**TABLE 15–3**
**Probabilities of Various Macrostates for 100 Coin Tosses**

| Macrostate | | Number of | |
|---|---|---|---|
| heads | tails | microstates | Probability |
| 100 | 0 | 1 | $8.0 \times 10^{-31}$ |
| 99 | 1 | $1.0 \times 10^{2}$ | $8.0 \times 10^{-29}$ |
| 90 | 10 | $1.7 \times 10^{13}$ | $1.0 \times 10^{-17}$ |
| 80 | 20 | $5.4 \times 10^{20}$ | $4.0 \times 10^{-10}$ |
| 60 | 40 | $1.4 \times 10^{28}$ | 0.01 |
| 55 | 45 | $6.1 \times 10^{28}$ | 0.05 |
| 50 | 50 | $1.0 \times 10^{29}$ | 0.08 |
| 45 | 55 | $6.1 \times 10^{28}$ | 0.05 |
| 40 | 60 | $1.4 \times 10^{28}$ | 0.01 |
| 20 | 80 | $5.4 \times 10^{20}$ | $4.0 \times 10^{-10}$ |
| 10 | 90 | $1.7 \times 10^{13}$ | $1.0 \times 10^{-17}$ |
| 1 | 99 | $1.0 \times 10^{2}$ | $8.0 \times 10^{-29}$ |
| 0 | 100 | 1 | $8.0 \times 10^{-31}$ |

arrangement greatly increases as the number of coins increases. These same ideas can be applied to the molecules of a system. For example, the most probable state of a gas (say, the air in a room) is one in which the molecules take up the whole space and move about randomly; this corresponds to the Maxwellian distribution, Fig. 15–19a (and see Chapter 13). On the other hand, the very orderly arrangement of all the molecules located in one corner of the room and all moving with the same velocity (Fig. 15–19b) is extremely unlikely.

From these examples, it is clear that probability is directly related to disorder and hence to entropy. That is, the most probable state is the one with greatest entropy, or greatest disorder and randomness.

*Entropy in terms of probability*

In terms of probability, the second law of thermodynamics—which tells us that entropy increases in any process—reduces to the statement that those processes occur which are most probable. The second law thus becomes a trivial statement. However, there is an additional element now. The second law in terms of probability does not *forbid* a decrease in entropy. Rather, it says the probability is extremely low. It is not impossible that salt and pepper should separate spontaneously into layers, or that a broken teacup should mend itself. It is even possible that a lake should freeze over on a hot summer day (that is, for heat to flow out of the cold lake into the warmer surroundings). But the probability for such events occurring is miniscule. In our coin examples, we saw that increasing the number of coins from 4 to 100 drastically reduced the probability of large deviations from the average, or most probable, arrangement. In ordinary systems, we are dealing not with 100 molecules, but with incredibly large numbers of molecules: in 1 mole alone there are $6 \times 10^{23}$ molecules. Hence the probability of deviation far from the average is incredibly tiny. For example, it has been calculated that the probability that a stone resting on the ground could transform 1 cal of thermal energy into mechanical energy and rise up into the air is much less likely than the probability that a group of monkeys typing randomly would by chance produce the complete works of Shakespeare.

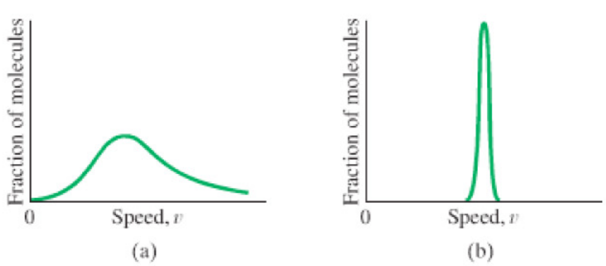


**FIGURE 15–19** (a) Most probable distribution of molecular speeds in a gas (Maxwellian, or random); (b) orderly, but highly unlikely, distribution of speeds in which all molecules have nearly the same speed.