as discussed under effusion; *i.e.*, the rate of passage is inversely proportional to the square root of the molecular weight.

If the holes of the diaphragm are very small, of the order of  $10^{-5}$  cm for gases at 1 atm, pressures may be obtained comparable to those calculated from the equation. For large holes ordinary flow occurs and the pressure Although maximum pressures are obtainable with very small is less. holes, clearly high transport of gas cannot be obtained in this case because of the high resistance. With large holes the rate of transport is low because of small pressure. At some intermediate size of pores the rate of transpiration will be a maximum. The usual porous diaphragm will contain openings of a variety of sizes so that thermal transpiration will occur in the smaller ones and ordinary fluid flow in the opposite direction through the larger ones, thus internally "short-circuiting" the diaphragm to a large extent. Therefore, the total transport of gas through the diaphragm usually is considerably less than might otherwise be anticipated. For example, when 2 or 3 in. of diatomaceous earth was rammed into a 1-in. porcelain tube, one end of which was left open to the atmosphere and heated to 1000°C and the other end closed and connected to a manometer, the pressure fell in a few minutes to 1 cm Hg less than atmospheric. When both ends were left open to the atmosphere, the rate of flow of air was about 20 cc/min. Most commercial bricks showed the effects to only about one-tenth the magnitude observed for diatomaceous earth. This effect may become important in industrial furnaces when it is necessary to maintain a controlled atmosphere, as in annealing or heat-treating.

Distribution of Velocities. Thus far, our simplified picture of gas molecules as mass points (since collisions have not been considered), onethird of which move in each of the three directions with a single constant velocity (at a given temperature), has led to several fruitful results. A more complete picture considers the molecules to have finite diameter and to move in all possible directions with all velocities but still does not consider them to occupy an appreciable fraction of the space or to have any forces acting between them. Some of the results of this extended kinetic theory will be given without derivation.

At constant temperature the probability that a given molecule has a velocity u at any instant is proportional to  $e^{-mu^{2/2kT}}$ , where k is Boltzmann's constant, that is, R, the gas constant, divided by N, Avogadro's number. If we let  $n_u$  be the number of molecules with velocity between zero and u, then  $dn_u$  is the number having velocity between u and u + du, which is clearly proportional to the above probability. A plot of  $dn_u/du$  vs. u is shown in Fig. 2-1. This ordinate has been chosen, since it is proportional to the probability of a given u and hence to the number of molecules.

way: To a steam engineer interested in the properties of water substance in the vicinity of its critical point, van der Waals' and Thomson's concept sheds considerable light, but to the metallurgist, interested in metals slightly above their melting point, the concept of the continuity between gaseous and liquid states contributes little but the incorrect inference that the atoms of the molten metal behave in the random manner characteristic of gases. For the present it will suffice to mention that the chemical forces between atoms or molecules are of very short range and play a predominant role in condensed phases (liquids or solids) but a very minor role in gases at a pressure of 1 atm or less.

In most metallurgical operations, involving gases at a pressure in the vicinity of 1 atm and particularly at elevated temperature, the ideal-gas law is adequate to describe the pressure-volume relations. As a general rule it may be expected that at low temperature the departures from this law are more pronounced for gases with higher boiling point. Thus. the following series is arranged in order of increasing boiling point: hydrogen, carbon monoxide, nitrogen or oxygen, carbon dioxide, water; and this is also the order of increasing deviation from ideality at low temperature. In the vicinity of room temperature and pressure the departure of carbon dioxide from ideality is 0.6 per cent (i.e., the volume occupied by a mole is 0.6 per cent less than that calculated from the ideal-gas law), and that of carbon monoxide is 0.1 per cent. If 100 cc of pure carbon monoxide is burned to carbon dioxide, as is done in gas analysis, only 99.5 cc of carbon dioxide is obtained, thus resulting in  $\frac{1}{2}$  per cent error in the analysis if no correction is made. Such a departure from ideality at low temperature is attributable principally to the intermolecular forces represented by the a constant of van der Waals' equation. Since these are the same forces which hold a liquid together, it is readily seen why these departures correlate with the boiling point and why they are negative in sign in the sense that the observed volume is less than the ideal-gas volume. At high temperature (steelmaking temperature) the departure from ideality becomes smaller but now is attributable principally to the molecular size, represented by van der Waals' b constant, and is therefore positive. As only the simpler (smaller) molecules are stable at such temperatures, the departures from ideality cannot be expected to exceed 0.01 to 0.02 per cent. At some intermediate temperature the positive and negative effects are equal and the gas behaves as a perfect gas up to a pressure of many atmospheres.

## GAS MIXTURES

When more than one component is present in a phase under consideration, the state is obviously not completely specified unless the relative amounts of the various components are designated. Of the several ways

n	l	m	8		
1	0	0	- <del>1</del>		
1	0	0			

For n = 2, *i.e.*, the second shell, there are eight possible sets of quantum numbers:

n	l	m	8
2 2 2 2 2 2 2 2 2 2 2	1 1 1 1 1 1 0 0	$ \begin{array}{c} 1 \\ 1 \\ 0 \\ -1 \\ -1 \\ 0 \\ 0 \end{array} $	

Table 3-2 shows the number of electrons in the shells and subshells, *i.e.*, those with various values of n and l, for each of the chemical elements. It will be noted that the maximum tota! number of electrons in any shell is  $2(n)^2$ , or 2, 8, 18, 32, ... Strictly this table refers to an isolated atom, i.e., one with no other atom in the vicinity. The arrangement given in each case corresponds to the lowest possible energy state, and hence the most stable state, for a given number of orbital electrons. This is seen from the fact that in the first three periods no electron with higher value of n (corresponding to higher energy) appears until all possible lower quantum states are occupied. Although n is called the principal quantum number in the sense that it is predominant in defining the energy state, the other quantum numbers also define a contribution to the energy. Thus, although the lowest energy state is always the most stable, it does not always happen that lower shells are completely filled before a higher one may be occupied; electrons enter the fourth and higher shells before the preceding ones are completely filled. This phenomenon gives rise to the so-called transition elements of the long periods (scandium through nickel and yttrium through palladium) and also to the group of elements known as the rare earths. The arrangement of Table 3-2 is quite consistent with the periodic chart of Table 3-1, it being noted that elements with electrons only with principal quantum number 1 fall in the first period, those with electrons of principal quantum number 2 (but no greater) fall in the second period, etc. Also the group number corre-

The symbol 11 indicates a pair of atomic or nonbonding electrons, • a bonding electron, and  $\circ$  a metallic orbital, normally open and accommodating the resonance. The second formulation, Sn B, may be imagined as derived from the first. Sn A, by the dropping of one bonding electron from 5p to 5s, forming there an electron pair; this leaves a vacant orbital in Sn B. By a similar step Sn C may be imagined as derived from Sn B: it will be noted that the configuration Sn C corresponds to that given for an isolated Sn atom in Table 3-2. Gray tin with its diamond-type structure and absence of metallic properties is assumed to consist exclusively of tetravalent Sn A. White tin might at first be thought to consist exclusively of bivalent Sn B atoms, as Sn B possesses the two requirements for the metallic bond-bonding electrons and an extra orbital. In accord with the principle mentioned in the preceding paragraph, however, only three-quarters of the atoms need have an extra orbital-the energy of two resonating bonds being roughly the same as that of four nonresonating bonds. Hence it seems likely that white tin is composed of 75 per cent Sn B atoms and 25 per cent Sn A atoms, leading to a valence of  $(\frac{3}{4})(2) + (\frac{1}{4})(4) = 2.5$ . This valence seems in accord with the properties of white tin, in particular with the valence (2.44, given later in Table 3-4) derived from the interatomic distances with the aid of Eq. (3-1), as will be discussed later in this chapter. It seems worth noting at this point that Pauling in his later work considers lead in the pure state to have a valence of 2.0 rather than 2.5, all atoms being analogous to Sn B with none of the A type; this is in accord with the softer and more metallic nature of lead.

One more example will be given. As in the case of tin, possible electronic configurations for zinc are shown below.

	Valence	3 <i>d</i>				48	4 <i>p</i>	
Zn A Zn B Zn C Zn D	6 4 2 0				• 11 11 11	• ↑↓ ↑↓	• • • †↓	

Clearly, metallic zinc cannot consist exclusively of Zn A atoms, for these have no extra orbitals to accommodate resonance. Similarly Zn D is excluded, as it has no bonding electrons at all. It might be expected that metallic Zn consists principally of Zn B atoms, as this type has the largest number of bonding electrons consistent with an extra orbital to accommodate resonance. In fact Pauling now considers that metallic zinc consists nearly entirely of these B type atoms, corresponding to a valence of 4.