is then:

$$E = N\bar{\varepsilon} = \frac{3}{2} NkT$$

Consider again the average kinetic energy of a molecule:

$$\bar{\varepsilon} = \frac{3}{2} kT ,$$

and

$$\begin{aligned} \bar{\varepsilon} &= \frac{1}{2} m_0 \overline{v^2} \\ \frac{3}{2} kT &= \frac{1}{2} m_0 \overline{v^2} , \\ \overline{v^2} &= \frac{3kT}{m_0} \end{aligned}$$

So the average value of the square of the velocity is proportional to the absolute temperature T . The square root of $\overline{v^2}$ is called root-mean-square speed v_{rms} :

$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m_0}} = \sqrt{\frac{3RT}{M}}$$

here we used that:

$$\begin{aligned} NkT &= \frac{m}{M} RT = \frac{m_0 N}{M} RT , \\ \frac{kT}{m_0} &= \frac{RT}{M} . \end{aligned}$$

As we calculated the internal energy of the gas we supposed that the molecules have only random translational motion and kinetic energy. It is true for a mono-atomic gas. In case of diatomic or polyatomic gas the molecules can rotate beside the translation

The number of velocity components needed to describe the motion of a molecule completely is called the number of degrees of freedom denoted by f :

for mono-atomic gas $f = 3$

for diatomic gas $f = 5$

for polyatomic gas $f = 6$

For a diatomic molecule there are two possible axes of rotation perpendicular to each other.

Using the concept of freedom energy of the ideal gas:

$$E = \frac{f}{2} pV = \frac{f}{2} NkT$$

The average energy of a molecule:

$$\bar{\varepsilon} = \frac{f}{2} kT$$

The principle of equipartition of energy states, that for any degree of freedom for any molecule the same average energy is associated that is:

$$\bar{\varepsilon}_1 = \frac{1}{2}kT$$

The finite change of the internal energy of the ideal gas with f degree of freedom:

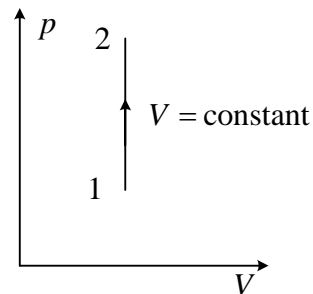
$$\Delta E = \frac{f}{2}Nk\Delta t = \frac{f}{2}\frac{m}{M}R\Delta t$$

4.6 The application of the First Law of Thermodynamics for special transformations of ideal gas

4.6.1 Isochoric transformation

In case of isochoric transformation the volume is kept constant:

$$V = \text{constant} .$$



The connection between pressure and temperature:

$$pV = \frac{m}{M}RT$$

$$\frac{p}{T} = \frac{mR}{MV} = \text{constant} ,$$

$$\frac{p_1}{T_1} = \frac{p_2}{T_2} .$$

Apply the first law of thermodynamics:

$$\Delta E_{12} = Q_{12} + W_{12}$$

As the volume is constant there is no work done by the environment, $W_{12} = 0$, therefore:

$$Q_{12} = \Delta E_{12} = \frac{f}{2}\frac{m}{M}R\Delta T_{12}$$

Introduce the next expression which is called specific heat at constant volume:

$$c_v = \frac{f}{2}\frac{R}{M}$$

This quantity is different for different gases. The unit is

$$[c_v] = \frac{J}{kgK} .$$

The heat can be written as:

$$Q_{12} = c_v m \Delta T$$

The product of the molar mass M and the specific heat is called molar specific heat:

$$C_V = c_V M = \frac{f}{2} R,$$

and its unit is:

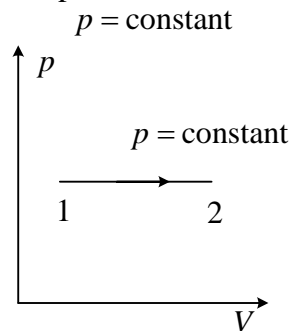
$$[C_V] = \frac{J}{molK}$$

Using the molar specific heat:

$$Q_{12} = C_V n \Delta T.$$

4.6.2 Constant-pressure process

We enclose the gas in a cylinder with a piston that moves so as to maintain constant pressure.



The ideal gas state equation:

$$pV = \frac{m}{M} RT$$

$$\frac{V}{T} = \frac{mR}{Mp} = \text{constant}$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2},$$

Apply the first law of thermodynamics:

$$\Delta E_{12} = Q_{12} + W_{12}$$

The change of the internal energy:

$$\Delta E_{12} = \frac{f}{2} \frac{m}{M} R \Delta T.$$

The work done by the environment in case of constant pressure process:

$$W_{12} = -\int_1^2 p dV = -p \int_1^2 dV = -p(V_2 - V_1)$$

Apply the state equation of the ideal gas for the first and second state:

$$pV_1 = \frac{m}{M} RT_1, \text{ and } pV_2 = \frac{m}{M} RT_2,$$

that is:

$$p(V_2 - V_1) = \frac{m}{M} R(T_2 - T_1) = \frac{m}{M} R \Delta T_{12}$$

Inserting into the first law:

$$\frac{f}{2} \frac{m}{M} R \Delta T_{12} = Q_{12} - \frac{m}{M} R \Delta T_{12}$$

$$Q_{12} = \left(\frac{f}{2} \frac{R}{M} + \frac{R}{M} \right) m \Delta T_{12} = \left(c_v + \frac{R}{M} \right) m \Delta T_{12}$$

Introduce the heat at constant pressure as:

$$c_p = \left(\frac{f}{2} + 1 \right) \frac{R}{M},$$

this quantity is different for different gases.

The heat:

$$Q_{12} = c_p m \Delta T_{12}$$

The same way as before the molar specific heat is defined as:

$$C_p = c_p M = \left(\frac{f}{2} + 1 \right) R.$$

Note that in all cases C_p is greater than C_v , because at constant volume all heat absorbed is stored as internal energy, but at constant pressure the heat absorbed is stored as the change of the internal energy and some additional work is done.

$$c_p = c_v + \frac{R}{M}, \text{ or } C_p = C_v + R$$

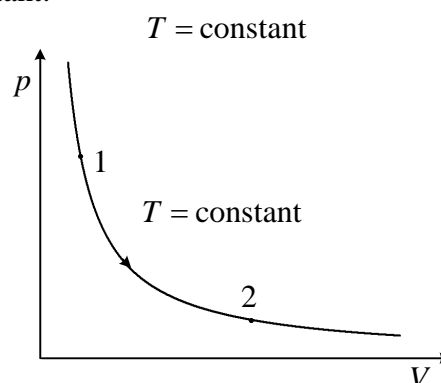
The above statement is called Robert-Mayer equation.

The ratio of the constant pressure specific heat to the constant volume specific heat is called adiabatic exponent:

$$\gamma = \frac{c_p}{c_v}, \text{ or } \gamma = \frac{C_p}{C_v} = \frac{\frac{f+2}{2} R}{\frac{f}{2} R} = \frac{f+2}{f}.$$

4.6.3 Isothermal process

The temperature is kept constant:



$$pV = \frac{m}{M} RT = \text{constant},$$

$$p_1 V_1 = p_2 V_2.$$

Apply the first law of thermodynamics:

$$\Delta E_{12} = Q_{12} + W_{12}.$$

In case of ideal gas the change of internal energy:

$$\begin{aligned}\Delta E_{12} &= \frac{f}{2} \frac{R}{M} M \Delta T_{12} = 0, \\ 0 &= Q_{12} + W_{12} \\ -W_{12} &= Q_{12} \\ W_{12}' &= Q_{12}\end{aligned}$$

The energy entering the system as heat Q_{12} is equal to the work done by the system W_{12}' .

Determine the work done by the environment, apply the definition of work done:

$$W_{12} = -\int_1^2 p dV = -\int_{V_1}^{V_2} \frac{p_1 V_1}{V} dV = -p_1 V_1 \ln \frac{V_2}{V_1}$$

we used that: $p_1 V_1 = pV$.

4.6.4 Adiabatic process

An adiabatic process is one in which there is no heat transfer either into or out of a system; in other words:

$$Q_{12} = 0$$

Such a system is called thermally insulated. Applying the first law:

$$\begin{aligned}\Delta E_{12} &= Q_{12} + W_{12} \\ \Delta E_{12} &= W_{12},\end{aligned}$$

In elementary form:

$$dE = \delta W$$

Use the other form of the internal energy of an ideal gas:

$$E = \frac{f}{2} pV$$

The infinitesimal change is:

$$dE = \frac{f}{2} dpV + \frac{f}{2} p dV,$$

therefore:

$$\frac{f}{2} dpV + \frac{f}{2} p dV = -p dV,$$

we have applied the elementary work: $\delta W = -p dV$

$$\begin{aligned}\frac{f}{2} dpV &= -\frac{f+2}{f} p dV \\ \frac{dp}{p} &= -\frac{f+2}{f} \frac{dV}{V}\end{aligned}$$

The adiabatic exponent is:

$$\begin{aligned}\gamma &= \frac{C_p}{C_v} = \frac{f+2}{f}, \\ \frac{dp}{p} &= -\gamma \frac{dV}{V}\end{aligned}$$

Taking the integral between two states:

$$\int_1^2 \frac{dp}{p} = -\gamma \int_1^2 \frac{dV}{V}$$

$$\ln \frac{p_2}{p_1} = -\gamma \ln \frac{V_2}{V_1},$$

$$\ln \frac{p_2}{p_1} = \ln \left(\frac{V_1}{V_2} \right)^\gamma$$

$$\frac{p_2}{p_1} = \left(\frac{V_1}{V_2} \right)^\gamma,$$

finally:

$$p_2 V_2^\gamma = p_1 V_1^\gamma, \quad p V^\gamma = \text{constant}.$$

This equation is called Poisson equation.

Using the state equation as:

$$pV = nRT,$$

$$p = \frac{nRT}{V}$$

$$nR \frac{T}{V} V^\gamma = \text{constant},$$

therefore the Poisson equation between T and V is:

$$TV^{\gamma-1} = \text{constant}.$$