# 5. THERMODYNAMICS

As we saw in the first part of this textbook, Newtonian mechanics explains a wide range of phenomena on a macroscopic scale, such as motion of various bodies, and the planets of our solar system. The thermodynamics is concerned with the concepts of heat and temperature. As we shall see, thermodynamics is very successful in explaining the bulk properties of matter and correlation between these properties and the mechanics of atoms and molecules. A quantitative description of thermal phenomena requires a careful definition of the concepts of **temperature, heat and internal energy. T**he laws of thermodynamics provide us with relationship between heat flow, work, and internal energy of a system. In practice, suitable observable quantities must be selected to describe the overall behavior of a system. For example, the macroscopic quantities, pressure, volume and temperature are used to characterize the properties of a gas.

## 5.1 Density and pressure

The density of a homogeneous substance is defined as its mass per unit area

$$\rho = \frac{m}{V}\,. \tag{6.1}$$

The unit of density is kg/m$^3$. The density varies with temperature, since the volume of a substance is temperature dependent. Note that under standard conditions (0°C and atmospheric pressure) the densities of gases are about 1/1000 of the densities of solids and liquids. This implies that the average molecular spacing in a gas under these conditions is about ten times greater than in solid or liquid.

The pressure is defined as a force per unit area, where the force is understood to be acting perpendicular to the surface $A$

$$p = \frac{F}{A}\,. \tag{6.2}$$

The SI unit of pressure is N/m$^2$, which is called Pascal (Pa).

## 5.2 Thermal expansion of gases. Macroscopic description of an ideal gas.

The volume of a gas depends very much on the pressure as well as on the temperature. These dependences can be expressed by **Gay-Lussac`s and Charles` laws**. It was found experimentally that at a constant volume, the pressure of a gas is directly proportional to the thermodynamics temperature $T$ as

$$\frac{p}{p_0} = \frac{T}{T_0}\ ; \qquad V = \text{const.} \tag{6.3}$$

Where $T_0$ is the thermodynamic temperature of the freezing point, i.e. $T_0 = 273.15\,K$ and $p_0$ is a corresponding pressure. The relation between Celsius scale and thermodynamics scale (it will be defined later) is given by

$$T = t + 273.15\,. \tag{6.4}$$

We can transform (6.4) to the form which corresponds to the Celsius scale as

$$p = p_0 \frac{t + 273.15}{273.15} = p_0 (1 + \gamma t) \tag{6.5}$$

Where $\gamma$ is called **the coefficient of thermal expansion** and its value is $\frac{1}{273.15} K^{-1}$.

For a given amount of gas it was found that the volume of gas is directly proportional to the thermodynamics temperature when the pressure is constant

$$\frac{V}{V_0} = \frac{T}{T_0}\ ; \qquad p = \text{const.} \tag{6.6}$$

Where $T_0$ the thermodynamic temperature of the freezing is point and $V_0$ is corresponding volume. By the same procedure as we used before we obtain

$$V = V_0 (1 + \gamma t) \tag{6.7}$$

Both laws are accurate for real gases only if the pressure and density of the gas are not to height (for the pressures up to $10^5$ Pa, approximately) and the gas is not close to condensation. Such a low density gas is commonly referred to as **an ideal gas**. Most gases at room temperature and atmospheric pressure behave as ideal gases.

Now suppose an ideal gas. For a given quantity of a gas it is found experimentally, that the volume of a gas is inversely proportional to the pressure to it when the temperature is kept constant

$$pV = \text{const.}\ ; \ T = \text{const.} \tag{6.8}$$

This relation is known as **Boyle`s law**.

If these three laws are combined into single general equation we obtain **the equation of state of an ideal gas**

$$\frac{pV}{T} = \frac{p_0 V_0}{T_0}$$

or

$$pV = \frac{p_0 V_0}{T_0} T = \text{constant} \times \text{T} \tag{6.9}$$

To determine the constant $\frac{p_0 V_0}{T_0}$ we must incorporate the effect of the amount.

It is convenient to express amount of gas in a given volume in terms of **number of moles**, ***n***. By the definition, one mole of any substance is that mass of the substance that contains a specific number of molecules called **Avogadro`s number, $N_A$**. Its value is

$$N_A = 6.022 \times 10^{23} \text{ molecules/mol} \qquad (6.10)$$

**Avogadro`s number is defined to be number of carbon atoms in 12 grams of the isotope carbon 12.** The number of moles of a substance is related to its mass, *m*, by the relation

$$n = \frac{m}{M} \qquad (6.11)$$

Where *M* is a quantity called **the molecular weight** of the substance, usually expressed in g/mol. For example, the molecular weight of oxygen $O_2$ is 32 g/mol. Therefore, the mass of one mole of oxygen is 32 grams.

By the Avogadro`s hypothesis one mole of gases at the same temperature and pressure occupy the same volume. Thus for, so called **standard conditions**, that are $T_0 = 273.15 \text{ K}$, $p_0 = 1.01325 \times 10^5 \text{ Pa}$ one mole of gas occupies a volume $V_m = 22.4 \times 10^{-3} \text{ m}^{-3}$. Then we can write

$$\frac{p_0 V_0}{T_0} = \frac{p_0 V_m}{T_0} n = Rn \qquad (6.12)$$

Where *n* represents the number of moles, $R = \frac{p_0 V_m}{T_0}$ is called **the universal gas constant.** This constant has the same value for all gases $R = 8.314 \text{ J/K.mol}$. Substituting eq.(6.12) into eq.(6.9) gives

$$pV = nRT \qquad (6.13)$$

**This equation is general form of the equation of state of an ideal gas**.

## 5.3 Kinetic theory of gases

Up to now we have been discussed the properties of an ideal gas using macroscopic variables as pressure, volume and temperature. We shall now show that such large-scale properties can be described on a microscopic scale, where matter is treated as a collection of molecules. Newton`s laws of motion applied in a statistical manner to a collection of particles provide a reasonable description of thermodynamics processes.

## 5.4 Molecular model for the pressure of an ideal gas

This model shows that the pressure that the gas exerts on the wall of the container is a consequence of the collisions of the gas molecules with the walls. **The following assumptions will be made:**

1. The number of molecules and the average separation between them is large compared with their dimensions.
2. The molecules obey Newton`s law of motion, but the individual molecules move in random motion.
3. The molecules undergo elastic collisions with each other. In the collisions both kinetic energy and momentum are conserved.
4. The forces between molecules are negligible except during a collision. The forces between them are short-range; it means the molecules interact with each other only during a collision.
5. All molecules of gas are identical.
6. The gas is in thermal equilibrium with the wall of container. Hence, a wall will eject as many molecules at it absorbs.

Now we derive an expression for determination the pressure of an ideal gas containing of *N* molecules in a container of volume *V*. The container is assumed to be in the shape of cube with edges of length *d*.

Consider the collision of one molecule moving with the velocity $v$ toward the left -hand face, for example, as is shown in Fig.6.1. The molecule has velocity components $v_x$, $v_y$ and $v_z$. If the molecule collides with the wall elastically its *x* components of velocity is reversed, while *y* and *z* components remain unaltered. Before the collision is *x* component of momentum of the molecule $mv_x$ before the collision, and $-mv_x$ afterward. The change of the momentum of the molecule is by the law of conservation of momentum given by

$$\Delta p_x = mv_x - (-mv_x) = 2mv_x \tag{6.14}$$

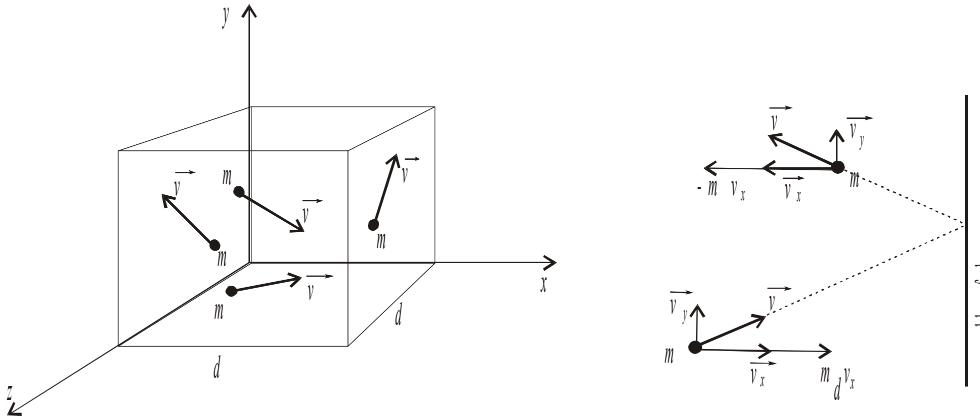

Fig.6. 1

In order that a molecule will make two successive collisions across the box and back again, it must travel a distance $2d$ along the *x* axis in a time $\Delta t$. If *F* is the average force exerted by a molecule on the wall in time $\Delta t$, then from Newton`s second law we have

$$F = \frac{\Delta p}{\Delta t} = \frac{2mv_x}{\Delta t} \tag{6.15}$$

This molecule will make many collisions with the wall, each separated by a time $\Delta t$ , which is the time it takes the molecule travel across the box and back again, a distance $2d$ . So

$$2d = v_x \Delta t$$

Rearranging of this expression gives the value of the time as

$$\Delta t = \frac{2d}{v_x} \tag{6.16}$$

Applying Newton`s second law of motion on this molecule gives

$$F = \frac{2mv_x}{\Delta t} = \frac{2mv_x}{2d / v_x} = \frac{mv_x^2}{d} \tag{6.17}$$

**The total force acting on the wall** is the sum of all such terms for all particles. Then **total pressure** is given by expression

$$P = \frac{\sum F_i}{A} = \frac{m}{d^3} \sum v_{xi}^2 \ . \tag{6.18}$$

The average value of $v_x^2$ is defined as

$$\overline{v}_x^2 = \frac{v_{x1}^2 + v_{x2}^2 + ... + v_{xn}^2}{N} = \frac{\sum_{i-1}^{n} v_{xi}^2}{N} , \tag{6.19}$$

Where *N* is the number of molecules and $V = d^3$ is the volume of container. Inserting the average value of $v_x^2$ into eq.(6.18) we can express the pressure in the form

$$P = \frac{Nm}{V} \overline{v}_x^2 \ . \tag{6.20}$$

From the vector analysis we know that the square of the speed for any particle is given by

$$v^2 = v_x^2 + v_y^2 + v_z^2 \ .$$

Where $v_x$ , $v_y$ , $v_z$ are *x, y, z,* components of velocity of the particle, respectively. Since there is no preferred direction for the molecules, the average values $\overline{v}_x^2$ , $\overline{v}_y^2$ and $\overline{v}_z^2$ are equal to each other. Then

$$\overline{v}_x^2 = \overline{v}_y^2 = \overline{v}_z^2 = \frac{1}{3} \overline{v}^2 . \tag{6.21}$$

Hence the pressure $P$ in eq.6.20 can be express as

$$P = \frac{1}{3} \frac{Nm}{V} \overline{v}^2 \tag{6.22}$$

or

$$P = \frac{2}{3}\frac{N}{V}\left(\frac{1}{2}m\overline{v}^2\right). \tag{6.23}$$

This tells us that **the pressure is proportional to the number of molecules per unit volume and to the average translational kinetic energy per molecule**.

## 5.5 Molecular interpretation of temperature

We can obtain some insight into the meaning of temperature by first writing the eq.(6.23) in more familiar form

$$PV = \frac{2}{3}N\left(\frac{1}{2}m\overline{v}^2\right). \tag{6.24}$$

Let us now compare this equation with the empirical equation of state for an ideal gas (eq.6.13):

$$PV = nkT \tag{6.25}$$

Recall that the equation of state is based on experimental facts concerning the macroscopic behavior of gases. Equating the right sides of these expressions, we find that

$$T = \frac{2}{3k}\left(\frac{1}{2}m\overline{v}^2\right), \tag{6.26}$$

where $k = \frac{R}{N_A}$ is the Boltzmann`s constant, $N_A = \frac{N}{n}$ is the Avogadro`s constant, *R* is the universal gas constant, *n* is the number of moles.

Since $\frac{1}{2}m\overline{v}^2$ is the average translational kinetic energy per molecule, we see that **temperature is a direct measure of the average molecular kinetic energy**.

By rearranging eq.(6.26) we can relate the translational molecular kinetic energy to the temperature:

$$\frac{1}{2}m\overline{v}^2 = \frac{3}{2}kT. \tag{6.27}$$

This equation says that **the average translational kinetic energy per molecule is** $\frac{3}{2}kT$ **.** Since

$$\overline{v}_x^2 = \frac{1}{3}\overline{v}^2$$

it follows, that

$$\frac{1}{2}m\overline{v}_x^2 = \frac{1}{2}kT. \tag{6.28}$$

In a similar manner, for the *y* and *z* motions it follows that

$$\frac{1}{2}m\bar{v}_y^2 = \frac{1}{2}kT \qquad (6.29)$$

$$\frac{1}{2}m\bar{v}_z^2 = \frac{1}{2}kT\,. \qquad (6.30)$$

Thus, each translational **degree of freedom** contributes an equal amount of energy to the gas $\frac{1}{2}kT$. Note that **the degree of freedom refers to the number of independent means by which a molecule can possess energy**.

This result, known as **the theorem of equipartition of energy**, says that the energy of a system in thermal equilibrium is equally divided among all degrees of freedom. Therefore we can say that the average kinetic energy per one degree of freedom is

$$K = \frac{1}{2}kT\,, \qquad \text{for one particle} \qquad (6.31)$$

$$K = \frac{1}{2}RT \ (6.32)$$

For a monoatomic gas with three degrees of freedom the average kinetic energy is

$$K = \frac{3}{2}kT \qquad (6.33)$$

or for one mole

$$K = \frac{3}{2}RT\,. \qquad (6.34)$$

**The total translational kinetic energy** of *N* molecules of gas is simply *N* times the average energy per molecule as

$$K = N\left(\frac{1}{2}m\bar{v}^2\right) = \frac{3}{2}NkT\,. \qquad (6.35)$$

The square root of $\bar{v}^2$ is called **the root mean square speed.**

$$v_{rms} = \sqrt{\bar{v}^2} = \sqrt{\frac{3kT}{m}}$$

## 6.6 Work and heat in thermodynamics processes.

## First law of thermodynamics.

We can say that **heat** represent that part of the internal kinetic energy of a body, which is transferred to another body due to the temperature difference between them. However, this statement is valid only for the case when the volume of the body remains constant. Heat transferred from one body to another can not only increase internal energy of the second body but it can also do work.

Let us now calculate the work done in a very simple and common type of thermodynamic process: when there is the change in volume, such as when a gas expands.

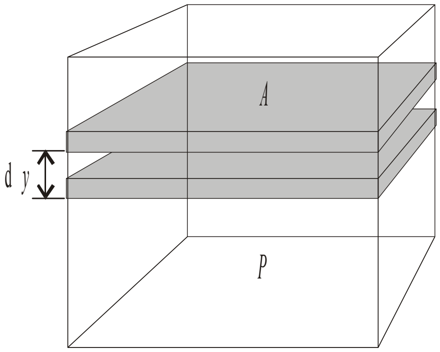

Fig.6. 2

The gas expands against the piston which area is *A*. The gas exerts a force $F = PA$ on the piston, where *P* is the pressure of the gas. The work done by the gas to move the piston an infinitesimal displacement $dy$ is

$$dW = F \cdot dy = PA\,dy = PdV \tag{6.37}$$

or

$$W = \int_V PdV\,, \tag{6.38}$$

Where $dV = Ady$ is the infinitesimal increase in volume. If the gas is compressed, so that $dy$ is pointed into a gas, the volume would be decreased and $dV < 0$. The work done by the gas in this case would then be negative.

We can now tie all these ideas together. We define the internal energy of the system as the sum of all the energy of the molecules of the system. We would expect that the internal energy of a system would be increased either doing work on a system, or by adding heat to it. The internal energy would be decreased if heat flowed out of the system, or work was done by the system on something else. Therefore it is reasonable to write **law of conservation of energy** in the following way

$$\Delta U = Q - W\,, \tag{6.39}$$

Where $\Delta U = U_f - U_i$ is the change in internal energy of the system between final state $U_f$ and initial $U_i$, *W* is the work done by the system.

Note that although both the *Q* and *W* depend on the path, the quantity $(Q - W)$ ( it is the change in internal energy) is independent on the path. This equation is called **the first law of thermodynamics**. The heat *Q* is positive when it enters the system and work *W* is positive when work is done by the system. When a system undergoes an infinitesimal change in state, where a small amount of heat, $dQ$, is transferred and a small amount of work, $\mathrm{d}W$, is done, the internal energy also changes by a small amount, $\mathrm{d}U$. Then **for infinitesimal processes we can express the first law of thermodynamics** as

$$\mathrm{d}U = \mathrm{d}Q - \mathrm{d}W . \tag{6.40}$$

Let us look at some special case. We consider **the isolated system** that is one that does not interact with the surroundings. In this case

$$\mathrm{d}Q = \mathrm{d}W = 0 \tag{6.41}$$

and from the first law of thermodynamics follows

$$\mathrm{d}U = 0 \tag{6.42}$$

and so $U_f = U_i$. We conclude that the internal energy of an isolated system remains constant.

## 5.6 Heat capacities of an ideal gas

Substances differ from one another in the quantity of heat needed to produce a given rise of temperature in a given mass. The amount of heat *Q* required to change the temperature of a system is found to be proportional to the mass *m* of the system and to change of $\Delta T$. It is expressed by equation

$$Q = mc\Delta T \tag{6.43}$$

Where *c* is the quantity characteristic of the material called **specific heat**. Its unit in SI units is J/kg.K. The specific heat also depends on how the process is heating. In eq.(6.43) we assume the process was carried out at constant atmospheric pressure. For such a process, we usually call *c*, **the specific heat at constant pressure** and use the symbol $c_P$. There is another possibility to add the heat, for example, the volume of material might to be kept constant and *c* is written as $c_V$, **the specific heat at constant volume**. However for solids and liquids the difference between $c_P$ and $c_V$ is small so that

$$c = c_V \doteq c_P = \frac{1}{m}\frac{Q}{\Delta T} = \frac{1}{m}\frac{\Delta U}{\Delta T} . \tag{6.44}$$

where *Q* is the heat added to the system, $\Delta U$ is the change in internal energy of a system and $\Delta T$ is the change in the temperature. However the specific heats of gases at constant volume $c_V$ and at constant pressure $c_P$ are quite different. This is easily explained in term of the first law of thermodynamics and kinetic energy.

We introduce **the molar capacity,** $C_V$, of a substance which is defined as the heat capacity per mole. It is the amount of heat required to raise one mol of the gas by one Kelvin at constant volume

$$C_V = \frac{1}{n}\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_{V = const.} = \frac{1}{n}\left(\frac{\mathrm{d}U}{\mathrm{d}t}\right) \qquad \text{(J/mol.K).} \tag{6.45}$$

Since $\mathrm{d}W = 0$ for a constant-volume process in eq.(6.40). Therefore, from eq.(6.35) we see that **the total internal energy *U* of molecules (or *n* moles) of an ideal and monatomic gas** is given by

$$U = \frac{3}{2} NkT = \frac{3}{2} nRT \tag{6.46}$$

If we differentiate this expression we give

$$\mathrm{d}U = \frac{3}{2} nR\mathrm{d}T \; . \tag{6.47}$$

For constant-volume process using eq.(6.45) we get

$$nC_V \mathrm{d}T = \frac{3}{2} nR\mathrm{d}T$$

or

$$C_V = \frac{3}{2} R \; . \tag{6.48}$$

**The molar heat capacity at constant pressure** $C_P$ is defined as

$$C_P = \frac{1}{n}\left(\frac{\mathrm{d}Q}{\mathrm{d}T}\right)_{P=const.} \qquad \text{(J/mol.K)}. \tag{6.49}$$

Now we can find **the relation between the molar heat capacity at constant pressure and the molar heat capacity at constant volume**. We use the first law of thermodynamics in form

$$dQ = dU + dW \; . \tag{6.50}$$

Where $dW = PdV$ .is the elementary work done by the gas

Inserting eq.6.50 into eq.6.49 gives

$$C_P = \frac{1}{n}\left(\frac{dU}{dT}\right) + \frac{P}{n}\left(\frac{dV}{dT}\right)_{P=const} \tag{6.51}$$

For an ideal gas we can use the equation of state given by eq.(6.25) in differential form as

$$P\mathrm{d}V + V\mathrm{d}P = nR\mathrm{d}T \; . \tag{6.52}$$

Second terms in this equation equals zero because the process is isobaric one ($P$=constant) and then we have

$$\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_{P=const} = \frac{nR}{P} \; . \tag{6.53}$$

Substituting this expression into eq.(6.51) and using equation (6.45) we obtain

$$C_P = C_V + R \; . \tag{6.54}$$

We define the ratio as

$$\frac{C_P}{C_V} = \kappa \tag{6.55}$$

where $K$ is called **Poisson`s constant**.

**Conclusions:**

1. The molar heat capacity at constant pressure is greater that the molar heat capacity at constant volume by an amount *R* (universal gas constant).
2. For monatomic gas the molar heat capacity at constant volume has the value $C_V = {}^3\!/_2 R = 12.5$ J/mol.K.
3. From eq.(6.54) follows that the molar heat capacity at constant pressure for a monatomic gas equals $C_P = {}^5\!/_2 R = 20.8$ J/mol.K.
4. $\kappa$ is dimensionless quantity. Its value depends on the degrees of freedom. For monatomic gas $\kappa = 1.67$ and diatomic gas $\kappa = 1.4$, for example.
5. The values of $C_P$ and $\kappa$ are in excellent agreement with experimental values for monatomic gases, but in disagreement with the values for the more complex gases. This is not surprising since the value $C_V = \frac{3}{2}R$ was derived for a monatomic ideal gas.
6. A diatomic molecule has additional degree of freedom. The molecule has a significant moment of inertia about two axes that are perpendicular to its length and to each other. If the angular velocities are $\omega_x$ and $\omega_y$, respectively, then the energies associated with these two degrees of freedom are $\frac{1}{2}I\omega_y^2, \frac{1}{2}I\omega_z^2$ as is shown in Fig.6.3. For this molecule we can neglect the rotation about *x* axis

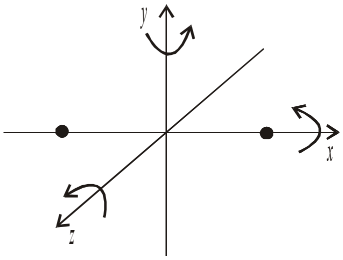

Fig.6 3

since the moment of inertia is negligible compared with those associated with the *z* and *y* axis. Thus there are five degrees of freedom: three associated with the translation motion and two associated with the rotational motion. Thus $C_V$ should be ${}^5\!/_2 R$ for one mole of a rigid rotator and $C_P = C_V + R = {}^7\!/_5 R$. Then $\kappa = \frac{C_P}{C_V} = 1.40$. But the agreement is not good for all diatomic molecules. For example, chlorine (Cl) has the value $\kappa = 1.35$ at room temperature. This is in contradiction with the equipartition theorem. The explanation of this disagreement can be given by the quantum theory only.

7.

## 5.7 Application of the first law of thermodynamics to some simple thermodynamics processes

For the quantities, which are expressed in the first law of thermodynamics

$$\mathrm{d}U = \mathrm{d}Q - \mathrm{d}W \tag{6.56}$$

Only the change in internal energy does not depend on the type of process (or path) but only on the temperature. The change of internal energy of *n* moles is expressed by equation (see expression 6.45) is given by

$$\mathrm{d}U = nC_V \mathrm{d}T\ . \tag{6.57}$$

The work done in taking a system from one state to another depends not only on the initial and final states but also on the type of process. We shall imagine that the gas is going from one state to another one **quasistatistically**, by which we mean that the process is carried out extremely slowly trough infinitesimally close equilibrium state. In this way pressure and temperature are defined for the system at all instant. Such a process is called **a reversible process**. For this process it is possible to determine dependences $P = P(V)$. For this case the infinitesimal work is expressed as

$$\mathrm{d}W = P\mathrm{d}V \tag{6.58}$$

and the total work

$$W = \int_{V_1}^{V_2} P(V)\mathrm{d}V\ . \tag{6.59}$$

Inserting eq.(6.57) and eq.(6.58) into first law of thermodynamics we obtain

$$\mathrm{d}Q = nC_V \mathrm{d}T + P(V)\mathrm{d}V\ . \tag{6.60}$$

We shall apply this law on different reversible processes.

### I.ISOCHORIC PROCESS (The constant-volume process)

In this process the volume is constant, it means $dV = 0$. Therefore the work done by the gas equals zero:

$$\mathrm{d}W = P\mathrm{d}V = 0\ . \tag{6.61}$$

Inserting this value into eq.(6.60) gives

$$\mathrm{d}Q = nC_V \mathrm{d}T$$

To find the total heat added to the system at constant volume we have to integrate this expression:

$$Q = nC_V \int_{T_i}^{T_f} dT$$

$$Q = nC_V (T_f - T_i). \tag{6.62}$$

From this equation we see that **all heat added to the gas is used to increase its internal energy**.

### II. ISOBARIC PROCESS (The constant-pressure process)

In this process the pressure of the gas remain constant, it means that $dP = 0$. The work done in this process equals

$$W = \int_{V_i}^{V_f} P\mathrm{d}V = P\int_{\mathrm{V_i}}^{\mathrm{V_f}} \mathrm{d}V = P(V_f - V_i) = nR(T_f - T_i) \tag{6.63}$$

Where we used the ideal gas law in differential form $PdV + VdP = nRdT$. From the first law of thermodynamics we obtain

$$Q = nC_V(T_f - T_i) + nR(T_f - T_i) = n(C_V + R)(T_f - T_i) = nC_P(T_f - T_i), \tag{6.64}$$

Where is used expression (6.54). When such a process occurs, the heat transferred and the work done is both nonzero.

### III. ISOTHERMAL PROCESS

If the temperature remains constant then $\mathrm{d}T = 0$ and therefore, the internal energy of the gas remains also constant, or

$$\mathrm{d}U = 0. \tag{6.65}$$

From eq.(6.60) we can see that all heat added to the gas is used to work done by the gas, or

$$Q = W = \int_{V_i}^{V_f} P(V)\mathrm{d}V = nRT\int_{\mathrm{V_i}}^{\mathrm{V_f}} \frac{\mathrm{d}V}{V} = nRT\ln\frac{V_f}{V_i} = nRT\ln\frac{P_i}{P_f}. \tag{6.66}$$

The isothermal expansion of the gas can be achieved by placing the gas in good thermal contact with a heat reservoir at the same temperature. If the gas expands isothermally, then $V_f \rangle V_i$ and we see that the work done by the gas is positive. If the gas is compressed isothermally, then $V_f \langle V_i$ and the work done by the gas is negative. Hence, for an isothermal process $\Delta U = 0$, and from the first law we conclude that the heat given up by the reservoir (and transferred to the gas) equals the work done by the gas, $Q = W$.

### IV. ADIABATIC PROCESS

In the adiabatic process no heat is allowed to flow into or out of the system, i.e. $\mathrm{d}Q = 0$. From the first law of thermodynamics we have

$$\mathrm{d}W = -\mathrm{d}U = -nC_V\mathrm{d}T$$

or

$$W = nC_V\left(T_i - T_f\right). \tag{6.67}$$

An adiabatic process can be achieved either by the thermally insulating system from its surroundings or by performing the process rapidly. From this result, we see that if the gas expands adiabatically, $W$ is positive, so $\Delta U$ is negative and the gas is lowered in temperature. Conversely, a gas is raised in temperature when it is compressed adiabatically.

Adiabatically processes are very important in engineering practice. Some common examples of adiabatic processes include the expansion of hot gases in an internal combustion engine, the compression stroke in a diesel machine or liquefaction of gases in a cooling system.

**Relation between *P* and *V* for an adiabatic process involving an ideal gas.**

In reality, true adiabatic processes cannot occur since a perfect heat insulator between a system and its surroundings does no exist. However, there are processes that are nearly adiabatic. For example, if a gas is compressed or expanded very rapidly, very little heat flows into or out the system. This process is nearly adiabatic such as in the cycle of a gasoline engine. For example, if a gas that is thermally insulated from its surroundings is allowed to expand slowly against the piston, the process is a quasi-static, adiabatic process.

Suppose that an ideal gas undergoes a quasi-static, adiabatic expansion. At any time during the process, we assume that the gas is in equilibrium state, so that the equation of state, $PV = nRT$, is valid. From the first law of thermodynamics follows that

$$p\mathrm{d}V + nC_V\mathrm{d}T = 0. \tag{6.68}$$

Let us differentiate the equation of state $PV = nRT$. We obtain

$$P\mathrm{d}V + V\mathrm{d}P = nR\mathrm{d}T \tag{6.69}$$

Or

$$\mathrm{d}T = \frac{P\mathrm{d}V + V\mathrm{d}P}{nR}. \tag{6.70}$$

Substituting $\mathrm{d}T$ into eq.(6.68) gives

$$\left(C_V + R\right)P\mathrm{d}V + C_V V\mathrm{d}P = 0. \tag{6.71}$$

Because $C_V + R = C_P$ we have

$$C_P P\mathrm{d}V + C_V V\mathrm{d}P = 0. \tag{6.72}$$

Using the definition of $\kappa$, (see eq.6.55) the equation (6.72) becomes

$$\frac{\mathrm{d}P}{P} + \kappa\frac{\mathrm{d}V}{V} = 0. \tag{6.73}$$

This equation is integrated to become

$$\ln P + \kappa \ln V = \text{constant} \tag{6.74}$$

or

$$PV^{\kappa} = \text{constant}\,. \tag{6.75}$$

This equation is one for the quasi-static adiabatic expansion or compression It is called **the Poisson's equation for the quasi-adiabatic process**..

**Example**

Air in the cylinder of a diesel machine at 20°C is compressed from an initial pressure of $10^5$ Pa. and volume of 800 $\text{cm}^3$ to a volume of 60 $\text{cm}^3$. Assuming the air behaves as an ideal gas ( $\kappa = 1.4$ ) and that compression is adiabatic, find the pressure and temperature.

Solution:

Using eq.(6.75) we find that

$$P_f = P_i \left( \frac{V_i}{V_f} \right)^{\kappa} = 37.6 \times 10^5 \text{ Pa}\,.$$

Since $PV = nRT$ is always valid during the process and sine no gas escapes from the cylinder

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f} \text{ or } T_f = T_i \frac{P_f V_f}{P_i V_i} = 826 \text{ K}\,.$$

**Example**

A cylinder contains 3 moles of helium gas at a temperature of 300 K. Determine

a) The amount of heat that must be transferred to the gas to increase its temperature to 500 K, if the gas is heated at constant volume

b) The amount of heat that must be transferred to the gas at constant pressure to raise the temperature to 500K.

Solution:

a) For the constant-volume process, the work done is zero. Therefore

$$Q_1 = nC_V \Delta T\,,$$

Where $C_V = 12.5 \text{ J/mol.K}$ for He and $T = 200 \text{ K}$. Calculation shows that

$$Q_1 = 7.5 \times 10^3 \text{ J}\,.$$

b) For a constant-pressure process is

$$Q_2 = nC_P \Delta T\,,$$

Where for He is $C_P = 20.8 \text{ J/mol.K}$. Then we give

$$Q_2 = 12.5 \times 10^3 \text{ J}\,.$$

In this process is the work done by the gas given

$$W = Q_2 - Q_1 = 5.0 \times 10^3 \text{ J}$$

.

## 5.8 ENTROPY. Reversible and irreversible processes

For the description of the thermodynamics processes introduced Clausius in 1860 a new quantity, which is called **entropy**. The entropy is state variable its value depends only on the state of system and not on the process taken. Consider a reversible (quasi-static) process between two equilibrium states. If $dQ_r$ is the heat absorb or expelled by the system during some small interval of the path we define the change in entropy between two equilibrium states as

$$\mathrm{d}S = \frac{\mathrm{d}Q_r}{T} \qquad \text{(J/K).} \qquad (6.76)$$

Where *T* is absolute temperature of the system in Kelvins.
It can be used to describe the state of system. The change in entropy, $\mathrm{d}S$, between two equilibrium states is given by the heat, $\mathrm{d}Q$, divided by the absolute temperature, *T*, of the system in this interval.

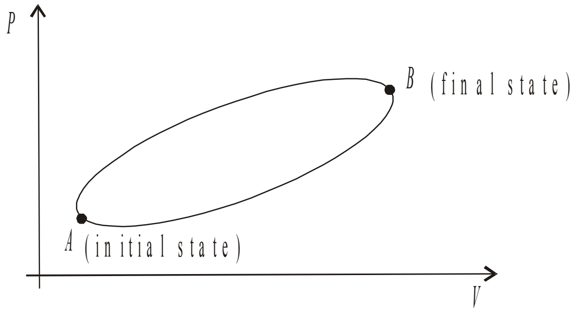

Fig.6 4

To calculate the change in entropy for a finite process, we must recognize that *T* is generally not constant. If $\mathrm{d}Q$ is the heat transferred when the system is at temperature *T*, then the change in entropy an arbitrary reversible process between initial and final states is

$$\Delta S = \int_i^f \frac{\mathrm{d}Q_r}{T} \qquad \text{(Reversible path).} \qquad (6.77)$$

That is, **the change in entropy of a system depends only on the properties of initial and final state**.

To calculate the change in entropy of an ideal gas going from one state to another state we can substitute the first law of thermodynamics eq.(6.56) and ideal gas equation (6.25) into definition of entropy. Thus we have

$$\mathrm{d}S = nC_V \frac{\mathrm{d}T}{T} + \frac{P}{T}\mathrm{d}V = nC_V \frac{\mathrm{d}T}{T} + nR\frac{\mathrm{d}V}{V}\,. \qquad (6.78)$$

To obtain the change in entropy we integrate this equation and we give

$$\Delta S = nC_V \int_{T_i}^{T_f} \frac{\mathrm{d}T}{T} + nR \int_{V_i}^{V_f} \frac{\mathrm{d}V}{V} = nC_V \ln\frac{T_f}{T_i} + nR\ln\frac{V_f}{V_i}. \tag{6.79}$$

**For a reversible process** Fig.(6.4) we have

$$\oint \mathrm{d}S = 0. \tag{6.80}$$

A process may be reversible if the system passes from the initial state to the final state through a succession of equilibrium states.

**An irreversible process** is one if the system and its surroundings cannot be returned to their initial states

Let us calculate the entropy changes during some particular processes.

**I. Isochoric process: $V$=constant ⇒ $V_i$=$V_f$**

$$\Delta S = nC_V \ln\frac{T_f}{T_i} = nC_V \ln\frac{P_f}{P_i}, \tag{6.81}$$

Where is used the equation of state in the form $\frac{P_i}{T_i} = \frac{P_f}{T_f}$.

**II. Isobaric process: $P$=constant ⇒ $P_i$=$P_f$**

Using equation of state for isobaric process we have $\frac{T_i}{T_f} = \frac{V_i}{V_f}$, then from eq.(6.79) we have

$$\Delta S = nC_V \ln\frac{T_f}{T_i} + nR\ln\frac{T_f}{T_i} = nC_P \ln\frac{T_f}{T_i} = nC_P \ln\frac{V_f}{V_i}. \tag{6.82}$$

**III. Isothermal process: $T$=constant**

$$\Delta S = nR\ln\frac{V_f}{V_i} = nR\ln\frac{P_i}{P_f}. \tag{6.83}$$

**IV. Adiabatic process:**

$$\mathrm{d}Q = 0 \;\Rightarrow\; \Delta S = 0. \tag{6.84}$$

## 5.9 CARNOT CYCLE. Carnot efficiency

It is easy to produce thermal energy by doing work. In 1824 a French engineer Sadi Carnot described a working cycle, now called **Carnot cycle** that showed that a heat engine operating in the ideal, reversible cycle between two heat reservoirs would be most efficient engine possible. Carnot engine works between four states as is shown in Fig. (6.5). The gas is **first expanded isothermally** path 1→2 at temperature *T*. To do so we can imagine the gas to be in contact with a height temperature heat reservoir at temperature *T*, which delivers heat $Q_{12}$ to working substance. **Next the gas is expanded**

**adiabatically path** 2→3, no heat is exchange and the temperature is reduced to $T_0$ . **The third step is isothermal compression**, 3→4, in contact with a low temperature heat reservoir at the temperature $T_0$ , during which heat $Q_{34}$ flow out of the gas. **In fourth step the gas is compressed adiabatically**, path 4→1, back to original state.

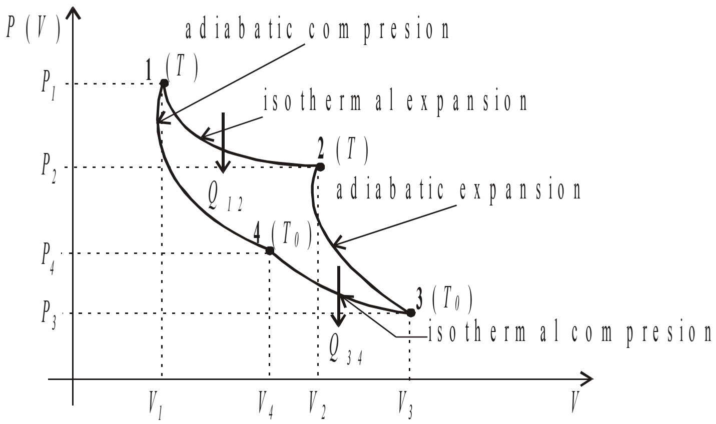

Fig.6 5

**I. Isothermal expansion (** *dT=0*)

*T* is constant it means that the internal energy remains constant. From first law the heat added to the gas from the high temperature reservoir equals the work done by the gas

$$Q_{12} = W_{12} = nRT \ln \frac{V_2}{V_1} . \tag{6.85}$$

The change in entropy for this process is

$$\Delta S_{12} = nR \ln \frac{V_2}{V_1} . \tag{6.86}$$

**II. Adiabatic expansion (** $\mathrm{d}Q = 0$ **)**

$$W_{23} = nC_V \left( T - T_0 \right) \tag{6.87}$$

and

$$Q_{23} = \Delta S_{23} = 0 . \tag{6.88}$$

**III. Isothermal compression (** d*T*=0 )

$$W_{34} = Q_{34} = nRT_0 \ln \frac{V_4}{V_3} < 0 \tag{6.89}$$

$$\Delta S_{34} = nR \ln \frac{V_4}{V_3} . \tag{6.90}$$

**IV. Adiabatic compression** (d*Q*=0)

$$W_{41} = nC_V(T - T_0) \langle 0 \tag{6.91}$$

$$\Delta S_{41} = Q_{41} = 0\,. \tag{6.92}$$

The net work done in one cycle by a Carnot engine is given by

$$\begin{aligned} W &= W_{12} + W_{23} + W_{34} + W_{41} = nRT\ln\frac{V_2}{V_1} + nRT_0\ln\frac{V_4}{V_3} + nC_V(T - T_0) + nC_V(T - T_0) = \\ &= nRT\ln\frac{V_2}{V_1} - nRT_0\ln\frac{V_3}{V_4} \end{aligned} \tag{6.93}$$

For the change in entropy for a reversible process we have

$$\Delta S_{12} + \Delta S_{23} + \Delta S_{34} + \Delta S_{41} = 0\,. \tag{6.94}$$

Inserting into this equation the changes in entropy during corresponding processes we have

$$nR\ln\frac{V_2}{V_1} + 0 + nR\ln\frac{v_4}{V_3} + 0 = \ln\frac{V_2}{V_1} + \ln\frac{v_4}{V_3} = 0 \tag{6.95}$$

From this equation we have expressed the relation between the volumes $V_1$, $V_2$, $V_3$ and $V_4$ :

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}\,. \tag{6.96}$$

Inserting eq.(6.96) into eq.(6.93) gives

$$W = nR(T - T_0)\ln\frac{V_2}{V_1}\,. \tag{6.97}$$

We denote the heat obtained by the gas from the high temperature reservoir with temperature $T$ in eq. (6.85) as $Q_{12} = Q$, so

$$Q = nRT\ln\frac{V_2}{V_1}\,. \tag{6.98}$$

**The efficiency of a heat engine** is the ratio of the net work done by the engine during one cycle to the heat taken in from the high temperature reservoir in one cycle

$$\eta = \frac{W}{Q} = \frac{T - T_0}{T} = 1 - \frac{T_0}{T}\,. \tag{6.99}$$

We can denote $Q_0 = |Q_{34}| = - Q_{34}$. Using eqs.(6.89, 6.93, 6.97) we obtain

$$W = Q - Q_0 \tag{6.100}$$

Then efficiency equals

$$\eta = \frac{Q - Q_0}{Q} = 1 - \frac{Q_0}{Q}\,. \tag{6.101}$$

**The efficiency of a heat machine depends on the height and low reservoirs temperatures**, respectively, as is shown in eq.6.99. Equation (6.101) shows that the efficiency is less that 1 as long as the heat $Q_0$ delivered to the low temperature reservoir is not zero.

## 5.10 The second law of thermodynamics

The second law of thermodynemics can be stated in many ways:

1. **The Kelvin-Planck statement** of this law is as follows: No cyclic process is possible whose only result is to transfer an amount of heat $Q$ from source at a single temperature totally into work.
2. **A perpetual-motion machine** of the second kind cannot be built.
3. **The Clausius statement** of second law of thermodynamics is as follows: No cycle process is possible whose only result is a flow of heat out of a system at one temperature and equal magnitude flow of heat into a second system at a higher temperature.

This statement tells us that heat does not flow spontaneously from a cold object to a hot object. On the base of second law of thermodynamics we can state so called **Carnot`s theorem:** All reversible engines operating between the same two temperatures have the same efficiency; no reversible engine operating between the same two temperatures can have a efficiency greater that this.

## 5.11 Thermodynamics temperature scale

The efficiency of reversible engine is independent of the working substance, it depends only on the two temperatures between which the engine works. The efficiency of heat machine is given by eq.(6.99) and eq.(6.101)

$$\eta = 1 - \frac{T_0}{T}$$

On the other hand the efficiency is given by the equation

$$\eta = 1 - \frac{Q_0}{Q}.$$

Equating of these equations follows immediately

$$\frac{T}{T_0} = \frac{Q}{Q_0}$$

or

$$T = T_0 \frac{Q}{Q_0}. \tag{6.102}$$

This equation is the basis for Kelvin or thermodynamics scale. To complete this definition we assign the arbitrary value of 273.16 to the temperature of the triple point of water and denote it as $T_{tr} = 273.16\ \mathrm{K}$ .

Then for a Carnot engine operating between two reservoirs at the temperature *T* and $T_{tr}$ we have

$$T = T_{tr} \frac{Q}{Q_{tr}}, \tag{6.103}$$

Where *Q* and $Q_{tr}$ are the heats exchange by a Carnot cycle with reservoirs at temperature *T* and $T_{tr}$. Eq.(6.102) is the definition of **the thermodynamic scale**. The thermodynamic scale is used the standard scale. It is independent of the substance used.

**The temperature of any substance can be obtained in the following manner**:

1. Take the substance through the Carnot cycle
2. Measure the heat *Q* absorb or expelled by the system at some temperature *T*
3. Measure the heat absorb or expelled by the system when it is at the temperature of the triple point of the water ( water, ice and vapor in equilibrium state)

Very low temperatures are difficult to obtain experimentally, because the fundamental feature of all cooling process is that the lower temperatures, the more difficult they are to go still lower. This experience has led to the formulation of the **third law of thermodynamics,** which states**: It is not possible to actually absolute zero in any finite number of processes**.

From equation (6.99) follows

$$\eta = 1 - \frac{T_0}{T}, \tag{6.104}$$

We can see that to obtain 100 % efficiency, the temperature $T_0$ must be equal zero. Since $T_0$ can never been zero, we see that a 100 % efficient heat engine is not possible.

**Example**

A cold reservoir is at 273 K, and the hotter reservoir is at 373 K. Show that it is impossible for a small amount of heat energy, say 8 J, to be transferred from the cold reservoir to the hot reservoir without decreasing the entropy of the universe and hence violating the second law.

Solution:

We assume that during the heat transfer, the two reservoirs don`t undergo a temperature change. The entropy change of the hot reservoir is given by

$$\Delta S_{hot} = \frac{Q}{T_{hot}} = 0.0214\ \mathrm{J/K}\ .$$

The cold reservoir loses heat, and its entropy change is

$$\Delta S_{cold} = \frac{Q}{T_{cold}} = -0.0293 \text{ J/K} .$$

The net entropy change of the universe is

$$\Delta S_{univ} = \Delta S_{cold} + \Delta S_{hot} = -0.0079 \text{ J/K} .$$

This is in violation of the concept that the entropy of the universe always increases in natural processes. That is, the spontaneous transfer of heat from a cold to a hot object cannot exist.