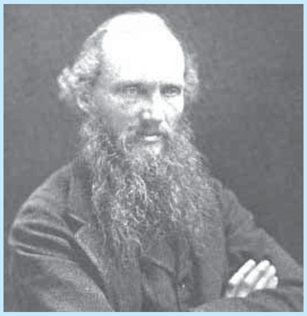
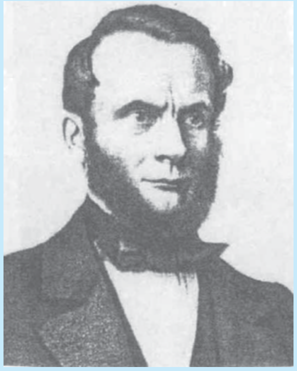
Pioneers of Thermodynamics



Lord Kelvin (William Thomson) (1824-1907), born in Belfast, Ireland, is among the foremost British scientists of the nineteenth century. Thomson played a key role in the development of the law of conservation of energy suggested by the work of James Joule (1818-1889), Julius Mayer (1814-1878) and Hermann Helmholtz (1821-1894). He collaborated with Joule on the so-called Joule-Thomson effect : cooling of a gas when it expands into vacuum. He introduced the notion of the absolute zero of temperature and proposed the absolute temperature scale, now called the Kelvin scale in his honour. From the work of Sadi Carnot (1796-1832), Thomson arrived at a form of the Second Law of Thermodynamics. Thomson was a versatile physicist, with notable contributions to electromagnetic theory and hydrodynamics.



Rudolf Clausius (1822-1888), born in Poland, is generally regarded as the discoverer of the Second Law of Thermodynamics. Based on the work of Carnot and Thomson, Clausius arrived at the important notion of entropy that led him to a fundamental version of the Second Law of Thermodynamics that states that the entropy of an isolated system can never decrease. Clausius also worked on the kinetic theory of gases and obtained the first reliable estimates of molecular size, speed, mean free path, etc.

A heat pump is the same as a refrigerator. What term we use depends on the purpose of the device. If the purpose is to cool a portion of space, like the inside of a chamber, and higher temperature reservoir is surrounding, we call the device a refrigerator; if the idea is to pump heat into a portion of space (the room in a building when the outside environment is cold), the device is called a heat pump.

In a refrigerator the working substance (usually, in gaseous form) goes through the following steps : (a) sudden expansion of the gas from high to low pressure which cools it and converts it into a vapour-liquid mixture, (b) absorption by the cold fluid of heat from the region to be cooled converting it into vapour, (c) heating up of the vapour due to external work done on the system, and (d) release of heat by the vapour to the surroundings, bringing it to the initial state and completing the cycle.

The coefficient of performance (α) of a refrigerator is given by

$$\alpha = \frac{Q_2}{W} \qquad (12.21)$$

where Q_2 is the heat extracted from the cold reservoir and W is the work done on the system–the refrigerant. (α for heat pump is defined as Q_1/W) Note that while η by definition can never exceed 1, α can be greater than 1. By energy conservation, the heat released to the hot reservoir is

$$Q_1 = W + Q_2$$

i.e.,

$$\alpha = \frac{Q_2}{Q_1 - Q_2} \qquad (12.22)$$

In a heat engine, heat cannot be fully converted to work; likewise a refrigerator cannot work without some external work done on the system, i.e., the coefficient of performance in Eq. (12.21) cannot be infinite.

12.11 SECOND LAW OF THERMODYNAMICS

The First Law of Thermodynamics is the principle of conservation of energy. Common experience shows that there are many conceivable processes that are perfectly allowed by the First Law and yet are never observed. For example, nobody has ever seen a book lying on a table jumping to a height by itself. But such a thing would be possible if the principle of conservation of energy were the only restriction. The table could cool spontaneously, converting some of its internal energy into an equal amount of mechanical energy of the book, which would then hop to a height with potential energy equal to the mechanical energy it acquired. But this never happens. Clearly, some additional basic principle of nature forbids the above, even though it satisfies the energy conservation principle. This principle, which disallows many phenomena consistent with the First Law of Thermodynamics is known as the Second Law of Thermodynamics.

The Second Law of Thermodynamics gives a fundamental limitation to the efficiency of a heat engine and the co-efficient of performance of a refrigerator. In simple terms, it says that efficiency of a heat engine can never be unity. According to Eq. (12.20), this implies that heat released to the cold reservoir can never be made zero. For a refrigerator, the Second Law says that the co-efficient of performance can never be infinite. According to Eq. (12.21), this implies that external work (W) can never be zero. The following two statements, one due to Kelvin and Planck denying the possibility of a perfect heat engine, and another due to Clausius denying the possibility of a perfect refrigerator or heat pump, are a concise summary of these observations.

Second Law of Thermodynamics

Kelvin-Planck statement

No process is possible whose sole result is the absorption of heat from a reservoir and the complete conversion of the heat into work.

Clausius statement

No process is possible whose sole result is the transfer of heat from a colder object to a hotter object.

It can be proved that the two statements above are completely equivalent.

12.12 REVERSIBLE AND IRREVERSIBLE PROCESSES

Imagine some process in which a thermodynamic system goes from an initial state i to a final state f. During the process the system absorbs heat Q from the surroundings and performs work W on it. Can we reverse this process and bring both the system and surroundings to their initial states with no other effect anywhere ? Experience suggests that for most processes in nature this is not possible. The spontaneous processes of nature are irreversible. Several examples can be cited. The base of a vessel on an oven is hotter than its other parts. When the vessel is removed, heat is transferred from the base to the other parts, bringing the vessel to a uniform temperature (which in due course cools to the temperature of the surroundings). The process cannot be reversed; a part of the vessel will not get cooler spontaneously and warm up the base. It will violate the Second Law of Thermodynamics, if it did. The free expansion of a gas is irreversible. The combustion reaction of a mixture of petrol and air ignited by a spark cannot be reversed. Cooking gas leaking from a gas cylinder in the kitchen diffuses to the entire room. The diffusion process will not spontaneously reverse and bring the gas back to the cylinder. The stirring of a liquid in thermal contact with a reservoir will convert the work done into heat, increasing the internal energy of the reservoir. The process cannot be reversed exactly; otherwise it would amount to conversion of heat entirely into work, violating the Second Law of Thermodynamics. Irreversibility is a rule rather an exception in nature.

Irreversibility arises mainly from two causes: one, many processes (like a free expansion, or an explosive chemical reaction) take the system to non-equilibrium states; two, most processes involve friction, viscosity and other dissipative effects (e.g., a moving body coming to a stop and losing its mechanical energy as heat to the floor and the body; a rotating blade in a liquid coming to a stop due to viscosity and losing its mechanical energy with corresponding gain in the internal energy of the liquid). Since dissipative effects are present everywhere and can be minimised but not fully eliminated, most processes that we deal with are irreversible.

A thermodynamic process (state $i \rightarrow$ state f) is reversible if the process can be turned back such that both the system and the surroundings return to their original states, with no other change anywhere else in the universe. From the preceding discussion, a reversible process is an idealised notion. A process is reversible only if it is quasi-static (system in equilibrium with the surroundings at every stage) and there are no dissipative effects. For example, a quasi-static isothermal expansion of an ideal gas in a cylinder fitted with a frictionless movable piston is a reversible process.

Why is reversibility such a basic concept in thermodynamics ? As we have seen, one of the concerns of thermodynamics is the efficiency with which heat can be converted into work. The Second Law of Thermodynamics rules out the possibility of a perfect heat engine with 100% efficiency. But what is the highest efficiency possible for a heat engine working between two reservoirs at temperatures T_1 and T_2 ? It turns out that a heat engine based on idealised reversible processes achieves the highest efficiency possible. All other engines involving irreversibility in any way (as would be the case for practical engines) have lower than this limiting efficiency.

12.13 CARNOT ENGINE

Suppose we have a hot reservoir at temperature T_1 and a cold reservoir at temperature T_2. What is the maximum efficiency possible for a heat engine operating between the two reservoirs and what cycle of processes should be adopted to achieve the maximum efficiency ? Sadi Carnot, a French engineer, first considered this question in 1824. Interestingly, Carnot arrived at the correct answer, even though the basic concepts of heat and thermodynamics had yet to be firmly established.

We expect the ideal engine operating between two temperatures to be a reversible engine. Irreversibility is associated with dissipative effects, as remarked in the preceding section, and lowers efficiency. A process is reversible if it is quasi-static and non-dissipative. We have seen that a process is not quasi-static if it involves finite temperature difference between the system and the reservoir. This implies that in a reversible heat engine operating between two temperatures, heat should be absorbed (from the hot reservoir) isothermally and released (to the cold reservoir) isothermally. We thus have identified two steps of the reversible heat engine : isothermal process at temperature T_1 absorbing heat Q_1 from the hot reservoir, and another isothermal process at temperature T_2 releasing heat Q_2 to the cold reservoir. To complete a cycle, we need to take the system from temperature T_1 to T_2 and then back from temperature T_2 to T_1. Which processes should we employ for this purpose that are reversible? A little reflection shows that we can only adopt reversible adiabatic processes for these purposes, which involve no heat flow from any reservoir. If we employ any other process that is not adiabatic, say an isochoric process, to take the system from one temperature to another, we shall need a series of reservoirs in the temperature range T_2 to T_1 to ensure that at each stage the process is quasi-static. (Remember again that for a process to be quasi-static and reversible, there should be no finite temperature difference between the system and the reservoir.) But we are considering a reversible engine that operates between only two temperatures. Thus adiabatic processes must bring about the temperature change in the system from T_1 to T_2 and T_2 to T_1 in this engine.

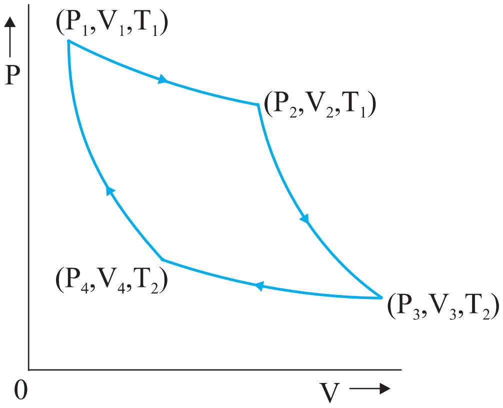


Fig. 12.11 *Carnot cycle for a heat engine with an ideal gas as the working substance.*

A reversible heat engine operating between two temperatures is called a Carnot engine. We have just argued that such an engine must have the following sequence of steps constituting one cycle, called the Carnot cycle, shown in Fig. 12.11. We have taken the working substance of the Carnot engine to be an ideal gas.

(a) *Step* 1 → 2 Isothermal expansion of the gas taking its state from (P_1, V_1, T_1) to (P_2, V_2, T_1).

The heat absorbed by the gas (Q_1) from the reservoir at temperature T_1 is given by

Eq. (12.12). This is also the work done ($W_{1\rightarrow 2}$) by the gas on the environment.

$$W_{1\rightarrow 2} = Q_1 = \mu R T_1 \ \ln\left(\frac{V_2}{V_1}\right) \tag{12.23}$$

(b) *Step* $2 \rightarrow 3$ Adiabatic expansion of the gas from (P_2, V_2, T_1) to (P_3, V_3, T_2) Work done by the gas, using Eq. (12.16), is

$$W_{2\rightarrow 3} = \frac{\mu R\,(T_1 - T_2)}{\gamma - 1} \tag{12.24}$$

(c) *Step* $3 \rightarrow 4$ Isothermal compression of the gas from (P_3, V_3, T_2) to (P_4, V_4, T_2).

Heat released (Q_2) by the gas to the reservoir at temperature T_2 is given by Eq. (12.12). This is also the work done ($W_{3\rightarrow 4}$) on the gas by the environment.

$$W_{3\rightarrow 4} = Q_2 = \mu R T_2 \ln\left(\frac{V_3}{V_4}\right) \tag{12.25}$$

(d) *Step* $4 \rightarrow 1$ Adiabatic compression of the gas from (P_4, V_4, T_2) to (P_1,V_1, T_1).

Work done on the gas, [using Eq.(12.16)], is

$$W_{4\rightarrow 1} = \mu R\left(\frac{T_1 - T_2}{\gamma - 1}\right) \tag{12.26}$$

From Eqs. (12.23) to (12.26) total work done by the gas in one complete cycle is

$$W = W_{1\rightarrow 2} + W_{2\rightarrow 3} - W_{3\rightarrow 4} - W_{4\rightarrow 1}$$

$$= \mu R T_1 \ \ln\left(\frac{V_2}{V_1}\right) - \mu R T_2 \ \ln\left(\frac{V_3}{V_4}\right) \tag{12.27}$$

The efficiency η of the Carnot engine is

$$\eta = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

$$= 1 - \left(\frac{T_2}{T_1}\right)\frac{\mathrm{In}\left(\frac{V_3}{V_4}\right)}{\mathrm{In}\left(\frac{V_2}{V_1}\right)} \tag{12.28}$$

Now since step $2 \rightarrow 3$ is an adiabatic process,

$$T_1\, V_2^{\ \gamma-1} = T_2\, V_3^{\ \gamma-1}$$

i.e. $$\frac{V_2}{V_3} = \left(\frac{T_2}{T_1}\right)^{1/(\gamma-1)} \tag{12.29}$$

Similarly, since step $4 \rightarrow 1$ is an adiabatic process

$$T_2\, V_4^{\ \gamma-1} = T_1\, V_1^{\ \gamma-1}$$

i.e. $$\frac{V_1}{V_4} = \left(\frac{T_2}{T_1}\right)^{1/\gamma-1} \tag{12.30}$$

From Eqs. (12.29) and (12.30),

$$\frac{V_3}{V_4} = \frac{V_2}{V_1} \tag{12.31}$$

Using Eq. (12.31) in Eq. (12.28), we get

$$\eta = 1 - \frac{T_2}{T_1} \quad \text{(Carnot engine)} \tag{12.32}$$

We have already seen that a Carnot engine is a reversible engine. Indeed it is the only reversible engine possible that works between two reservoirs at different temperatures. Each step of the Carnot cycle given in Fig. 12.11 can be reversed. This will amount to taking heat Q_2 from the cold reservoir at T_2, doing work W on the system, and transferring heat Q_1 to the hot reservoir. This will be a reversible refrigerator.

We next establish the important result (sometimes called Carnot's theorem) that (a) working between two given temperatures T_1 and T_2 of the hot and cold reservoirs respectively, no engine can have efficiency more than that of the Carnot engine and (b) the efficiency of the Carnot engine is independent of the nature of the working substance.

To prove the result (a), imagine a reversible (Carnot) engine R and an irreversible engine I working between the same source (hot reservoir) and sink (cold reservoir). Let us couple the engines, I and R, in such a way so that I acts like a heat engine and R acts as a refrigerator. Let I absorb heat Q_1 from the source, deliver work W' and release the heat Q_1- W' to the sink. We arrange so that R returns the same heat Q_1 to the source, taking heat Q_2 from the sink and requiring work $W = Q_1 - Q_2$ to be done on it.

Now suppose $\eta_R < \eta_I$ i.e. if R were to act as an engine it would give less work output than that of I i.e. $W < W'$ for a given Q_1. With R acting like a refrigerator, this would mean $Q_2 = Q_1 - W > Q_1 - W'$. Thus on the whole, the coupled I-R system extracts heat $(Q_1 - W) - (Q_1 - W') = (W' - W)$ from the cold reservoir and delivers the same amount of work in one cycle, without any change in the source or anywhere else. This is clearly against the Kelvin-Planck statement of the Second Law of Thermodynamics. Hence the assertion $\eta_I > \eta_R$ is wrong. No engine can have efficiency greater than that of the Carnot engine. A similar argument can be constructed to show that a reversible engine with one particular substance cannot be more efficient than the one using another substance. The maximum efficiency of a Carnot engine given by Eq. (12.32) is independent of the nature of the system performing the Carnot cycle of operations. Thus we are justified in using an ideal gas as a system in the calculation of efficiency η of a Carnot engine. The ideal gas has a simple equation of state, which allows us to readily calculate η, but the final result for η, [Eq. (12.32)], is true for any Carnot engine.

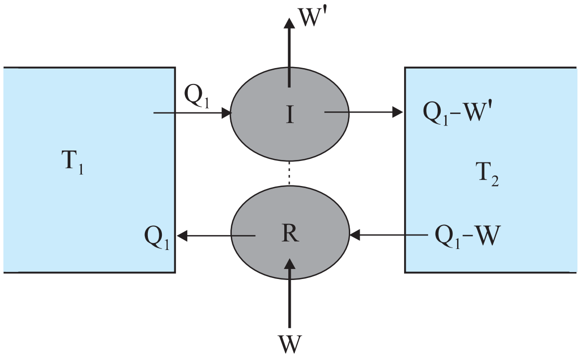


Fig. 12.12 *An irreversible engine (I) coupled to a reversible refrigerator (R). If W ′ > W, this would amount to extraction of heat W′ – W from the sink and its full conversion to work, in contradiction with the Second Law of Thermodynamics.*

This final remark shows that in a Carnot cycle,

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \qquad (12.33)$$

is a universal relation independent of the nature of the system. Here Q_1 and Q_2 are respectively, the heat absorbed and released isothermally (from the hot and to the cold reservoirs) in a Carnot engine. Equation (12.33), can, therefore, be used as a relation to define a truly universal thermodynamic temperature scale that is independent of any particular properties of the system used in the Carnot cycle. Of course, for an ideal gas as a working substance, this universal temperature is the same as the ideal gas temperature introduced in section 12.11.

SUMMARY

1. The zeroth law of thermodynamics states that '*two systems in thermal equilibrium with a third system are in thermal equilibrium with each other*'. The Zeroth Law leads to the concept of temperature.
2. Internal energy of a system is the sum of kinetic energies and potential energies of the molecular constituents of the system. It does not include the over-all kinetic energy of the system. Heat and work are two modes of energy transfer to the system. Heat is the energy transfer arising due to temperature difference between the system and the surroundings. Work is energy transfer brought about by other means, such as moving the piston of a cylinder containing the gas, by raising or lowering some weight connected to it.
3. The first law of thermodynamics is the general law of conservation of energy applied to any system in which energy transfer from or to the surroundings (through heat and work) is taken into account. It states that

$$\Delta Q = \Delta U + \Delta W$$

where ΔQ is the heat supplied to the system, ΔW is the work done by the system and ΔU is the change in internal energy of the system.

4. The specific heat capacity of a substance is defined by

$$s = \frac{1}{m}\frac{\Delta Q}{\Delta T}$$

where m is the mass of the substance and ΔQ is the heat required to change its temperature by ΔT. The molar specific heat capacity of a substance is defined by

$$C = \frac{1}{\mu}\frac{\Delta Q}{\Delta T}$$

where μ is the number of moles of the substance. For a solid, the law of equipartition of energy gives

$$C = 3R$$

which generally agrees with experiment at ordinary temperatures.

Calorie is the old unit of heat. 1 calorie is the amount of heat required to raise the temperature of 1 g of water from 14.5 °C to 15.5 °C. 1 cal = 4.186 J.

5. For an ideal gas, the molar specific heat capacities at constant pressure and volume satisfy the relation

$$C_p - C_v = R$$

where R is the universal gas constant.

6. Equilibrium states of a thermodynamic system are described by state variables. The value of a state variable depends only on the particular state, not on the path used to arrive at that state. Examples of state variables are pressure (P), volume (V), temperature (T), and mass (m). Heat and work are not state variables. An Equation of State (like the ideal gas equation $PV = \mu RT$) is a relation connecting different state variables.

7. A quasi-static process is an infinitely slow process such that the system remains in thermal and mechanical equilibrium with the surroundings throughout. In a quasi-static process, the pressure and temperature of the environment can differ from those of the system only infinitesimally.

8. In an isothermal expansion of an ideal gas from volume V_1 to V_2 at temperature T the heat absorbed (Q) equals the work done (W) by the gas, each given by

$$Q = W = \mu R T \ln\left(\frac{V_2}{V_1}\right)$$

9. In an adiabatic process of an ideal gas

$$PV^{\gamma} = \text{constant}$$

where $$\gamma = \frac{C_p}{C_v}$$

Work done by an ideal gas in an adiabatic change of state from (P_1, V_1, T_1) to (P_2, V_2, T_2) is

$$W = \frac{\mu R(T_1 - T_2)}{\gamma - 1}$$

10. Heat engine is a device in which a system undergoes a cyclic process resulting in conversion of heat into work. If Q_1 is the heat absorbed from the source, Q_2 is the heat released to the sink, and the work output in one cycle is W, the efficiency η of the engine is:

$$\eta = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

11. In a refrigerator or a heat pump, the system extracts heat Q_2 from the cold reservoir and releases Q_1 amount of heat to the hot reservoir, with work W done on the system. The co-efficient of performance of a refrigerator is given by

$$\alpha = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2}$$

12. The second law of thermodynamics disallows some processes consistent with the First Law of Thermodynamics. It states

Kelvin-Planck statement

No process is possible whose sole result is the absorption of heat from a reservoir and complete conversion of the heat into work.

Clausius statement

No process is possible whose sole result is the transfer of heat from a colder object to a hotter object.

Put simply, the Second Law implies that no heat engine can have efficiency η equal to 1 or no refrigerator can have co-efficient of performance α equal to infinity.

13. A process is reversible if it can be reversed such that both the system and the surroundings return to their original states, with no other change anywhere else in the universe. Spontaneous processes of nature are irreversible. The idealised reversible process is a quasi-static process with no dissipative factors such as friction, viscosity, etc.

14. Carnot engine is a reversible engine operating between two temperatures T_1 (source) and T_2 (sink). The Carnot cycle consists of two isothermal processes connected by two adiabatic processes. The efficiency of a Carnot engine is given by

$$\eta = 1 - \frac{T_2}{T_1} \qquad \text{(Carnot engine)}$$

No engine operating between two temperatures can have efficiency greater than that of the Carnot engine.

15. If $Q > 0$, heat is added to the system

If $Q < 0$, heat is removed to the system

If $W > 0$, Work is done by the system

If $W < 0$, Work is done on the system

Quantity	Symbol	Dimensions	Unit	Remark
Co-efficienty of volume expansion	α_v	$[K^{-1}]$	K^{-1}	$\alpha_v = 3\,\alpha_1$
Heat supplied to a system	ΔQ	$[ML^2 T^{-2}]$	J	Q is not a state variable
Specific heat	s	$[L^2 T^{-2} K^{-1}]$	$J\,kg^{-1}\,K^{-1}$	
Thermal Conductivity	K	$[MLT^{-3} K^{-1}]$	$J\,s^{-1}\,K^{-1}$	$H = -KA\frac{dt}{dx}$

POINTS TO PONDER

1. Temperature of a body is related to its average internal energy, not to the kinetic energy of motion of its centre of mass. A bullet fired from a gun is not at a higher temperature because of its high speed.
2. Equilibrium in thermodynamics refers to the situation when macroscopic variables describing the thermodynamic state of a system do not depend on time. Equilibrium of a system in mechanics means the net external force and torque on the system are zero.
3. In a state of thermodynamic equilibrium, the microscopic constituents of a system are not in equilibrium (in the sense of mechanics).
4. Heat capacity, in general, depends on the process the system goes through when heat is supplied.
5. In isothermal quasi-static processes, heat is absorbed or given out by the system even though at every stage the gas has the same temperature as that of the surrounding reservoir. This is possible because of the infinitesimal difference in temperature between the system and the reservoir.

EXERCISES

12.1 A geyser heats water flowing at the rate of 3.0 litres per minute from 27 °C to 77 °C. If the geyser operates on a gas burner, what is the rate of consumption of the fuel if its heat of combustion is 4.0×10^4 J/g ?

12.2 What amount of heat must be supplied to 2.0×10^{-2} kg of nitrogen (at room temperature) to raise its temperature by 45 °C at constant pressure ? (Molecular mass of $N_2 = 28$; $R = 8.3$ J mol^{-1} K^{-1}.)

12.3 Explain why

(a) Two bodies at different temperatures T_1 and T_2 if brought in thermal contact do not necessarily settle to the mean temperature $(T_1 + T_2)/2$.

(b) The coolant in a chemical or a nuclear plant (i.e., the liquid used to prevent the different parts of a plant from getting too hot) should have high specific heat.

(c) Air pressure in a car tyre increases during driving.

(d) The climate of a harbour town is more temperate than that of a town in a desert at the same latitude.

12.4 A cylinder with a movable piston contains 3 moles of hydrogen at standard temperature and pressure. The walls of the cylinder are made of a heat insulator, and the piston is insulated by having a pile of sand on it. By what factor does the pressure of the gas increase if the gas is compressed to half its original volume ?

12.5 In changing the state of a gas adiabatically from an equilibrium state *A* to another equilibrium state *B*, an amount of work equal to 22.3 J is done on the system. If the gas is taken from state *A* to *B* via a process in which the net heat absorbed by the system is 9.35 cal, how much is the net work done by the system in the latter case ? (Take 1 cal = 4.19 J)

12.6 Two cylinders *A* and *B* of equal capacity are connected to each other via a stopcock. *A* contains a gas at standard temperature and pressure. *B* is completely evacuated. The entire system is thermally insulated. The stopcock is suddenly opened. Answer the following :

(a) What is the final pressure of the gas in *A* and *B* ?

(b) What is the change in internal energy of the gas ?

(c) What is the change in the temperature of the gas ?

(d) Do the intermediate states of the system (before settling to the final equilibrium state) lie on its *P-V-T* surface ?

12.7 A steam engine delivers 5.4×10^8J of work per minute and services 3.6×10^9J of heat per minute from its boiler. What is the efficiency of the engine? How much heat is wasted per minute?

12.8 An electric heater supplies heat to a system at a rate of 100W. If system performs work at a rate of 75 joules per second. At what rate is the internal energy increasing?

12.9 A thermodynamic system is taken from an original state to an intermediate state by the linear process shown in Fig. (12.13)

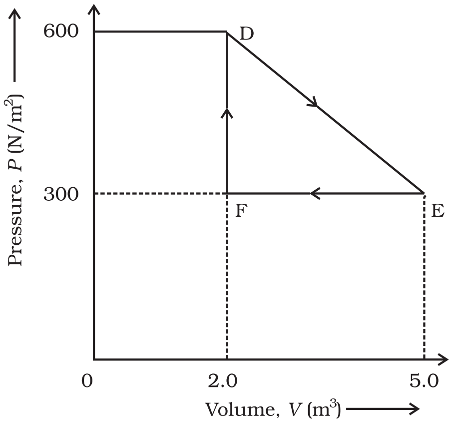


Fig. 12.13

Its volume is then reduced to the original value from E to F by an isobaric process. Calculate the total work done by the gas from D to E to F

12.10 A refrigerator is to maintain eatables kept inside at 9^0C. If room temperature is 36^0C, calculate the coefficient of performance.

CHAPTER THIRTEEN

KINETIC THEORY

13.1 INTRODUCTION

Boyle discovered the law named after him in 1661. Boyle, Newton and several others tried to explain the behaviour of gases by considering that gases are made up of tiny atomic particles. The actual atomic theory got established more than 150 years later. Kinetic theory explains the behaviour of gases based on the idea that the gas consists of rapidly moving atoms or molecules. This is possible as the inter-atomic forces, which are short range forces that are important for solids and liquids, can be neglected for gases. The kinetic theory was developed in the nineteenth century by Maxwell, Boltzmann and others. It has been remarkably successful. It gives a molecular interpretation of pressure and temperature of a gas, and is consistent with gas laws and Avogadro's hypothesis. It correctly explains specific heat capacities of many gases. It also relates measurable properties of gases such as viscosity, conduction and diffusion with molecular parameters, yielding estimates of molecular sizes and masses. This chapter gives an introduction to kinetic theory.

13.2 MOLECULAR NATURE OF MATTER

Richard Feynman, one of the great physicists of 20th century considers the discovery that "Matter is made up of atoms" to be a very significant one. Humanity may suffer annihilation (due to nuclear catastrophe) or extinction (due to environmental disasters) if we do not act wisely. If that happens, and all of scientific knowledge were to be destroyed then Feynman would like the 'Atomic Hypothesis' to be communicated to the next generation of creatures in the universe. Atomic Hypothesis: All things are made of atoms - little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another.

Speculation that matter may not be continuous, existed in many places and cultures. Kanada in India and Democritus

Atomic Hypothesis in Ancient India and Greece

Though John Dalton is credited with the introduction of atomic viewpoint in modern science, scholars in ancient India and Greece conjectured long before the existence of atoms and molecules. In the Vaiseshika school of thought in India founded by Kanada (Sixth century B.C.) the atomic picture was developed in considerable detail. Atoms were thought to be eternal, indivisible, infinitesimal and ultimate parts of matter. It was argued that if matter could be subdivided without an end, there would be no difference between a mustard seed and the Meru mountain. The four kinds of atoms (**Paramanu** — Sanskrit word for the smallest particle) postulated were Bhoomi (Earth), Ap (water), Tejas (fire) and Vayu (air) that have characteristic mass and other attributes, were propounded. Akasa (space) was thought to have no atomic structure and was continuous and inert. Atoms combine to form different molecules (e.g. two atoms combine to form a diatomic molecule dvyanuka, three atoms form a tryanuka or a triatomic molecule), their properties depending upon the nature and ratio of the constituent atoms. The size of the atoms was also estimated, by conjecture or by methods that are not known to us. The estimates vary. In Lalitavistara, a famous biography of the Buddha written mainly in the second century B.C., the estimate is close to the modern estimate of atomic size, of the order of 10^{-10} m.

In ancient Greece, Democritus (Fourth century B.C.) is best known for his atomic hypothesis. The word 'atom' means 'indivisible' in Greek. According to him, atoms differ from each other physically, in shape, size and other properties and this resulted in the different properties of the substances formed by their combination. The atoms of water were smooth and round and unable to 'hook' on to each other, which is why liquid /water flows easily. The atoms of earth were rough and jagged, so they held together to form hard substances. The atoms of fire were thorny which is why it caused painful burns. These fascinating ideas, despite their ingenuity, could not evolve much further, perhaps because they were intuitive conjectures and speculations not tested and modified by quantitative experiments - the hallmark of modern science.

in Greece had suggested that matter may consist of indivisible constituents. The scientific 'Atomic Theory' is usually credited to John Dalton. He proposed the atomic theory to explain the laws of definite and multiple proportions obeyed by elements when they combine into compounds. The first law says that any given compound has, a fixed proportion by mass of its constituents. The second law says that when two elements form more than one compound, for a fixed mass of one element, the masses of the other elements are in ratio of small integers.

To explain the laws Dalton suggested, about 200 years ago, that the smallest constituents of an element are atoms. Atoms of one element are identical but differ from those of other elements. A small number of atoms of each element combine to form a molecule of the compound. Gay Lussac's law, also given in early 19th century, states: When gases combine chemically to yield another gas, their volumes are in the ratios of small integers. Avogadro's law (or hypothesis) says: Equal volumes of all gases at equal temperature and pressure have the same number of molecules. Avogadro's law, when combined with Dalton's theory explains Gay Lussac's law. Since the elements are often in the form of molecules, Dalton's atomic theory can also be referred to as the molecular theory of matter. The theory is now well accepted by scientists. However even at the end of the nineteenth century there were famous scientists who did not believe in atomic theory !

From many observations, in recent times we now know that molecules (made up of one or more atoms) constitute matter. Electron microscopes and scanning tunnelling microscopes enable us to even see them. The size of an atom is about an angstrom (10^{-10} m). In solids, which are tightly packed, atoms are spaced about a few angstroms (2 Å) apart. In liquids the separation between atoms is also about the same. In liquids the atoms are not as rigidly fixed as in solids, and can move around. This enables a liquid to flow. In gases the interatomic distances are in tens of angstroms. The average distance a molecule can travel without colliding is called the **mean free path**. The mean free path, in gases, is of the order of thousands of angstroms. The atoms are much freer in gases and can travel long distances without colliding. If they are not enclosed, gases disperse away. In solids and liquids the closeness makes the interatomic force important. The force has a long range attraction and a short range repulsion. The atoms attract when they are at a few angstroms but repel when they come closer. The static appearance of a gas is misleading. The gas is full of activity and the equilibrium is a dynamic one. In dynamic equilibrium, molecules collide and change their speeds during the collision. Only the average properties are constant.

Atomic theory is not the end of our quest, but the beginning. We now know that atoms are not indivisible or elementary. They consist of a nucleus and electrons. The nucleus itself is made up of protons and neutrons. The protons and neutrons are again made up of quarks. Even quarks may not be the end of the story. There may be string like elementary entities. Nature always has surprises for us, but the search for truth is often enjoyable and the discoveries beautiful. In this chapter, we shall limit ourselves to understanding the behaviour of gases (and a little bit of solids), as a collection of moving molecules in incessant motion.

13.3 BEHAVIOUR OF GASES

Properties of gases are easier to understand than those of solids and liquids. This is mainly because in a gas, molecules are far from each other and their mutual interactions are negligible except when two molecules collide. Gases at low pressures and high temperatures much above that at which they liquefy (or solidify) approximately satisfy a simple relation between their pressure, temperature and volume given by (see Ch. 11)

$$PV = KT \qquad (13.1)$$

for a given sample of the gas. Here T is the temperature in kelvin or (absolute) scale. K is a constant for the given sample but varies with the volume of the gas. If we now bring in the idea of atoms or molecules then K is proportional to the number of molecules, (say) N in the sample. We can write $K = N\,k$. Observation tells us that this k is same for all gases. It is called Boltzmann constant and is denoted by k_B.

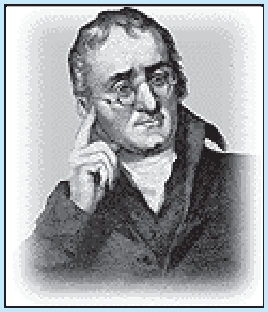
$$\text{As } \frac{P_1V_1}{N_1T_1} = \frac{P_2V_2}{N_2T_2} = \text{constant} = k_B \qquad (13.2)$$

if P, V and T are same, then N is also same for all gases. This is Avogadro's hypothesis, that the number of molecules per unit volume is same for all gases at a fixed temperature and pressure. The number in 22.4 litres of any gas is 6.02×10^{23}. This is known as Avogadro number and is denoted by N_A. The mass of 22.4 litres of any gas is equal to its molecular weight in grams at S.T.P (standard temperature 273 K and pressure 1 atm). This amount of substance is called a mole (see Chapter 2 for a more precise definition). Avogadro had guessed the equality of numbers in equal volumes of gas at a fixed temperature and pressure from chemical reactions. Kinetic theory justifies this hypothesis.

The perfect gas equation can be written as

$$PV = \mu\, RT \qquad (13.3)$$

where μ is the number of moles and $R = N_A k_B$ is a universal constant. The temperature T is absolute temperature. Choosing kelvin scale for



John Dalton (1766- 1844)

He was an English chemist. When different types of atoms combine, they obey certain simple laws. Dalton's atomic theory explains these laws in a simple way. He also gave a theory of colour blindness.

Amedeo Avogadro (1776 – 1856)

He made a brilliant guess that equal volumes of gases have equal number of molecules at the same temperature and pressure. This helped in understanding the combination of different gases in a very simple way. It is now called Avogadro's hypothesis (or law). He also suggested that the smallest constituent of gases like hydrogen, oxygen and nitrogen are not atoms but diatomic molecules.

absolute temperature, R = 8.314 J mol^{-1}K^{-1}. Here

$$\mu = \frac{M}{M_0} = \frac{N}{N_A} \qquad (13.4)$$

where M is the mass of the gas containing N molecules, M_0 is the molar mass and N_A the Avogadro's number. Using Eqs. (13.4) and (13.3) can also be written as

$PV = k_B NT$ or $P = k_B nT$

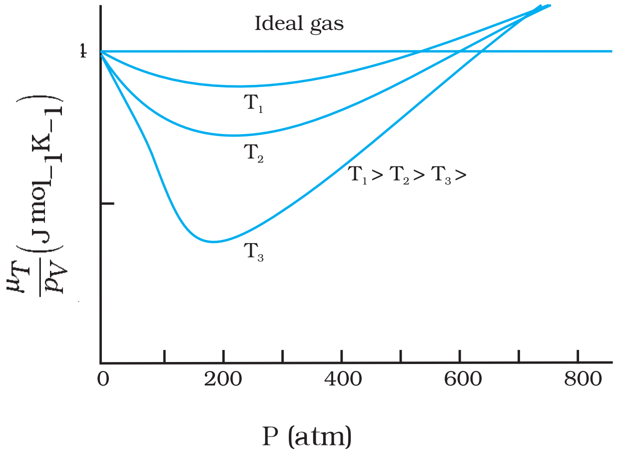


Fig.13.1 *Real gases approach ideal gas behaviour at low pressures and high temperatures.*

where n is the number density, i.e. number of molecules per unit volume. k_B is the Boltzmann constant introduced above. Its value in SI units is 1.38 × 10^{-23} J K^{-1}.

Another useful form of Eq. (13.3) is

$$P = \frac{\rho RT}{M_0} \qquad (13.5)$$

where ρ is the mass density of the gas.

A gas that satisfies Eq. (13.3) exactly at all pressures and temperatures is defined to be an **ideal gas**. An ideal gas is a simple theoretical model of a gas. No real gas is truly ideal. Fig. 13.1 shows departures from ideal gas behaviour for a real gas at three different temperatures. Notice that all curves approach the ideal gas behaviour for low pressures and high temperatures.

At low pressures or high temperatures the molecules are far apart and molecular interactions are negligible. Without interactions the gas behaves like an ideal one.

If we fix μ and T in Eq. (13.3), we get

$$PV = \text{constant} \qquad (13.6)$$

i.e., keeping temperature constant, pressure of a given mass of gas varies inversely with volume. This is the famous **Boyle's law**. Fig. 13.2 shows comparison between experimental P-V curves and the theoretical curves predicted by Boyle's law. Once again you see that the agreement is good at high temperatures and low pressures. Next, if you fix P, Eq. (13.1) shows that $V \propto T$ i.e., for a fixed pressure, the volume of a gas is proportional to its absolute temperature T **(Charles' law)**. See Fig. 13.3.

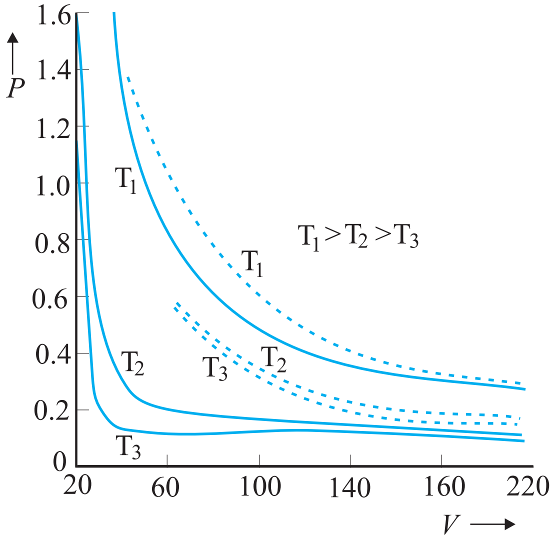


Fig.13.2 *Experimental P-V curves (solid lines) for steam at three temperatures compared with Boyle's law (dotted lines). P is in units of 22 atm and V in units of 0.09 litres.*

Finally, consider a mixture of non-interacting ideal gases: μ_1 moles of gas 1, μ_2 moles of gas 2, etc. in a vessel of volume V at temperature T and pressure P. It is then found that the equation of state of the mixture is :

$$PV = (\mu_1 + \mu_2 + \dots)\, RT \qquad (13.7)$$

$$\text{i.e. } P = \mu_1 \frac{RT}{V} + \mu_2 \frac{RT}{V} + \dots \qquad (13.8)$$

$$= P_1 + P_2 + \dots \qquad (13.9)$$

Clearly $P_1 = \mu_1 RT/V$ is the pressure gas 1 would exert at the same conditions of volume and temperature if no other gases were present. This is called the partial pressure of the gas. Thus, the total pressure of a mixture of ideal gases is the sum of partial pressures. This is Dalton's law of partial pressures.

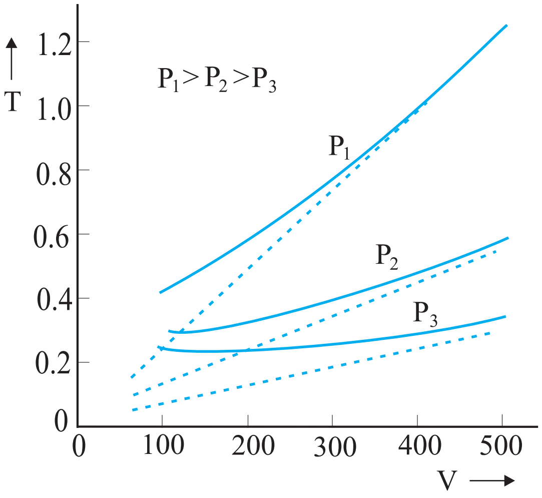


Fig. 13.3 *Experimental T-V curves (solid lines) for CO_2 at three pressures compared with Charles' law (dotted lines). T is in units of 300 K and V in units of 0.13 litres.*

We next consider some examples which give us information about the volume occupied by the molecules and the volume of a single molecule.

Example 13.1 The density of water is 1000 kg m^{-3}. The density of water vapour at 100 °C and 1 atm pressure is 0.6 kg m^{-3}. The volume of a molecule multiplied by the total number gives ,what is called, molecular volume. Estimate the ratio (or fraction) of the molecular volume to the total volume occupied by the water vapour under the above conditions of temperature and pressure.

Answer For a given mass of water molecules, the density is less if volume is large. So the volume of the vapour is $1000/0.6 = /(6 \times 10^{-4})$ times larger. If densities of bulk water and water molecules are same, then the fraction of molecular volume to the total volume in liquid state is 1. As volume in vapour state has increased, the fractional volume is less by the same amount, i.e. 6×10^{-4}.

Example 13.2 Estimate the volume of a water molecule using the data in Example 13.1.

Answer In the liquid (or solid) phase, the molecules of water are quite closely packed. The density of water molecule may therefore, be regarded as roughly equal to the density of bulk water = 1000 kg m^{-3}. To estimate the volume of a water molecule, we need to know the mass of a single water molecule. We know that 1 mole of water has a mass approximately equal to

(2 + 16)g = 18 g = 0.018 kg.

Since 1 mole contains about 6×10^{23} molecules (Avogadro's number), the mass of a molecule of water is $(0.018)/(6 \times 10^{23})$ kg = 3×10^{-26} kg. Therefore, a rough estimate of the volume of a water molecule is as follows :

Volume of a water molecule

$= (3 \times 10^{-26} \text{ kg})/ (1000 \text{ kg m}^{-3})$

$= 3 \times 10^{-29} \text{ m}^3$

$= (4/3)\, \pi\, (\text{Radius})^3$

Hence, Radius $\approx 2 \times 10^{-10}$ m = 2 Å

Example 13.3 What is the average distance between atoms (interatomic distance) in water? Use the data given in Examples 13.1 and 13.2.

Answer : A given mass of water in vapour state has 1.67×10^3 times the volume of the same mass of water in liquid state (Ex. 13.1). This is also the increase in the amount of volume available for each molecule of water. When volume increases by 10^3 times the radius increases by $V^{1/3}$ or 10 times, i.e., 10 × 2 Å = 20 Å. So the average distance is 2 × 20 = 40 Å.

Example 13.4 A vessel contains two non-reactive gases : neon (monatomic) and oxygen (diatomic). The ratio of their partial pressures is 3:2. Estimate the ratio of (i) number of molecules and (ii) mass density of neon and oxygen in the vessel. Atomic mass of Ne = 20.2 u, molecular mass of O_2 = 32.0 u.

Answer Partial pressure of a gas in a mixture is the pressure it would have for the same volume and temperature if it alone occupied the vessel. (The total pressure of a mixture of non-reactive gases is the sum of partial pressures due to its constituent gases.) Each gas (assumed ideal) obeys the gas law. Since V and T are common to the two gases, we have $P_1 V = \mu_1 RT$ and $P_2 V = \mu_2 RT$, i.e. $(P_1/P_2) = (\mu_1 / \mu_2)$. Here 1 and 2 refer to neon and oxygen respectively. Since $(P_1/P_2) = (3/2)$ (given), $(\mu_1/ \mu_2) = 3/2$.

(i) By definition $\mu_1 = (N_1/N_A)$ and $\mu_2 = (N_2/N_A)$ where N_1 and N_2 are the number of molecules of 1 and 2, and N_A is the Avogadro's number. Therefore, $(N_1/N_2) = (\mu_1 / \mu_2) = 3/2$.

(ii) We can also write $\mu_1 = (m_1/M_1)$ and $\mu_2 = (m_2/M_2)$ where m_1 and m_2 are the masses of 1 and 2; and M_1 and M_2 are their molecular masses. (Both m_1 and M_1; as well as m_2 and M_2 should be expressed in the same units). If ρ_1 and ρ_2 are the mass densities of 1 and 2 respectively, we have

$$\frac{\rho_1}{\rho_2} = \frac{m_1/V}{m_2/V} = \frac{m_1}{m_2} = \frac{\mu_1}{\mu_2} \times \left(\frac{M_1}{M_2}\right)$$

$$= \frac{3}{2} \times \frac{20.2}{32.0} = 0.947$$ ◀

13.4 KINETIC THEORY OF AN IDEAL GAS

Kinetic theory of gases is based on the molecular picture of matter. A given amount of gas is a collection of a large number of molecules (typically of the order of Avogadro's number) that are in incessant random motion. At ordinary pressure and temperature, the average distance between molecules is a factor of 10 or more than the typical size of a molecule (2 Å). Thus the interaction between the molecules is negligible and we can assume that they move freely in straight lines according to Newton's first law. However, occasionally, they come close to each other, experience intermolecular forces and their velocities change. These interactions are called collisions. The molecules collide incessantly against each other or with the walls and change their velocities. The collisions are considered to be elastic. We can derive an expression for the pressure of a gas based on the kinetic theory.

We begin with the idea that molecules of a gas are in incessant random motion, colliding against one another and with the walls of the container. All collisions between molecules among themselves or between molecules and the walls are elastic. This implies that total kinetic energy is conserved. The total momentum is conserved as usual.

13.4.1 Pressure of an Ideal Gas

Consider a gas enclosed in a cube of side l. Take the axes to be parallel to the sides of the cube, as shown in Fig. 13.4. A molecule with velocity (v_x, v_y, v_z) hits the planar wall parallel to *yz*-plane of area A (= l^2). Since the collision is elastic, the molecule rebounds with the same velocity; its *y* and *z* components of velocity do not change in the collision but the *x*-component reverses sign. That is, the velocity after collision is $(-v_x, v_y, v_z)$. The change in momentum of the molecule is : $-mv_x - (mv_x) = -2mv_x$. By the principle of conservation of momentum, the momentum imparted to the wall in the collision $= 2mv_x$.

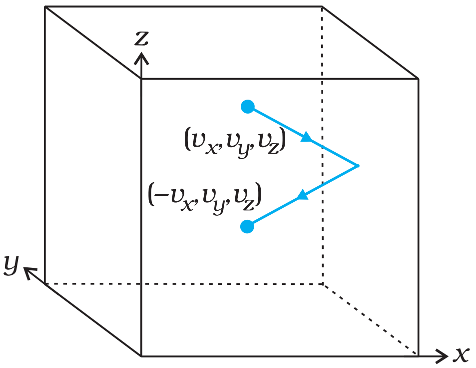


Fig. 13.4 *Elastic collision of a gas molecule with the wall of the container.*

To calculate the force (and pressure) on the wall, we need to calculate momentum imparted to the wall per unit time. In a small time interval Δt, a molecule with *x*-component of velocity v_x will hit the wall if it is within the distance $v_x \Delta t$ from the wall. That is, all molecules within the volume $Av_x\Delta t$ only can hit the wall in time Δt. But, on the average, half of these are moving towards the wall and the other half away from the wall. Thus the number of molecules with velocity (v_x, v_y, v_z) hitting the wall in time Δt is $½A\, v_x\, \Delta t\, n$ where n is the number of molecules per unit volume. The total momentum transferred to the wall by these molecules in time Δt is :

$$Q = (2mv_x)\,(½\, n\, A\, v_x\, \Delta t) \qquad (13.10)$$

The force on the wall is the rate of momentum transfer $Q/\Delta t$ and pressure is force per unit area :

$$P = Q/(A\,\Delta t) = n\, m\, v_x^2 \qquad (3.11)$$

Actually, all molecules in a gas do not have the same velocity; there is a distribution in velocities. The above equation therefore, stands for pressure due to the group of molecules with speed v_x in the *x*-direction and n stands for the number density of that group of molecules. The total pressure is obtained by summing over the contribution due to all groups:

$$P = n\,m\,\overline{v_x^2} \tag{13.12}$$

where $\overline{v_x^2}$ is the average of $v_x^{\,2}$. Now the gas is isotropic, i.e. there is no preferred direction of velocity of the molecules in the vessel. Therefore, by symmetry,

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

$$= (1/3)\,[\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}\,] = (1/3)\,\overline{v^2} \tag{13.13}$$

where v is the speed and $\overline{v^2}$ denotes the mean of the squared speed. Thus

$$P = (1/3)\,n\,m\,\overline{v^2} \tag{13.14}$$

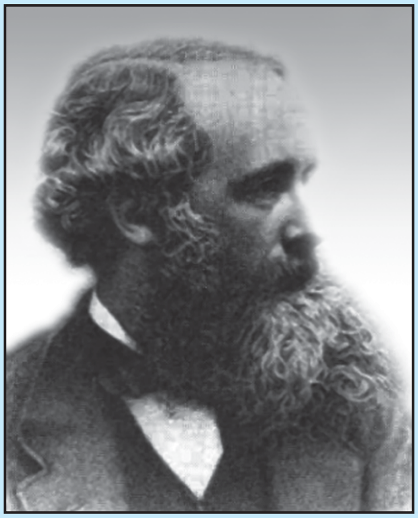
Some remarks on this derivation. First, though we choose the container to be a cube, the shape of the vessel really is immaterial. For a vessel of arbitrary shape, we can always choose a small infinitesimal (planar) area and carry through the steps above. Notice that both A and Δt do not appear in the final result. By Pascal's law, given in Ch. 10, pressure in one portion of the gas in equilibrium is the same as anywhere else. Second, we have ignored any collisions in the derivation. Though this assumption is difficult to justify rigorously, we can qualitatively see that it will not lead to erroneous results. The number of molecules hitting the wall in time Δt was found to be ½ $n A v_x \Delta t$. Now the collisions are random and the gas is in a steady state. Thus, if a molecule with velocity (v_x, v_y, v_z) acquires a different velocity due to collision with some molecule, there will always be some other molecule with a different initial velocity which after a collision acquires the velocity (v_x, v_y, v_z). If this were not so, the distribution of velocities would not remain steady. In any case we are finding $\overline{v_x^2}$. Thus, on the whole, molecular collisions (if they are not too frequent and the time spent in a collision is negligible compared to time between collisions) will not affect the calculation above.

13.4.2 Kinetic Interpretation of Temperature

Equation (13.14) can be written as

$$PV = (1/3)\,nV\,m\,\overline{v^2} \tag{13.15a}$$

Founders of Kinetic Theory of Gases



James Clerk Maxwell (1831 – 1879), born in Edinburgh, Scotland, was among the greatest physicists of the nineteenth century. He derived the thermal velocity distribution of molecules in a gas and was among the first to obtain reliable estimates of molecular parameters from measurable quantities like viscosity, etc. Maxwell's greatest achievement was the unification of the laws of electricity and magnetism (discovered by Coulomb, Oersted, Ampere and Faraday) into a consistent set of equations now called Maxwell's equations. From these he arrived at the most important conclusion that light is an electromagnetic wave. Interestingly, Maxwell did not agree with the idea (strongly suggested by the Faraday's laws of electrolysis) that electricity was particulate in nature.

Ludwig Boltzmann (1844 – 1906) born in Vienna, Austria, worked on the kinetic theory of gases independently of Maxwell. A firm advocate of atomism, that is basic to kinetic theory, Boltzmann provided a statistical interpretation of the Second Law of thermodynamics and the concept of entropy. He is regarded as one of the founders of classical statistical mechanics. The proportionality constant connecting energy and temperature in kinetic theory is known as Boltzmann's constant in his honour.

$$PV = (2/3)\, N \times ½\, m\, \overline{v^2} \qquad (13.15b)$$

where N (= nV) is the number of molecules in the sample.

The quantity in the bracket is the average translational kinetic energy of the molecules in the gas. Since the internal energy E of an ideal gas is purely kinetic*,

$$E = N \times (1/2)\, m\, \overline{v^2} \qquad (13.16)$$

Equation (13.15) then gives :

$$PV = (2/3)\, E \qquad (13.17)$$

We are now ready for a kinetic interpretation of temperature. Combining Eq. (13.17) with the ideal gas Eq. (13.3), we get

$$E = (3/2)\ k_B\, NT \qquad (13.18)$$

$$\text{or}\quad E/\,N = ½\ m\ \overline{v^2} \ = \ (3/2)\ k_BT \qquad (13.19)$$

i.e., the average kinetic energy of a molecule is proportional to the absolute temperature of the gas; it is independent of pressure, volume or the nature of the ideal gas. This is a fundamental result relating temperature, a macroscopic measurable parameter of a gas (a thermodynamic variable as it is called) to a molecular quantity, namely the average kinetic energy of a molecule. The two domains are connected by the Boltzmann constant. We note in passing that Eq. (13.18) tells us that internal energy of an ideal gas depends only on temperature, not on pressure or volume. With this interpretation of temperature, kinetic theory of an ideal gas is completely consistent with the ideal gas equation and the various gas laws based on it.

For a mixture of non-reactive ideal gases, the total pressure gets contribution from each gas in the mixture. Equation (13.14) becomes

$$P = (1/3)\ [n_1 m_1 \overline{v_1^2}\ + n_2\, m_2\ \overline{v_2^2}\ + \ldots\ ] \qquad (13.20)$$

In equilibrium, the average kinetic energy of the molecules of different gases will be equal. That is,

$$½\ m_1\ \overline{v_1^2}\ = ½\ m_2\ \overline{v_2^2} = (3/2)\ k_B\ T$$

so that

$$P = (n_1 + n_2 + \ldots\ )\ k_B\ T \qquad (13.21)$$

which is Dalton's law of partial pressures.

From Eq. (13.19), we can get an idea of the typical speed of molecules in a gas. At a temperature T = 300 K, the mean square speed of a molecule in nitrogen gas is :

$$m = \frac{M_{N_2}}{N_A} = \frac{28}{6.02 \times 10^{26}} = 4.65 \times 10^{-26}\ \text{kg}.$$

$$\overline{v^2}\ = 3\ k_B\ T\ /\ m \ = \ (516)^2\ \text{m}^2\text{s}^{-2}$$

The square root of $\overline{v^2}$ is known as root mean square (rms) speed and is denoted by v_{rms},

(We can also write $\overline{v^2}$ as $< v^2 >$.)

$$v_{\text{rms}}\ = \ 516\ \text{m s}^{-1}$$

The speed is of the order of the speed of sound in air. It follows from Eq. (13.19) that at the same temperature, lighter molecules have greater rms speed.

Example 13.5 A flask contains argon and chlorine in the ratio of 2:1 by mass. The temperature of the mixture is 27 °C. Obtain the ratio of (i) average kinetic energy per molecule, and (ii) root mean square speed v_{rms} of the molecules of the two gases. Atomic mass of argon = 39.9 u; Molecular mass of chlorine = 70.9 u.

Answer The important point to remember is that the average kinetic energy (per molecule) of any (ideal) gas (be it monatomic like argon, diatomic like chlorine or polyatomic) is always equal to (3/2) k_BT. It depends only on temperature, and is independent of the nature of the gas.

(i) Since argon and chlorine both have the same temperature in the flask, the ratio of average kinetic energy (per molecule) of the two gases is 1:1.

(ii) Now ½ $m\, v_{\text{rms}}{}^2$ = average kinetic energy per molecule = (3/2)) k_BT where m is the mass of a molecule of the gas. Therefore,

$$\frac{\left(\mathbf{v}_{rms}^2\right)_{\text{Ar}}}{\left(\mathbf{v}_{rms}^2\right)_{\text{Cl}}} = \frac{(m)_{\text{Cl}}}{(m)_{\text{Ar}}} = \frac{(M)_{\text{Cl}}}{(M)_{\text{Ar}}} = \frac{70.9}{39.9} = 1.77$$

where M denotes the molecular mass of the gas. (For argon, a molecule is just an atom of argon.) Taking square root of both sides,

$$\frac{\left(\mathbf{v}_{rms}\right)_{\text{Ar}}}{\left(\mathbf{v}_{rms}\right)_{\text{Cl}}} = 1.33$$

You should note that the composition of the mixture by mass is quite irrelevant to the above

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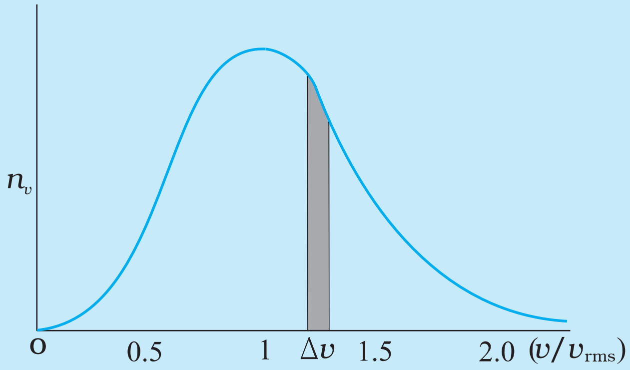
* *E denotes the translational part of the internal energy U that may include energies due to other degrees of freedom also. See section 13.5.*

Maxwell Distribution Function

In a given mass of gas, the velocities of all molecules are not the same, even when bulk parameters like pressure, volume and temperature are fixed. Collisions change the direction and the speed of molecules. However in a state of equilibrium, the distribution of speeds is constant or fixed.

Distributions are very important and useful when dealing with systems containing large number of objects. As an example consider the ages of different persons in a city. It is not feasible to deal with the age of each individual. We can divide the people into groups: children up to age 20 years, adults between ages of 20 and 60, old people above 60. If we want more detailed information we can choose smaller intervals, 0-1, 1-2,..., 99-100 of age groups. When the size of the interval becomes smaller, say half year, the number of persons in the interval will also reduce, roughly half the original number in the one year interval. The number of persons $dN(x)$ in the age interval x and $x+dx$ is proportional to dx or $dN(x) = n_x\, dx$. We have used n_x to denote the number of persons at the value of x.



Maxwell distribution of molecular speeds

In a similar way the molecular speed distribution gives the number of molecules between the speeds v and $v+dv$. $dN(v) = 4p\, N\, a^3 e^{-bv^2}\, v^2\, dv = n_v dv$. This is called Maxwell distribution. The plot of n_v against v is shown in the figure. The fraction of the molecules with speeds v and $v+dv$ is equal to the area of the strip shown. The average of any quantity like v^2 is defined by the integral $<v^2> = (1/N) \int v^2\, dN(v) = \sqrt{(3k_B\, T/m)}$ which agrees with the result derived from more elementary considerations.

calculation. Any other proportion by mass of argon and chlorine would give the same answers to (i) and (ii), provided the temperature remains unaltered. ◀

▶ ***Example 13.6*** Uranium has two isotopes of masses 235 and 238 units. If both are present in Uranium hexafluoride gas which would have the larger average speed ? If atomic mass of fluorine is 19 units, estimate the percentage difference in speeds at any temperature.

Answer At a fixed temperature the average energy $= \frac{1}{2}\, m <v^2>$ is constant. So smaller the mass of the molecule, faster will be the speed. The ratio of speeds is inversely proportional to the square root of the ratio of the masses. The masses are 349 and 352 units. So

$$v_{349}\, /\, v_{352} = (352/\, 349)^{1/2} = 1.0044\ .$$

Hence difference $\dfrac{\Delta V}{V} = 0.44\ \%$.

[^{235}U is the isotope needed for nuclear fission. To separate it from the more abundant isotope ^{238}U, the mixture is surrounded by a porous cylinder. The porous cylinder must be thick and narrow, so that the molecule wanders through individually, colliding with the walls of the long pore. The faster molecule will leak out more than the slower one and so there is more of the lighter molecule (enrichment) outside the porous cylinder (Fig. 13.5). The method is not very efficient and has to be repeated several times for sufficient enrichment.]. ◀

When gases diffuse, their rate of diffusion is inversely proportional to square root of the masses (see Exercise 13.12). Can you guess the explanation from the above answer?

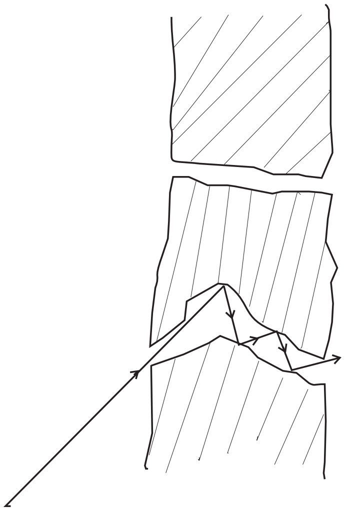


Fig. 13.5 *Molecules going through a porous wall.*

▶ ***Example 13.7*** (a) When a molecule (or an elastic ball) hits a (massive) wall, it rebounds with the same speed. When a ball hits a massive bat held firmly, the same thing happens. However, when the bat is moving towards the ball, the ball rebounds with a different speed. Does the ball move faster or slower? (Ch.6 will refresh your memory on elastic collisions.)

(b) When gas in a cylinder is compressed by pushing in a piston, its temperature rises. Guess at an explanation of this in terms of kinetic theory using (a) above.

(c) What happens when a compressed gas pushes a piston out and expands. What would you observe ?

(d) Sachin Tendulkar uses a heavy cricket bat while playing. Does it help him in anyway ?

Answer (a) Let the speed of the ball be u relative to the wicket behind the bat. If the bat is moving towards the ball with a speed V relative to the wicket, then the relative speed of the ball to bat is $V + u$ towards the bat. When the ball rebounds (after hitting the massive bat) its speed, relative to bat, is $V + u$ moving away from the bat. So relative to the wicket the speed of the rebounding ball is $V + (V + u) = 2V + u$, moving away from the wicket. So the ball speeds up after the collision with the bat. The rebound speed will be less than u if the bat is not massive. For a molecule this would imply an increase in temperature.

You should be able to answer (b) (c) and (d) based on the answer to (a).

(Hint: Note the correspondence, piston→ bat, cylinder → wicket, molecule → ball.) ◀

13.5 LAW OF EQUIPARTITION OF ENERGY

The kinetic energy of a single molecule is

$$\varepsilon_t = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 \qquad (13.22)$$

For a gas in thermal equilibrium at temperature T the average value of energy denoted by $<\varepsilon_t>$ is

$$\langle\varepsilon_t\rangle = \left\langle\frac{1}{2}mv_x^2\right\rangle + \left\langle\frac{1}{2}mv_y^2\right\rangle + \left\langle\frac{1}{2}mv_z^2\right\rangle = \frac{3}{2}k_BT \qquad (13.23)$$

Since there is no preferred direction, Eq. (13.23) implies

$$\left\langle\frac{1}{2}\ mv_x^2\right\rangle = \frac{1}{2}\ k_BT\ ,\left\langle\frac{1}{2}\ mv_y^2\right\rangle = \frac{1}{2}\ k_BT\ ,$$

$$\left\langle\frac{1}{2}\ mv_z^2\right\rangle = \frac{1}{2}\ k_BT \qquad (13.24)$$

A molecule free to move in space needs three coordinates to specify its location. If it is constrained to move in a plane it needs two;and if constrained to move along a line, it needs just one coordinate to locate it. This can also be expressed in another way. We say that it has one degree of freedom for motion in a line, two for motion in a plane and three for motion in space. Motion of a body as a whole from one point to another is called translation. Thus, a molecule free to move in space has three translational degrees of freedom. Each translational degree of freedom contributes a term that contains square of some variable of motion, e.g., ½ mv_x^2 and similar terms in v_y and v_z. In, Eq. (13.24) we see that in thermal equilibrium, the average of each such term is ½ k_BT.

Molecules of a monatomic gas like argon have only translational degrees of freedom. But what about a diatomic gas such as O_2 or N_2? A molecule of O_2 has three translational degrees of freedom. But in addition it can also rotate about its centre of mass. Figure 13.6 shows the two independent axes of rotation 1 and 2, normal to the axis joining the two oxygen atoms about which the molecule can rotate*. The molecule thus has two rotational degrees of freedom, each of which contributes a term to the total energy consisting of translational energy ε_t and rotational energy ε_r.

$$\varepsilon_t + \varepsilon_r = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \frac{1}{2}I_1\omega_1^2 + \frac{1}{2}I_2\omega_2^2 \qquad (13.25)$$

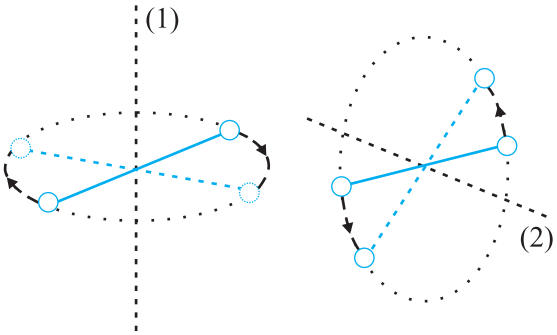


Fig. 13.6 *The two independent axes of rotation of a diatomic molecule*

where ω_1 and ω_2 are the angular speeds about the axes 1 and 2 and I_1, I_2 are the corresponding moments of inertia. Note that each rotational degree of freedom contributes a term to the energy that contains square of a rotational variable of motion.

We have assumed above that the O_2 molecule is a 'rigid rotator', i.e. the molecule does not vibrate. This assumption, though found to be true (at moderate temperatures) for O_2, is not always valid. Molecules like CO even at moderate temperatures have a mode of vibration, i.e. its atoms oscillate along the interatomic axis like a one-dimensional oscillator, and contribute a vibrational energy term ε_v to the total energy:

$$\varepsilon_v = \frac{1}{2}m\left(\frac{dy}{dt}\right)^2 + \frac{1}{2}ky^2$$

$$\varepsilon = \varepsilon_t + \varepsilon_r + \varepsilon_v \qquad (13.26)$$

where k is the force constant of the oscillator and y the vibrational co-ordinate.

Once again the vibrational energy terms in Eq. (13.26) contain squared terms of vibrational variables of motion y and dy/dt .

At this point, notice an important feature in Eq.(13.26). While each translational and rotational degree of freedom has contributed only one 'squared term' in Eq.(13.26), one vibrational mode contributes two 'squared terms' : kinetic and potential energies.

Each quadratic term occurring in the expression for energy is a mode of absorption of energy by the molecule. We have seen that in thermal equilibrium at absolute temperature T, for each translational mode of motion, the average energy is ½ k_BT. A most elegant principle of classical statistical mechanics (first proved by Maxwell) states that this is so for each mode of energy: translational, rotational and vibrational. That is, in equilibrium, the total energy is equally distributed in all possible energy modes, with each mode having an average energy equal to ½ k_BT. This is known as the **law of equipartition of energy**. Accordingly, each translational and rotational degree of freedom of a molecule contributes ½ k_BT to the energy while each vibrational frequency contributes $2 \times ½\, k_BT = k_BT$, since a vibrational mode has both kinetic and potential energy modes.

The proof of the law of equipartition of energy is beyond the scope of this book. Here we shall apply the law to predict the specific heats of gases theoretically. Later we shall also discuss briefly, the application to specific heat of solids.

13.6 SPECIFIC HEAT CAPACITY

13.6.1 Monatomic Gases

The molecule of a monatomic gas has only three translational degrees of freedom. Thus, the average energy of a molecule at temperature T is $(3/2)k_BT$. The total internal energy of a mole of such a gas is

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* *Rotation along the line joining the atoms has very small moment of inertia and does not come into play for quantum mechanical reasons. See end of section 13.6.*