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# Perfect Gases

*In this chapter we shall introduce the idea of atoms and show how it has been outstandingly successful in giving a quantitative explanation of the mechanical properties of the simplest types of gases. In Section 1.2 we shall deduce the pressure of a gas and other simple properties in terms of atomic or molecular motion, and in Section 1.3 we shall go on to consider the distribution of velocities among the gas particles. This leads to various other topics such as the density of the earth's atmosphere, distribution of energy among the particles and their modes of motion, specific heats, random thermal motion and adiabatic changes. Finally, in Section 1.9 we take account of the collisions which limit the mean free paths of gas particles and show in the remaining sections how this leads to a simple understanding of thermal conductivity, viscosity and diffusion in gases.*

## 1.1 ATOMIC STRUCTURE OF MATTER

One of the oldest ideas in science is that the ordinary matter of the world consists of large numbers of small atoms. It seemed impossible that a piece of matter could be cut up repeatedly into smaller and smaller parts; there must come an end to this when it was reduced to ultimate constituents. It was also felt that the sensations of heat, cold and the force of the wind might be brought about by the impacts of innumerable small particles flying about.

The atomic theory became popular in the 16th and 17th centuries, when it was used to explain the structures and properties of solids. The denseness and the hardness of solids suggested that atoms in them must be packed together particularly closely. Really close packing has to be done

in a systematic orderly way, and this agreed with what was known then about crystals. Their flat faces, sharp edges and regular angles suggested that crystals are a form of matter in which the atoms are arranged in orderly patterns, such as may be produced by stacking large numbers of equal spheres together. Robert Hooke, in fact, showed that the various common shapes of alum crystals could all be reproduced from a pile of musket shot stacked in a single regular pattern. Other people tried to explain the plasticity and fracture of solids, the nature of alloyed metals and changes of crystal structure in terms of the ways in which atoms pack together and move about in crystals.

This early theory failed to take root, however, because it was speculative and lacked proof, even though it has since been proved broadly correct. Some of the best evidence for the atomic structure of matter has in fact

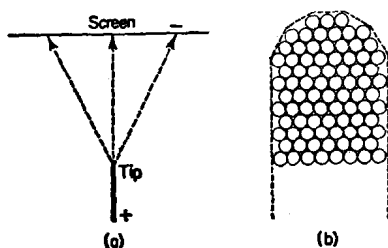


Fig. 1.1. Field-ion microscopy. (a) Arrangement of specimen and screen; (b) schematic section through tip, showing atomic structure.

come from the study of crystals during the present century. The ability of crystals to act as diffraction gratings for X-rays has proved beyond all doubt the regularity of atomic structure in them. In recent years even more direct methods have been developed, based on electron microscopy and other high-resolution microscopical techniques. In one such method, called *field-ion* microscopy, an extremely fine hemispherical tip of a specimen is examined, as shown in Fig. 1.1. This tip is positively charged electrically, so that lines of electric force radiate from it to a nearby fluorescent screen. A trace of gas such as helium is allowed to enter a vacuum chamber which surrounds the specimen. These atoms become positively charged when they touch the atoms of the tip and then accelerate down the lines of force to the screen, where they produce a visible image of the tip. The magnification and resolution of this image are high enough to show the individual atoms of the tip. The frontispiece shows an example. This is of course a flat picture of a hemispherical surface, so that there is some distortion; but the atoms and crystal facets of the surface are clearly visible.

The idea of atoms helped chemistry to make great progress in the 19th century. Striking regularities were observed in the proportions by which the chemical elements combine together. A table of unit chemical weights was drawn up, each element being given its own individual value in such a way that unit weight of one element always combines with one or a few unit weights of another. This suggested that each unit weight was proportional to the mass of a *unit particle* of the element and that chemical combination involves the joining together of such unit particles in definite and reproducible small numbers. It was also discovered that gases of the elements combine chemically in simple proportions by volume as well as by weight. The observed proportions suggested that equal volumes of gases contain equal numbers of particles at the same temperature and pressure (*Avogadro's hypothesis*). A complicating factor was that in most gases of elements the particles are not single atoms but *molecules* containing two or more atoms in chemical combination, e.g.  $O_2$ ,  $O_3$ ,  $H_2$ ,  $N_2$ ,  $Cl_2$ . Two tables were thus necessary, one for single atoms and one for molecules. These are of course the familiar tables of *atomic* and *molecular weights* of the elements.

The scales were chosen so that a single oxygen atom has a weight of 16. The molecular weights of oxygen ( $O_2$ ) and ozone ( $O_3$ ) are thus 32 and 48, respectively. A sample of an element contains 1 *mole* of particles (atoms or molecules) when its atomic or molecular weight is measured in grammes weight. A mole is now known to contain  $6.025 \times 10^{23}$  particles, this number being known as *Avogadro's number* ( $N_0$ ). Thus, a single oxygen atom weighs  $16 N_0^{-1}$ , i.e.  $2.66 \times 10^{-23}$  g. The quantity  $1.66 \times 10^{-24}$  g (i.e.  $N_0^{-1}$  g) is the *atomic mass unit*. Atomic weights are given in Table 1.1. Their wide range should be noticed, particularly as the densities of liquids and solids depend mainly on the weights of their atoms. A sample of an element with density  $\rho$  and atomic weight  $A$  contains  $N_0 \rho / A$  atoms/cm<sup>3</sup>.

Atoms and molecules are of course very small. The volume of 1 mole of gas at NTP (i.e. 0°C and 760 mm of mercury pressure) is 22,400 cm<sup>3</sup>. Divided into Avogadro's number, this gives *Loschmidt's number*,  $2.7 \times 10^{19}$  particles/cm<sup>3</sup>, which corresponds to an average distance of about  $33 \times 10^{-8}$  cm from one particle to the next. The particles themselves are even smaller. When a vapour is condensed to a liquid or solid, it shrinks to about one-thousandth of its volume at NTP. The atoms or molecules are thus only about  $3 \times 10^{-8}$  cm across. Atomic sizes can now be measured accurately by X-ray diffraction analysis of crystals. Because of their smallness, it is convenient to use a special unit of length, the Ångström ( $1 \text{ Å} = 10^{-8}$  cm) for them.

TABLE 1.1  
Physical Properties of Elements

Atomic number	Element	Atomic weight	Density at 20°C, g/cm <sup>3</sup>	Melting point, °C	Boiling point, °C	Specific heat at 20°C, 0.1 cal g <sup>-1</sup> °C <sup>-1</sup>	Coefficient of linear thermal expansion, 10 <sup>-6</sup> °C <sup>-1</sup>	Thermal conductivity, 0-100°C, 0.1 cal cm <sup>-1</sup> sec <sup>-1</sup> °C <sup>-1</sup>	Young's modulus, 10 <sup>9</sup> psi	Shear modulus, 10 <sup>9</sup> psi	Poisson's ratio	Viscosity at 20°C, 10 <sup>-3</sup> poises
1	Hydrogen (H)	1.008	0.00009	-259.2	-252.7	34.5		4 × 10 <sup>-3</sup>				0.0085
2	Helium (He)	4.003	0.00018		-268.9	12.5		3.4 × 10 <sup>-3</sup>				0.0194
3	Lithium (Li)	6.94	0.534	180.5	1330	7.9	56	1.7	1.66			
4	Beryllium (Be)	9.013	1.848	1277	2770	4.5	12.4	3.8	43	21	0.08	
5	Boron (B)	10.82	2.34	(2100)	(2550)	3.09	8.3					
6	Carbon (C)	12.011	2.25	3700 <sup>a</sup>	4830	1.65	3	0.57	{ 144 (in basal plane only) 1 (bulk polycrystalline)			
7	Nitrogen (N)	14.008	0.00125	-210	-196	1.22	1.2	38	120	50	0.25	0.0174
8	Oxygen (O)	16.00	0.00143	-219	-183	2.18		5.8 × 10 <sup>-4</sup>				0.020
9	Fluorine (F)	19.00	0.0017	-219.6	-188	1.8		5.8 × 10 <sup>-4</sup>				
10	Neon (Ne)	20.183	0.0009	-249	-246			1.1 × 10 <sup>-3</sup>				0.031
11	Sodium (Na)	22.997	0.971	97.8	892	2.95	71	3.2	1.3			
12	Magnesium (Mg)	24.32	1.74	650	1105	2.45	26	3.8	6.5	2.5	0.3	3



# Perfect Gases

13	Aluminium (Al)	26.98	2.699	660	2450	2.15	24	5.3	10	3.8	0.34	
14	Silicon (Si)	28.09	2.33	1410	2680	1.62	7.6	2.0	16			
15	Phosphorus (P) (white)	30.975	1.83	44.2	280	1.77	125					
16	Sulphur (S) (yellow)	32.066	2.07	119	445	1.75	64					
17	Chlorine (Cl)	35.457	0.0032	-101	-34.7	1.16						0.0132
18	Argon (A)	39.994	0.0018	-189.4	-186	1.25						0.0222
19	Potassium (K)	39.10	0.86	63.7	760	1.77	83	2.4	0.5			
20	Calcium (Ca)	40.08	1.55	838	1440	1.49	22	3.0	3	1	0.31	
21	Scandium (Sc)	44.96	2.99	1540	2730	1.34						
22	Titanium (Ti)	47.90	4.507	1670	3260	1.24	8.5	0.36	16.8	6	0.34	
23	Vanadium (V)	50.95	6.1	1860	3400	1.19	7.8	0.85	20	7.3	0.36	
24	Chromium (Cr)	52.01	7.19	1875	2665	1.1	6.2	1.6	36			
25	Manganese (Mn)	54.94	7.43	1245	2150	1.15	22		23			
26	Iron (Fe)	55.85	7.87	1536	3000	1.1	11.7	1.8	28.5	11.5	0.28	
27	Cobalt (Co)	58.94	8.85	1495	2900	0.99	12.3	1.65	30		0.31	
28	Nickel (Ni)	58.71	8.90	1453	2730	1.05	13.3	2.2	31	11.5	0.31	
29	Copper (Cu)	63.54	8.96	1083	2600	0.92	16.5	9.4	18	6.7	0.35	
30	Zinc (Zn)	65.38	7.13	419.5	906	0.915	40	2.7	14	5	0.35	
31	Gallium (Ga)	69.72	5.91	29.8	2240	0.79	18		1.4			
32	Germanium (Ge)	72.60	5.32	937	2830	0.73	6	1.5	11			
33	Arsenic (As)	74.91	5.72	613 <sup>a</sup>		0.82	4.7		11			
34	Selenium (Se)	78.96	4.79	217	685	0.84	37					
35	Bromine (Br)	79.916	3.12	-7.2	58	0.70						
36	Krypton (Kr)	83.8	0.0037	-157	-152							
37	Rubidium (Rb)	85.48	1.53	38.9	688	0.8	90		0.34			
38	Strontium (Sr)	87.63	2.60	768	1380				2.5	1	0.28	
39	Yttrium (Y)	88.92	4.47	1510	3030	0.71						

Table 1.1 (continued)

Atomic number	Element	Atomic weight	Density at 20°C, g/cm <sup>3</sup>	Melting point, °C	Boiling point, °C	Specific heat at 20°C, 0.1 cal g <sup>-1</sup> °C <sup>-1</sup>	Coefficient of linear thermal expansion, 10 <sup>-6</sup> °C <sup>-1</sup>	Thermal conductivity, 0-100°C, 0.1 cal cm <sup>-1</sup> sec <sup>-1</sup> °C <sup>-1</sup>	Young's modulus, 10 <sup>6</sup> psi	Shear modulus, 10 <sup>6</sup> psi	Poisson's ratio	Viscosity at 20°C, 10 <sup>-2</sup> poises
40	Zirconium (Zr)	91.22	6.49	1852	3580	0.67	5.8	0.4	14	5	0.34	
41	{ Niobium (Nb) Columbium (Cb)	92.91	8.57	2470	4900	0.65	7.1	1.4	15	5.4	0.38	
42	Molybdenum (Mo)	95.95	10.22	2610	5550	0.66	4.9	3.5	50			
43	Technetium (Tc)	98		(2100)	(3900)				59			
44	Ruthenium (Ru)	101.1	12.2	(2500)	(4900)	0.57	9.1		60	27	0.25	
45	Rhodium (Rh)	102.91	12.44	1965	4500	0.59	8.3	2.1	42			
46	Palladium (Pd)	106.7	12.02	1552	4000	0.58	11.8	1.7	17	7	0.39	
47	Silver (Ag)	107.88	10.49	960.8	1761	0.56	19.7	10	11	4	0.38	
48	Cadmium (Cd)	112.41	8.65	320.9	765	0.55	30	2.2	8	4	0.29	
49	Indium (In)	114.82	7.31	156.2	2000	0.57	33	0.57	1.6			
50	Tin (Sn)	118.70	7.298	231.9	2270	0.54	23	1.6	6.8	2.5	0.36	
51	Antimony (Sb)	121.76	6.62	630.5	1380	0.49	9.5	0.45	11			
52	Tellurium (Te)	127.61	6.24	449.5	990	0.47	16.8	0.14	6			
53	Iodine (I)	126.91	4.94	113.7	183	0.52	93	0.01				
54	Xenon (Xe)	131.30	0.0059	-112	-108			1.24 × 10 <sup>-3</sup>				

55	Caesium (Cs)	132.91	1.903	28.7	690	0.48	97			0.25
56	Barium (Ba)	137.36	3.5	714	1640	0.68			1.8	
57	Lanthanum (La)	138.92	6.19	920	3470	0.48			10	
(Rare earth elements here)										
72	Hafnium (Hf)	178.58	13.09	2250	5400	0.35		6.0	20	5 0.37
73	Tantalum (Ta)	180.95	16.6	2980	5400	0.34	6.5	1.3	27	
74	Tungsten (W)	183.86	19.3	3410	5900	0.33	4.3	4.5	50	22 0.17
75	Rhenium (Re)	186.22	21.04	3170	5900	0.33	6.7	1.7	70	30 0.26
76	Osmium (Os)	190.2	22.57	(3000)	5500	0.31	4.6		80	34 0.25
77	Iridium (Ir)	192.2	22.5	2455	5300	0.31	6.8	1.4	75	32 0.26
78	Platinum (Pt)	195.09	21.45	1769	4530	0.31	8.9	1.7	21	8 0.39
79	Gold (Au)	197.0	19.32	1063	2970	0.31	14.2	7.1	12	4 0.42
80	Mercury (Hg)	200.61	13.55	-38.36	357	0.33	61	0.2		1.556
81	Thallium (Tl)	204.39	11.85	303	1457	0.31			1	0.4 0.45
82	Lead (Pb)	207.21	11.36	327.4	1725	0.31	28	0.93	2.6	0.8 0.45
83	Bismuth (Bi)	209.00	9.80	271.3	1560	0.31	29.3	0.83		
84	Polonium (Po)	210		250			13.3	0.2	4.6	
85	Astatine (At)	211		(300)						
86	Radon (Rn)	222	0.01	(-70)	-61.8					
87	Francium (Fr)	223		(27)						
88	Radium (Ra)	226.05	5.0	700						
89	Actinium (Ac)	227		(1000)						
90	Thorium (Th)	232.05	11.66	1750	(3850)	0.34	12		11	4 0.30
91	Protactinium (Pa)	231.1	15.4	(1200)						
92	Uranium (U)	238.07	19.07	1132	3820	0.28	17	0.63	25	11 0.24

(Transuranic elements here; e.g. 93 Np, 94 Pu, 95 Am, 96 Cm, 97 Bk, 98 Cf, 99 E, 100 Fm, 101 Mv, 102 No, etc.)

• Sublimes.

## 1.2 KINETIC THEORY OF GASES

The other outstanding success of the atomic theory in the 19th century was its quantitative explanation of the mechanical properties of gases. Gases are simple forms of matter. They have low densities, expand to fill their containers and are easily compressed. These properties suggested that the particles in gases are mostly too far apart to exert forces on one another. Moreover, because equal numbers of gas particles in equal volumes at equal temperatures produce the same pressure (at low densities and high temperatures), *whatever their chemical species*, it seemed that this pressure was produced by the particles acting in a purely mechanical way as point centres of mass.

A gas was thus pictured as a collection of small elastic spheres, each of mass  $m$ , velocity  $c$ , momentum  $mc$  and kinetic energy  $\frac{1}{2}mc^2$ , flying about ceaselessly as separate individuals, moving in straight lines and bouncing off the walls of their containers and also, when they happen to meet, off one another. When a gas is allowed to remain undisturbed in its container for a length of time, these collisions cause it to settle down into a *state of equilibrium* in which it is *uniform* (i.e. its particles are distributed impartially throughout the whole container—we ignore for the moment the effect of gravity), is *isotropic* (i.e. its particles move impartially in all directions) and is *constant* in its bulk properties such as pressure and temperature.

When the gas is in this state, the theory of its properties becomes much simpler. We can, for example, pretend that the gas particles bounce off the walls of their container like perfect elastic spheres rebounding from a perfectly smooth, reflecting surface, even though it is known experimentally that they do not do this but tend to stick to the surface for a little time before flying off in some unrelated direction. The reason is that, because the gas is uniform and isotropic, particles approach and leave the walls in random directions, so that the *overall* distribution of directions of motion is unaffected by the walls. Also, when the gas is constant in its properties, the particles on average approach and leave the walls in the same numbers and with the same kinetic energies. The walls thus behave to the gas as a whole, even though not to individual particles, as if they were perfect reflectors of its particles. By the same argument, the distribution of particle motions is unaffected by collisions among the particles themselves; on average, as many particles are knocked into a particular direction and speed as are knocked out of it. It also follows that the shape of the container does not affect the equilibrium properties of the gas; particles re-enter the gas from a wall in just the same numbers and with just the same velocities as they would if that wall were not there and they

had come instead from another part of the gas behind it. The container can thus be altered in shape (at constant volume), by removing some walls and building others in other positions, without altering the properties of the gas.

The leading idea in the kinetic theory of gases is that gas pressure is caused by the impacts of gas particles on the walls of the container. The equilibrium properties mentioned above enable us to calculate the pressure in terms of the behaviour of a single gas particle moving in a cubical box with perfectly reflecting sides of length  $L$ , as shown two-dimensionally in Fig. 1.2. We resolve its velocity  $c$  into component velocities  $u$ ,  $v$  and  $w$ ,

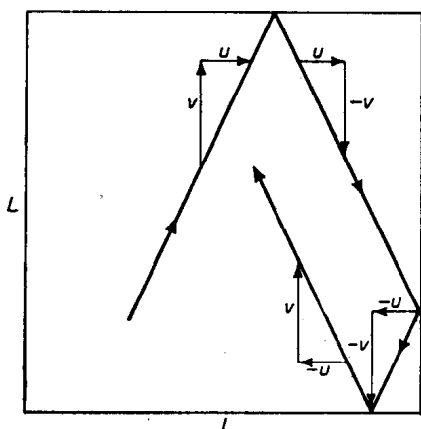


Fig. 1.2. Path of a gas particle in a box.

parallel to the edges of the box. At each collision the velocity component perpendicular to the wall is exactly reversed and the other two components unchanged. Each collision which changes, say,  $+u$  to  $-u$ , also changes the momentum of the particle by  $2mu$  and hence, because momentum is conserved, gives an outward momentum  $2mu$  to the wall in question. This wall is hit  $u/2L$  times per second by the particle and so receives momentum from it at a rate  $mu^2/L$  per second. From Newton's second law (*force = rate of momentum change*) this gives a force  $mu^2/L$  on the wall. The pressure  $p$ , i.e. force per unit area, on this wall due to all particles in the gas is then given by

$$p = \frac{\sum mu^2}{L^3} = \frac{m}{V} \sum u^2, \quad (1.1)$$

where  $V (=L^3)$  is the volume and the sum is over all particles. We see that each particle contributes independently to the total pressure. This remains

true if the particles are of different chemical species and have different masses  $m_1, m_2, \dots$  etc., the sum then being replaced by  $m_1 u_1^2 + m_2 u_2^2 + \dots$  etc. This gives *Dalton's law*: the total pressure exerted by a mixture of different gases is the sum of the *partial pressures* of each of these gases separately.

The pressures on the other faces are found similarly. Since the gas is uniform and isotropic, they are all equal. Hence,

$$\sum u^2 = \sum v^2 = \sum w^2 = \frac{1}{3} \sum (u^2 + v^2 + w^2) = \frac{1}{3} \sum c^2 = \frac{1}{3} N \overline{c^2}, \quad (1.2)$$

where  $\overline{c^2}$  is the mean-square velocity and  $N$  is the number of particles in volume  $V$ . Substituting in Equation (1.1), we obtain

$$\frac{1}{3} N m \overline{c^2} = \frac{2}{3} E = pV, \quad (1.3)$$

where  $E (= \frac{1}{2} N m \overline{c^2})$  is the total kinetic energy of the particles. Since  $Nm = \rho V$ , where  $\rho$  is the *density*, the mean-square speed is given by

$$\overline{c^2} = \frac{3p}{\rho}. \quad (1.4)$$

The densities of hydrogen and nitrogen at NTP are  $9 \times 10^{-5}$  and  $1.25 \times 10^{-3}$  g cm $^{-3}$ , respectively. If  $p \simeq 10^6$  dyn cm $^{-2}$  (atmospheric pressure), this gives the speed (root mean-square) of hydrogen molecules at NTP as about  $1.8 \times 10^5$  cm sec $^{-1}$  ( $\simeq 1$  mile sec $^{-1}$ ) and that of nitrogen molecules as about  $5 \times 10^4$  cm sec $^{-1}$ . These are about the muzzle velocities of rifle bullets. There is direct evidence for these high speeds from the fact that sound waves in air, which are transmitted by the motion of air molecules, travel at about  $3.3 \times 10^4$  cm sec $^{-1}$  under ordinary conditions (cf. Section 12.4).

When a gas is heated at constant pressure, it expands; when heated at constant volume, its pressure rises. Thus,  $pV$  increases as heat energy is given to the gas. Since  $pV$  is proportional to the kinetic energy of the particles, we suppose that this kinetic energy is *heat energy*. The hotness of the gas, i.e. the *temperature*, is thus a measure of the average kinetic energy per particle. Of all the various ways in which we could define temperature in terms of this kinetic energy, the simplest and most useful is to make it directly proportional, i.e.  $T \propto E$ . In fact, the *absolute temperature*  $T$  on the *perfect gas scale* is defined from the relation

$$\frac{1}{2} m \overline{c^2} = \frac{3}{2} kT, \quad (1.5)$$

where  $k$  is a constant. Substituted into Equation (1.3), this becomes

$$pV = NkT, \quad (1.6)$$

the familiar *equation of state* of a *perfect gas*. It summarizes the two laws

of a perfect gas: *Charles' law* ( $V$  is proportional to  $T$  at constant  $p$ ) and *Boyle's law* ( $pV$  is constant at constant  $T$ ). We also see that the *specific heat* (rate of increase of energy with temperature) belonging to the translational motion of the particles of a perfect gas is the same at all temperatures; this follows from the fact that we have *defined* temperature as proportional to the energy of such a gas.

For 1 mole of gas ( $N = N_0 = \text{Avogadro's number}$ ), the equation of state becomes

$$pV = RT, \quad (1.7)$$

where

$$R = N_0 k. \quad (1.8)$$

The constants  $k$  and  $R$  are *universal* constants, the same for all substances. This can be proved in a very general way from statistical mechanics. It also follows directly from Avogadro's hypothesis. Consider two gases with particles of masses  $m_1$  and  $m_2$  and mean-square velocities  $\overline{c_1^2}$  and  $\overline{c_2^2}$ , which are at the same temperature  $T$  and which have the same volume  $V$  and pressure  $p$ . Then, by Avogadro's hypothesis, they have the same number of particles,  $N_1 = N_2$ . Since  $pV = \frac{1}{3}N_1m_1\overline{c_1^2} = \frac{1}{3}N_2m_2\overline{c_2^2}$ , it follows that

$$m_1\overline{c_1^2} = m_2\overline{c_2^2} \quad (1.9)$$

and, hence, that  $k$  in Equation (1.5) is the same for both gases.

We see that light particles move faster than heavy ones at the same temperature. This enables us to separate two gases from a mixture by allowing them to leak out of small holes in their container. The rate of *effusion* from such a hole is proportional to the thermal velocity of a gas particle, and so varies inversely with the square root of the mass (*Graham's law*). Thus, hydrogen escapes four times as fast as oxygen. The holes must be small to prevent the gas from streaming out in bulk and thereby sweeping heavy and light particles along together. A porous membrane (e.g. unglazed porcelain) is often used, in which case the effect is referred to as *transpiration*. The method is important for separating gases of similar properties, such as *isotopes* (atoms of different masses belonging to the same chemical element). When the isotopes differ only slightly in mass, as in the separation of uranium isotopes by the gaseous diffusion method, the degree of separation achieved by the passage through a single membrane is small. It is usual then to pass the gas (e.g. uranium hexafluoride) through a series or *cascade* of separations, each stage of which consists of a membrane with ingoing and outgoing chambers, together with pumps to send the enriched gas forward to later stages and the impoverished gas back to earlier stages.

To find the numerical value of  $R$  in Equation (1.7), we fit this equation to real gases; these always obey this equation at sufficiently low densities. When  $R$  and  $N_0$  are known, then  $k$  in Equations (1.6) and (1.8) can be found. The temperature scale is chosen so that there are 100 degrees between the freezing and boiling points of water at 1 atm pressure; we then have  $k = \text{Boltzmann's constant} = 1.38 \times 10^{-16} \text{ erg deg}^{-1}$  and  $R = \text{the gas constant} = 8.313 \times 10^7 \text{ erg deg}^{-1} = 1.986 \text{ cal deg}^{-1} \text{ mole}^{-1}$ . At the freezing point of water a gas at normal pressure decreases in volume by about 1 part in 273 for each degree fall in temperature. Thus, a *perfect* gas (which obeys Equation (1.6) under all circumstances) should shrink to zero volume and lose all its kinetic energy at about  $-273^\circ\text{C}$ . The temperature  $T$  in Equation (1.6) is the *absolute temperature*, measured in *degrees Kelvin* ( $^\circ\text{K}$ ). The *absolute zero* of temperature is  $0^\circ\text{K}$  ( $= -273.16^\circ\text{C} = -459.69^\circ\text{F}$ ).

### 1.3 THE MAXWELL-BOLTZMANN DISTRIBUTION LAW

Owing to gains and losses of energy in chance collisions, the actual energy of a particle at any instant fluctuates widely about its average value. Although these individual fluctuations are highly erratic, the average distribution of a large number of particles over various levels of energy is a steady and calculable property of a gas, provided there is thermal equilibrium among its particles.

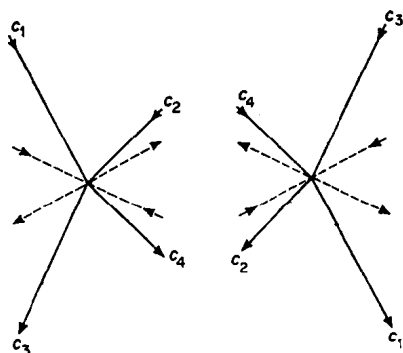


Fig. 1.3. A collision and its inverse. The broken lines show each collision as seen by an observer moving with the centre of mass of the particles.

Let all particles have the same mass. Let  $f$  be the number of particles with velocity  $c$ ; or, more precisely, let  $f(c) dc$  be the number within a small range  $dc$  of velocities centred about the value  $c$ . We expect  $f$  to depend on  $c$  and so write it as  $f(c)$ . In Fig. 1.3 we show a collision in which two



particles change their velocities from  $c_1$  and  $c_2$  to  $c_3$  and  $c_4$ . The total kinetic energy of the particles is conserved; hence,

$$c_1^2 + c_2^2 = c_3^2 + c_4^2. \quad (1.10)$$

The chance of such a collision occurring in a given time is proportional to the numbers,  $f(c_1)$  and  $f(c_2)$ , of both kinds of particles in the gas. The rate of such collisions is thus given by  $\alpha f(c_1)f(c_2)$ , where  $\alpha$  is a proportionality factor. Consider next the inverse collision in which two particles change their velocities from  $c_3$  and  $c_4$  to  $c_1$  and  $c_2$  (Fig. 1.3). The rate of this may similarly be written  $\alpha' f(c_3)f(c_4)$ . Since the gas is in equilibrium,

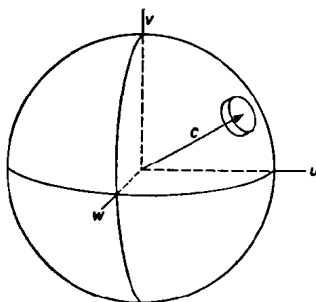


Fig. 1.4. Velocity diagram.

these two rates are equal. We must also have  $\alpha = \alpha'$ , since observers moving with the centres of mass of the particles would see the two collisions as *completely equivalent*, as shown by the broken lines in Fig. 1.3. Hence,  $f(c_1)f(c_2) = f(c_3)f(c_4)$ , i.e.

$$\ln f(c_1) + \ln f(c_2) = \ln f(c_3) + \ln f(c_4). \quad (1.11)$$

A solution of Equations (1.10) and (1.11) suggests itself immediately. It is simply  $\ln f(c) \propto c^2$ , or

$$f(c) = A e^{-\beta c^2}, \quad (1.12)$$

where  $A$  and  $\beta$  are constants. The minus sign is introduced since, for a finite kinetic energy,  $f(c)$  must decrease as  $c^2$  increases. It can be proved by further analysis that this equation is the only solution.

We sometimes need to know the numbers of particles moving at various speeds, *irrespective of direction*. In the velocity diagram of Fig. 1.4,  $c$  is represented by the vector shown and  $f(c) dc$  is the number of particles whose velocities are represented by points lying in the element shown at the end of this vector. This element is of thickness  $dc$  and stands on unit area of a sphere of radius  $c$ . To find the total number of particles  $N(c) dc$