Probability, Distributions, and Equilibrium

If nature does not answer first what we want, it is better to take what answer we get.

—Josiah Willard Gibbs, Lecture XXX, Monday, February 5, 1900

1.1 Chemical Change

What makes chemicals react? Do substances react to give the more stable product? Is it the release of heat that drives chemical processes? Or is it something else? It isn't hard to demonstrate that although most reactions give off heat, some actually absorb heat as they occur. (Did you know that if you add salt to ice water, it gets *really* cold? Why is that?) In addition, many chemical reactions seem to stop before they're complete. They just seem to never use all of their limiting reactant. Why is that? More practically, how can we predict what is going to happen, and how can we make chemistry work in our favor?

Your body is an incredibly complex mixture of chemicals. Is there a special life force that governs the chemistry in your body, or is it, like all nonliving things, governed by the force of nature?

Why does a drop of food coloring in a glass of water spread until the entire solution is colored? Why does ice melt in a glass of lemonade? If your answer to either of these questions is, "It just does!" you aren't too far from the mark. There's something about diffusion and melting that common experience tells us is irreversible. Imagine watching a movie where a glass of green liquid suddenly separates into half blue on the left and half yellow on the right. Would you believe it? What if a puddle of water suddenly came together and formed an ice sculpture?

These are questions of *thermodynamics*, the study of the driving force behind chemical and physical change. We all know from our experience that certain things happen only in one direction. Anything else would be ridiculous and totally unbelievable. The premise of this entire discussion is that the force of nature driving all chemical reactions in all systems, living and nonliving, is really nothing more than the *statistics* of blind chance. *All chemical reactions proceed because they are going from a less probable state to a more probable one*. For some of you this is going to be a hard pill to swallow. What about free will? How can it be that all natural processes are simply a result of chance?

You may not be comfortable with the idea that chance is behind all natural processes. That's OK. Albert Einstein, a pretty smart guy, whose discovery of quantum statistical mechanics underlies all of what we are about to discuss, to his death refused to believe that simple chance could be the real driving force behind all of life and all of the beauty of nature. His famous assertion, "Surely, God does not play dice," says it all. Einstein simply could not believe that his own discovery was truly fundamental and not just a trick.

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But, trick or not, over the 80 years since that discovery, no one—Einstein included—has been able to find any simpler, more powerful driving force than simple blind chance to explain and predict all of nature's wonders. Basically, the argument here is going to be that chemical reactions proceed not because they release energy, but, instead, because the chance of their doing anything *else* is incredibly small.

The interesting thing is that rather than just throwing up our hands and saying, "So what happens, happens—too bad," understanding chemistry in this way gives us the opportunity to direct it in ways we want it to go. Just because a chemical reaction *by itself* is headed in one direction doesn't mean we can't direct it otherwise. Sure we can. We can be *agents of change* if we want to, but in order to do that, we need to understand what it is that is causing the change (or lack thereof) in the first place. This, then, is what thermodynamics is all about.

The really exciting thing about getting a feeling for thermodynamics is that by understanding the underlying means by which chemical changes occur, we might be able to *direct* those reactions the way we want them to go (or to stop them altogether). This is true whether we are talking about the chemistry of cancer or the chemistry of ozone depletion.

1.2 Chemical Equilibrium

Much of this book is an attempt to help you understand why chemical reactions happen and why, once started, they always proceed toward a state we call *equilibrium*. We will say that a chemical system is at equilibrium if there is no tendency for it to change in any way *of its own accord*. Equilibrium is the end of the road, the state of "no observable reaction." We say that chemical reactions continue until they "reach equilibrium," at which point we can observe no further changes in pressure, volume, temperature, concentration, or color. Nonetheless, we shall see in this chapter that chemical equilibrium is very *dynamic*, much like the constant shuffling of a deck of cards.

We want to understand both what equilibrium is and how chemical reactions proceed toward it. The goal, then, of this chapter is to convince you of two ideas:

1. The equilibrium state (especially, *equilibrium constants*) can be predicted based on probability alone, and
2. The predictive nature of probability is especially well suited to chemical systems due to the sheer magnitude of the number of particles involved.

First, though, we need to discuss just the basics of probability.

1.3 Probability Is "(Ways of getting *x*)/(Ways total)"

Imagine throwing a standard six-sided die. What is the probability of rolling a 4? If you said, "one sixth," or "one in six," you were right. There is one way a die can land as a 4 out of a total of six possible ways it can land. Provided the die is not "loaded," that is, that it is not constructed or damaged in some way that makes it land one way more often than another, we can say

$$P_4 = \frac{(\text{Ways of getting 4})}{(\text{Ways total})} = 1/6$$

where "P_4" is the probability of rolling a 4. We say that the probability of rolling a 4 is "1/6" or "one chance in 6" or "16.66%" or 0.16666 . . . . In general, when each possibility is equally probable, we can just write that the probability of some outcome "*x*" is simply

$$P_x = \frac{(\text{Ways of getting } x)}{(\text{Ways total})} \tag{1.1}$$

This simple definition of probability as "ways of getting something divided by ways total" is fundamental to everything in this book.

1.4 AND Probability Multiplies

Now imagine throwing that same die 10 times. What is the probability of rolling a 4 ten times in a row? That is, what is the probability of it landing a 4 the first time *and* a 4 the second time *and* the third time *and* the fourth time, etc.? How probable do you think that is? Your intuition probably says, "not very!" But *exactly* how (im)probable is it? The answer is fairly intuitive:

$$P = \frac{1}{6} \times \frac{1}{6} \times \frac{1}{6} \times \frac{1}{6} \times \frac{1}{6} \times \frac{1}{6} \times \frac{1}{6} \times \frac{1}{6} \times \frac{1}{6} \times \frac{1}{6} = \left(\frac{1}{6}\right)^{10}$$

This number is quite small, 1.65×10^{-8}. But probability is more than just a number, it is (ways of getting x)/(ways total). Let's work it out as a fraction:

$$P = \left(\frac{1}{6}\right)^{10} = \frac{1}{60466176}$$

In fact, there is *one* way to roll a 4 ten times in a row, and there are 60,466,176 ways of rolling a die ten times. There is about a 1 in 60,000,000 chance of rolling that 4 ten times in a row. No wonder it's not very likely to happen!

The sorts of events we are talking about here are called *independent* events, because the outcome of one does not influence the probability of the outcome of the next. No matter how many times we roll a 4, the probability that the *next* roll will produce a 4 is still 1/6.

But here's another example, where the outcome of the second event is not independent of the first: What is the probability of drawing two hearts off the top of a standard well-shuffled deck of cards (13 spades, 13 hearts, 13 diamonds, and 13 clubs)? Can you see how to do it? Here is the calculation:

$$P_{\heartsuit\heartsuit} = \left(\frac{13}{52} \times \frac{12}{51}\right) = \frac{156}{2652} = 0.0588$$

The first fraction, 13/52, is the number of ways of drawing a heart for the first card divided by the total number of cards; the second fraction, 12/51, is the number of ways of drawing a heart *once one is removed from the deck* divided by the total number of cards *now in the deck*. Our calculation shows that there are 156 ways of drawing two hearts off the top of the deck out of a total of 2652 ways of drawing two cards. This amounts to about a 6% chance.

1.5 OR Probability Adds

What is the probability of throwing one normal six-sided die and rolling a 2 *or* a 3? The answer is 2/6:

$$P_{2 \text{ or } 3} = P_2 + P_3 = \frac{1}{6} + \frac{1}{6} = \frac{2}{6}$$

The probability of throwing a 2 is 1/6, and the probability of throwing a 3 is also 1/6. There are two ways to throw "a 2 or a 3" out of 6 total ways, for a probability of 2/6. Another way of saying this is that there is a "33% chance" of throwing a 2 or a 3.

1.6 AND and OR Probability Can Be Combined

Probability starts getting more interesting when we consider somewhat more complicated examples. For example, throw two normal six-sided dice. What is the probability of rolling an 8? This is trickier and can be solved more than one way. Based on the idea that $P_8 =$ (number of ways to roll 8) / (total ways), we could work out all the ways to get 8 and divide by the total number of ways of rolling two dice:

$$(\text{number of ways to roll 8}) = \text{five: } (2, 6), \ (6, 2), \ (3, 5), \ (5, 3), \ (4, 4)$$

$$(\text{total number of ways of rolling two dice}) = 6 \times 6 = 36$$

Thus, $P_8 = 5/36$. Another way of doing this, though, is by figuring out the different probabilities of all the independent possibilities and combining them. Thus, throwing an 8 is the same as throwing (a 2 *and* a 6) *or* (a 6 *and* a 2) *or* (a 3 *and* a 5) *or* (a 5 *and* a 3) *or* (two 4s):

$$P_8 = P_{2,6} + P_{6,2} + P_{3,5} + P_{5,3} + P_{4,4}$$
$$= \left(\frac{1}{6} \times \frac{1}{6}\right) + \left(\frac{1}{6} \times \frac{1}{6}\right) + \left(\frac{1}{6} \times \frac{1}{6}\right) + \left(\frac{1}{6} \times \frac{1}{6}\right) + \left(\frac{1}{6} \times \frac{1}{6}\right)$$
$$= \frac{5}{36}$$

Each of these five possibilities is independent and gives the desired outcome. Thus, we add them to give the overall probability of rolling 8.

This second way may seem more cumbersome at first, but consider this next example: What is the probability that *exactly one* of the top two cards of a standard well-shuffled deck of cards is a heart? In this case figuring out all the possibilities by hand (there are 1014) is much more difficult than using AND and OR.

We must calculate the probability of first drawing a heart (13/52) *and* then a card which is not a heart (39/51) *or* first drawing a card which is not a heart (39/52) *and* then the heart (13/51):

$$P = \left(\frac{13}{52} \times \frac{39}{51}\right) + \left(\frac{39}{52} \times \frac{13}{51}\right) = \frac{1014}{2652} = 0.382$$

Thus, there is a 38.2% chance of exactly one of the first two cards being a heart. Note that once again we have to consider the fact that after the first card is accounted for, there are only 51 cards remaining in the deck.

1.7 The Probability of "Not X" Is One Minus the Probability of "X"

There are two ways of thinking about determining the probability that when two cards are drawn off the top of the deck, neither card is a heart. The first approach is the same one we used to determine the probability that both cards would be hearts. We need to calculate the probability of first drawing a card that is not a heart (39/52) *and* then a card which is also not a heart (38/51):

$$P = \frac{39}{52} \times \frac{38}{51} = \frac{1482}{2652} = 0.559$$

Thus, there is a 55.9% chance that when two cards are drawn off the top of the deck, neither one of them will be a heart.

The second approach takes advantage of the fact that we already know the probability of all the outcomes except one. In this example of drawing two cards off the top of a deck, there are three possible outcomes: both of the cards will be hearts, one of the cards will be a

heart, or neither of the cards will be a heart. This is illustrated with a pie chart in Figure 1.1. Each slice of the pie represents a possible outcome. The probability of drawing two hearts is a slice accounting for 5.9% of the total pie. The probability of drawing one heart and one non-heart accounts for another 38.2% of the pie. Since the entire pie represents 100%, the remaining 55.9% must be the probability that neither card drawn will be a heart.

A more mathematical way to say this is

$$P_{\text{not } x} = 1 - P_x$$

In this example, the probability that neither card drawn will be a heart is the probability that the cards drawn are *not* "one (0.382) or both (0.059) are hearts." So in this case we could have calculated

$$P = 1 - (0.382 + 0.059) = 0.559$$

We arrive at the same result, that the probability of not drawing a heart is 56%! In this case the second approach was the easiest since we already knew the probabilities of all the outcomes except the one we wanted.

Figure 1.1
The three possible outcomes of drawing two cards off the top of a deck add up to 100%.

1.8 Probability Can Be Interpreted Two Ways

It's important to realize that in all of the above example we didn't have to do any multiplication or addition at all if we didn't want to. All we really had to do, for example, was count all the ways of getting a "neither card a heart" (A♠ 2♠, A♠ 3♠, etc., 1482 ways, believe it or not) and divide by all the possible ways of getting any two cards (of which there are 2652) to get our 55.9%. Similarly, for rolling a 4 ten times in a row, there is just *one* way to do it out of a total of 60,466,176 possibilities. Ultimately, probability always boils down to a fraction: the number of ways of x divided by the total number of ways possible. Everything else is just a trick to make the calculation of that fraction a little easier.

It's also important to realize that all of this works only when each "way" is equally probable. If the dice are loaded, or the cards are sticky, or the dealer is cheating, all bets are off! We'll see that this "fair game" sort of probability is all we need to understand the "force" behind chemical reactions.

The perspective we have been taking up to this point, counting all the ways of this or that outcome, is that of the gambler. From this perspective, probability gives some sort of indication of what to expect next: "If I roll this die or pick up that card, my chances of winning are . . . ." But there is another perspective, which turns out to be more appropriate to chemistry. This is the casino's perspective. From this perspective, probability gives an indication (a *strong* indication) of what to expect over the long haul: "If this game is played 10,000 times, we should expect a profit of . . . ."

Clearly in the case of casino gambling, the "odds are in favor of the house." For example, a slot machine is constructed to "deliver" a certain percentage of the time. You may get lucky and win the jackpot, but there are an awful lot of times that handle is pulled and no money comes out. As long as a casino operator can get someone to place a bet (and they do not mismanage their expenses), then over the long haul the casino is going to make a profit. It's not that they can't lose, just that it is *sooooo* unlikely that they will lose overall when the handle has been pulled 10,000 times. If they do, then something's wrong with that slot machine!

The casino operator's advantage is precisely why probability works to explain chemical reactions. If you think the odds are pretty likely to work out after 10,000 games are played, try 602,213,670,000,000,000,000,000 (a mole)!
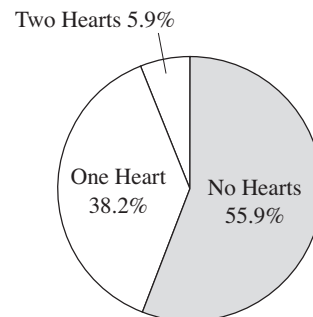
1.9 Distributions

After shuffling cards, we often deal them out, creating *hands*, or sets of cards. If you take a deck of cards and deal them *all* out into hands, we say you have *distributed* the cards. For example, take a deck of just four cards, one of each suit: a heart ($\heartsuit$), a diamond ($\diamondsuit$), a club ($\clubsuit$), and a spade ($\spadesuit$). This deck of cards can be distributed into two hands of two cards each. We will see that there is an excellent analogy between such distributions of a deck of cards into hands and the distribution of a collection of atoms into molecules in a chemical reaction. To understand the likelihood of different molecules being produced in a chemical reaction, we first look at how probability applies to this simple, four-card deck, containing just one card of each of the four suits.

What is the probability, then, that, distributed into two hands of two cards each, one hand has both red cards ($\heartsuit\diamondsuit$) and the other has both black ($\clubsuit\spadesuit$)? First we will just work out all the possibilities. There are 24 in all, as shown in Table 1.1. The answer to our question is that only in eight cases (those indicated with asterisks) are both cards in the same hand the same color. There is an 8/24 chance of one hand having both red while the other has both black. All the other possibilities (16 of 24 total) have one red and one black card in each hand.

If we ignore the distinction between spades and clubs, just calling both black cards "B" and similarly consider both hearts and diamonds to be just red cards, calling them "R", we can say that there are only two distinct *distributions* of cards. One possible distribution might be characterized as "$B_2 + R_2$", where one hand is both black and the other is both red. The other distinct distribution is where there are two hands, both the same, having one black and one red card each: "2 RB". Overall we have

Distribution A:	$R_2 + B_2$	8 ways	$P_A = 8/24 = 0.33$
Distribution B:	2 RB	16 ways	$P_B = 16/24 = 0.67$

Clearly Distribution B is twice as likely as Distribution A. We expect, if we were to shuffle the deck and deal out all the cards in pairs over and over many times, that roughly 33% of the time we would end up with Distribution A and roughly 67% of the time we would end up with Distribution B.

Table 1.1
All 24 distributions of four different cards into two hands. Asterisks indicate "2 R + 2 B."

Hand 1	Hand 2	Hand 1	Hand 2
$\heartsuit \diamondsuit$ *	$\spadesuit \clubsuit$	$\diamondsuit \heartsuit$ *	$\spadesuit \clubsuit$
$\heartsuit \diamondsuit$ *	$\clubsuit \spadesuit$	$\diamondsuit \heartsuit$ *	$\clubsuit \spadesuit$
$\heartsuit \spadesuit$	$\diamondsuit \clubsuit$	$\spadesuit \heartsuit$	$\diamondsuit \clubsuit$
$\heartsuit \spadesuit$	$\clubsuit \diamondsuit$	$\spadesuit \heartsuit$	$\clubsuit \diamondsuit$
$\heartsuit \clubsuit$	$\diamondsuit \spadesuit$	$\clubsuit \heartsuit$	$\diamondsuit \spadesuit$
$\heartsuit \clubsuit$	$\spadesuit \diamondsuit$	$\clubsuit \heartsuit$	$\spadesuit \diamondsuit$
$\diamondsuit \spadesuit$	$\heartsuit \clubsuit$	$\spadesuit \diamondsuit$	$\heartsuit \clubsuit$
$\diamondsuit \spadesuit$	$\clubsuit \heartsuit$	$\spadesuit \diamondsuit$	$\clubsuit \heartsuit$
$\diamondsuit \clubsuit$	$\heartsuit \spadesuit$	$\clubsuit \diamondsuit$	$\heartsuit \spadesuit$
$\diamondsuit \clubsuit$	$\spadesuit \heartsuit$	$\clubsuit \diamondsuit$	$\spadesuit \heartsuit$
$\spadesuit \clubsuit$ *	$\heartsuit \diamondsuit$	$\clubsuit \spadesuit$ *	$\heartsuit \diamondsuit$
$\spadesuit \clubsuit$ *	$\diamondsuit \heartsuit$	$\clubsuit \spadesuit$ *	$\diamondsuit \heartsuit$

Surely there is a more sophisticated way of calculating these probabilities. With any more than four cards it could be pretty difficult to lay out all the possibilities. Doing the calculation using AND and OR goes like this:

- Consider the first pair of cards off the deck. Since there are two red cards and four total, the probability of the first card being red is 2/4:

$$P_{1R} = \frac{2}{4}$$

- The probability now of the second card being red is 1 in 3, or 1/3, because now there are only three cards, one red and two black. So the probability of having the two red cards in the first hand is

$$P_{RR} = \frac{2}{4} \times \frac{1}{3}$$

- Now, for the second pair, there are only two black cards left. The probability that the first is black, of course, is 2/2; after that card is taken there is only one card left and its chance of being black is 1/1. So the probability of getting first two red cards *and* then two black cards is

$$P_{RRBB} = \frac{2}{4} \times \frac{1}{3} \times \frac{2}{2} \times \frac{1}{1}$$

- Similarly, the probability of getting first two black cards *and* then two red cards is also

$$P_{BBRR} = \frac{2}{4} \times \frac{1}{3} \times \frac{2}{2} \times \frac{1}{1}$$

- Thus, the probability of drawing off two red cards *and* then two black cards *or* the other way around is

$$P_{R_2+B_2} = P_{RRBB} + P_{BBRR}$$

$$= \left(\frac{2}{4} \times \frac{1}{3} \times \frac{2}{2} \times \frac{1}{1} \right) + \left(\frac{2}{4} \times \frac{1}{3} \times \frac{2}{2} \times \frac{1}{1} \right) = \frac{8}{24} = 0.33$$

Either way you do it, you get the same result: There are 8 ways out of 24 to get "R_2+B_2", Distribution A, and (by default, then) 16 ways out of 24 to get anything else ("2 RB", Distribution B). Since Distribution B is more likely than Distribution A, we refer to it as the *most probable distribution.* (Technically, perhaps, we should say *more* probable, since there are only two possible distributions in this case.) We will find that it is important to identify which distribution is the most probable, because we will argue that the approach to equilibrium is simply the natural development of a system to this state.

1.10 For Large Populations, We Approximate

What if these were hydrogen atoms, and we had 1000 of them? Instead of red and black cards, we might talk about ^{1}H isotopes ("H") and ^{2}H isotopes ("D", for *deuterium*). Say we had 800 H atoms and 200 D atoms in a box. They would naturally combine to form three distinct *molecular* species: H_2, D_2, and HD. In total, we would expect these 1000 atoms to combine to form 500 diatomic molecules.

And if we could somehow put a catalyst in the box (some platinum metal would do the trick), maybe we could get the following two-atom–scrambling, or *isotope exchange,* reactions to take place:

$$H_2 + D_2 \longrightarrow 2\,HD$$

$$2\,HD \longrightarrow H_2 + D_2$$
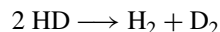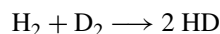
What would you expect to find after these reactions went on for a while? (Perhaps we could monitor the situation and wait until it looks like the reaction is over or at least settled into some final state.) Surely there is going to be some of each type of molecule present in the end. Two important questions could now be considered based on the idea that these isotopes are just getting scrambled randomly by the catalyst.

First, what is the probability that, if we select one *atom* out of the box at random, it would be H? D? Easy. We just take the number of ways of getting an H or D atom divided by the total number of atoms:

$$P_H = \frac{800}{1000}$$

$$P_D = \frac{200}{1000}$$

Second, what is the probability that any one *molecule* we select will be H_2? D_2? HD? This is trickier. But basically, it is just like taking cards off the top of a deck:

$$P_{H_2} = \frac{800}{1000} \times \frac{799}{999} \approx \frac{800}{1000} \times \frac{800}{1000} = 0.64$$

$$P_{D_2} = \frac{200}{1000} \times \frac{199}{999} \approx \frac{200}{1000} \times \frac{200}{1000} = 0.04$$

$$P_{HD} = \frac{800}{1000} \times \frac{200}{999} + \frac{200}{1000} \times \frac{800}{999}$$

$$\approx \frac{800}{1000} \times \frac{200}{1000} + \frac{200}{1000} \times \frac{800}{1000} = 0.32$$

Our calculation predicts that it is twice as likely for a molecule to be H_2 as HD in the end, and there is only a 4% chance of pulling out a D_2 from the mix. Notice that to be absolutely correct here, we have to consider the first and second atoms to be dependent, as for the first two cards in a deck. Thus, technically, we have to take into consideration that the first atom is no longer in the collection in calculating the probability.

Here, though, we see a new trick. Due to the fact that we are dealing with the sampling of large populations, *we can just ignore the dependency of the sampling*. The values of "799/999" and "800/999" are so close to "800/1000" that we can just use "800/1000" anywhere we are considering the probability of an atom being H. (The difference is less than one part in one thousand.) Note that here we don't *have* to make any approximations, but it turns out that if we do, the solution takes a nice form:

$$P_{H_2} \approx P_H \times P_H$$

$$P_{D_2} \approx P_D \times P_D$$

$$P_{HD} \approx P_H \times P_D + P_D \times P_H$$

How does this analysis relate to what we would expect to observe? Those observations will be distributions—so many H_2, D_2, and HD present at a particular instant—and there will be exactly 101 distinct *distributions*, as shown in Table 1.2. We can't ever have fewer than 300 molecules of H_2 because at that point we run out of D_2 to react with it. We might refer to D_2 in this case as the *limiting reactant*.

Table 1.2
There are 101 distinct *molecular* distributions of 800 H atoms and 200 D atoms.

	H_2	D_2	HD
#1	400	100	0
#2	399	99	2
#3	398	98	4
⋮			
#101	300	0	200

But which of these 101 distributions is the most probable one? Now, *this* is a very interesting question. We determined the probabilities of fishing out each of the specific types of molecules, H_2 (0.64), D_2 (0.04), and HD (0.32). What does it mean that the approximate probability of fishing out a molecule of H_2 is 0.64? Doesn't it mean that about 64% of the molecules are H_2? Surely it does! Here the "ways" of getting H_2 corresponds to the actual number of H_2 molecules in the system, and the "ways total" corresponds to the total number of molecules, 500. (Note that we had 1000 *atoms* but only 500 *molecules*.) We can write

$$P_{H_2} = \frac{N_{H_2}}{N_{\text{molecules}}} \quad \text{or} \quad 0.64 = \frac{N_{H_2}}{500}$$

Solving this for N_{H_2} we get $0.64 \times 500 = 320$. Likewise, we find $N_{D_2} = 0.04 \times 500 = 20$, and $N_{HD} = 0.32 \times 500 = 160$. We conclude that the *most probable* distribution in this case is $320\,H_2 + 20\,D_2 + 160\,HD$.

Finally, how probable is this most probable distribution? This is a difficult question. It can be calculated, but it's not a pretty sight. One way to do it is to list all the possible distributions (101 in this case) and determine the number of ways of getting each one. Adding all these ways together, we have the total number of ways possible. Then all we have to do is divide the number of ways of getting this particular distribution by the total number of ways possible. For example, it turns out that the number of possible ways of getting 800 H atoms and 200 D atoms to arrange themselves as $320\,H_2 + 20\,D_2 + 160\,HD$ is roughly 7.35×10^{214}. And the total number of ways there are to distribute 800 H atoms and 200 D atoms in any way turns out to be 6.6×10^{215}. Thus, the probability of actually getting this particular distribution is only about 11.1%. Still, this is the most probable distribution. The next most probable, characterized by $319\,H_2 + 19\,D_2 + 162\,HD$, has a probability of just 10.9%.

1.11 Relative Probability and Fluctuations

Although we have little hope in general of determining exactly how probable the most probable distribution is, still valuable will be how probable this distribution is in relation to some other distribution. If we divide the probabilities of the various distributions by the probability of the most probable one, we obtain what are called *relative probabilities*, P_{rel}, as shown in Table 1.3. Note that just these eleven distributions account for a full 88% of the possible ways of distributing the atoms. For example, the most probable distribution in this case is #81, consisting of $320\,H_2$, $20\,D_2$, and 160 HD molecules, with 7.35×10^{214} possible ways of finding this arrangement of atoms. This is more ways than any other possible distribution can be found, and we assign this distribution a relative probability of 1.

Table 1.3
Percent HD, number of ways, absolute probabilities, and relative probabilities for the eleven most probable molecular distributions of 800 H atoms and 200 D atoms. Distribution #81 is the *most probable distribution*, but not by much.

	H_2	D_2	HD	% HD	Ways	P	P_{rel}
#76	325	25	150	30.0%	2.64×10^{214}	0.040	0.36
#77	324	24	152	30.4%	3.74×10^{214}	0.057	0.51
#78	323	23	154	30.8%	4.94×10^{214}	0.075	0.67
#79	322	22	156	31.2%	6.07×10^{214}	0.092	0.83
#80	321	21	158	31.6%	6.93×10^{214}	0.105	0.94
#81	**320**	**20**	**160**	**32.0%**	$\mathbf{7.35 \times 10^{214}}$	**0.111**	**1.00**
#82	319	19	162	32.4%	7.21×10^{214}	0.109	0.98
#83	318	18	164	32.8%	6.54×10^{214}	0.099	0.89
#84	317	17	166	33.2%	5.47×10^{214}	0.083	0.74
#85	316	16	168	33.6%	4.20×10^{214}	0.064	0.57
#86	315	15	170	34.0%	2.96×10^{214}	0.045	0.40

Figure 1.2
Relative probabilities of specific number of HD molecules in the equilibration of 800 H atoms and 200 D atoms into 500 molecules of H_2, D_2, and HD. The most probable distribution has 160 HD molecules (32% HD).
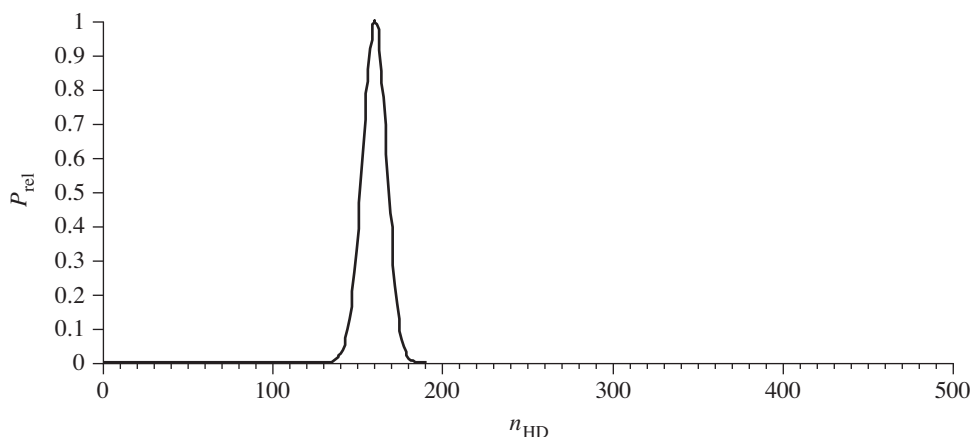
The slightly different distribution #82, characterized by 319 H_2 + 19 D_2 + 162 HD, is only slightly less probable than the most probable distribution, with "only" 7.21×10^{214} possible ways of being found. We could say that this distribution is 7.21×10^{214} / 7.35×10^{214} = 0.98 (that is, 98%) as probable as #81. A graph of the relative probabilities vs. number of HD molecules for all 101 possible distributions is shown in Figure 1.2. Notice that even our most probable distribution really has a probability of turning up only about 11% of the time. If we check our box of 500 molecules now and then, we will not always observe the most probable distribution any more than we would expect a flip of 100 pennies to always end up 50 heads and 50 tails. That is, we expect to see some *fluctuation* in the observations. Sometimes we will see more than 160 HD molecules, and other times we will see fewer.

However, a very interesting characteristic of all probability-based systems is that as the number of particles grows, our capability of *discerning* those fluctuations decreases exponentially. The reason this happens has to do with how we would measure the identity of the distributions. We wouldn't really count any molecules. Instead, we might weigh them, or titrate them, or somehow measure a property such as light absorbance that is unique to only one of the molecules in the mix.
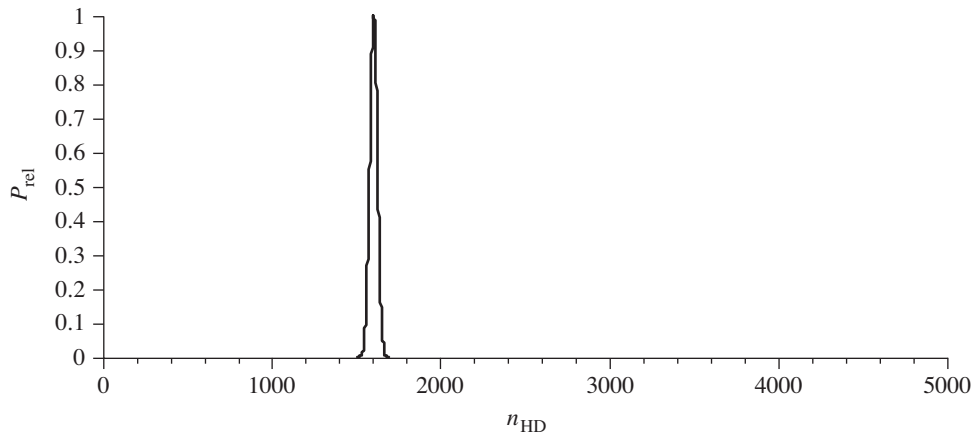
Figure 1.3
Relative probabilities of specific number of HD molecules in the equilibration of 8000 H atoms and 2000 D atoms into 5000 molecules of H_2, D_2, and HD. The most probable distribution is still 32% HD, but now the relative probability of finding 30% HD (1500 HD molecules) in the mix is only about 1 in 12,000.

In all such measurements there is a limit to our precision. For example, in the case we have been studying, Figure 1.2 shows that the most probable distribution could be characterized as being 32% HD ($160/500 \times 100\% = 32\%$). However, the relative probability of instead finding 30% HD (150 HD molecules) is 0.36. So that distribution is 36% *as probable* as the most probable distribution and will be seen a significant fraction of the time.

On the other hand, if we were to go to a system having ten times as many atoms—8000 H and 2000 D (now 5000 molecules)—then the most probable distribution would have the same percent H_2, D_2, and HD, and would be characterized as $3200\,H_2 + 200\,D_2 + 1600$ HD, still with 32% HD. But the relative probability of finding $3250\,H_2 + 250\,D_2 + 1500$ HD (30% HD) instead would be only about one chance in 12,000. This is seen in Figure 1.3.

And if we had 50,000 molecules, our chances of finding only 30% HD instead of 32% HD when we measured would be only about one chance in 10^{43}. With a *mole* of molecules, our relative chances of finding even 31.999999999% HD instead of 32% HD turns out to be only one part in 10^{105}.

What this means is that on a *mole* scale, the way real chemistry is carried out, we could not possibly expect to see any fluctuation at all. The fluctuations would be there of course, it's just that we couldn't *detect* them even with the most sensitive devices we could ever build. Our graph would be essentially a sharp spike at 32% HD, the most probable distribution.

Importantly, we could still use the technique described above to calculate the most probable distribution of molecules in our system. For example, if we started with 4.0 mol of H_2 and 1.0 mol of D_2, we would have 8.0 mol of H atoms and 2.0 mol of D atoms in the box, for a total of 10.0 mol of atoms, and we could calculate the *atomic* probabilities as

$$P_H = \frac{8.0 \text{ mol}}{10.0 \text{ mol}} = 0.80$$

$$P_D = \frac{2.0 \text{ mol}}{10.0 \text{ mol}} = 0.20$$

From that, we could calculate the approximate *molecular* probabilities:

$$P_{H_2} \approx P_H \times P_H = 0.80 \times 0.80 = 0.64$$

$$P_{D_2} \approx P_D \times P_D = 0.20 \times 0.20 = 0.04$$

$$P_{HD} \approx P_H \times P_D + P_D \times P_H = (0.80 \times 0.20) + (0.20 \times 0.80) = 0.32$$

Since we know that we have a total of 5.0 mol of *molecules* (H_2, D_2, and HD), we conclude that in this case the most probable distribution is characterized by:

$$N_{H_2} = P_{H_2} \times N_{total} = 0.64(5.0 \text{ mol}) = 3.2 \text{ mol } H_2$$

$$N_{D_2} = P_{D_2} \times N_{total} = 0.04(5.0 \text{ mol}) = 0.2 \text{ mol } D_2$$

$$N_{HD} = P_{HD} \times N_{total} = 0.32(5.0 \text{ mol}) = 1.6 \text{ mol HD}$$

These are the amounts of H_2, D_2, and HD we expect to find in the system any time we looked, even with fluctuations. Sure these are approximations, but they are very *good* approximations. Even with fluctuations, our calculation for the most probable distribution gives precisely what, with great certainty, *must* be observed.

1.12 Equilibrium and the Most Probable Distribution

Now imagine starting with this same "deck" of 8 mol H atoms and 2 mol D atoms already "stacked" in the form of 4.0 mol H_2 and 1.0 mol D_2 molecules. Start shuffling. What would you expect to happen? The relative probability of this starting distribution, with absolutely no HD, is essentially 0. Think it will last long? The most probable distribution we found above to be 3.2 mol H_2, 0.2 mol D_2, and 1.6 mol HD. How will that arise? Surely we will see some HD formed from what we might call the *forward* reaction:

$$H_2 + D_2 \longrightarrow 2 \text{ HD}$$
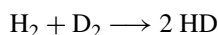
The amount of HD will build up, and then we will probably start to see the *reverse* reaction taking place:

$$2 \text{ HD} \longrightarrow H_2 + D_2$$
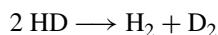
At some point, the rate of the forward reaction and the rate of the reverse reaction will become equal: Roughly as many HD will split up in any shuffle as are made. Isn't this what we call *equilibrium*? But we have also learned that the outcome of this shuffling is most certainly going to be the most probable distribution, or at the very least, with these kind of numbers, something very close to it. Thus, what we call the *equilibrium state* is really just the most probable distribution, along with the generally undetectable set of fluctuations very similar to it. That is, chemical equilibrium is a dynamic, fluctuating state centered around the most probable distribution.

1.13 Equilibrium Constants Describe the Most Probable Distribution

Consider again our small system containing just 800 H atoms and 200 D atoms, with a most probable distribution of 320 H_2, 20 D_2, and 160 HD molecules. For this equilibrium we might write

$$H_2 + D_2 \rightleftharpoons 2 \text{ HD} \qquad K = \frac{[HD]^2}{[H_2][D_2]}$$

If equilibrium is really the most probable distribution, then we should be able to substitute our values for the most probable distribution number of H_2, D_2, and HD molecules for equilibrium concentrations. If we do that, we get

$$K = \frac{160^2}{(320)(20)} = 4$$

OK, if that is really an equilibrium *constant*, then we should be able to start with *any* initial conditions (number of molecules, % H, and % D) and still get 4. Let's check it out by calculating this value, which we call the *reaction quotient*, *Q*, for the most probable distribution in each case:

N_{atoms}	% H	% D	Most Probable Distribution	Q
2000	80	20	$640 H_2 + 40 D_2 + 320 HD$	4
2000	50	50	$250 H_2 + 250 D_2 + 500 HD$	4
2000	10	90	$10 H_2 + 810 D_2 + 180 HD$	4

That is,

$$\frac{320^2}{(640)(40)} = \frac{500^2}{(250)(250)} = \frac{180^2}{(10)(810)} = 4$$

Note that each of these distributions is determined exactly as above, by first determining the atomic probabilities, P_H and P_D, then the molecular probabilities, P_{H_2}, P_{D_2}, and P_{HD}, and finally multiplying those probabilities by the total number of molecules (1000). Sure enough! No matter how much H or D we start with, we always get the same value for Q!

1.14 Le Châtelier's Principle Is Based on Probability

If a system at equilibrium is disturbed, a reaction will occur which will reduce (but not eliminate) that disturbance and create a new, shifted, equilibrium. This is Le Châtelier's principle, and it is supposed to apply to all chemical equilibria. Let's see if it works here. In Figure 1.4 we see three distributions. Distribution A is once again the most probable distribution for 500 molecules arising from mixing 800 H atoms with 200 D atoms. There are 320 H_2, 20 D_2, and 160 HD in this distribution. Note that it has $P_{rel} = 1$, because it is the most probable distribution.

Upon adding 300 D_2 molecules (600 D atoms), the equilibrium is disturbed, giving Distribution B. Notice that P_{rel} drops tremendously even though the number of ways, W, increases. This is because now we are comparing this distribution to others having many more atoms than before. Once the system starts scrambling, it is very unlikely that it will ever be found in this distribution again. Rather, the most probable distribution after this disturbance, Distribution C, is characterized by 200 H_2, 200 D_2, and 400 HD molecules.
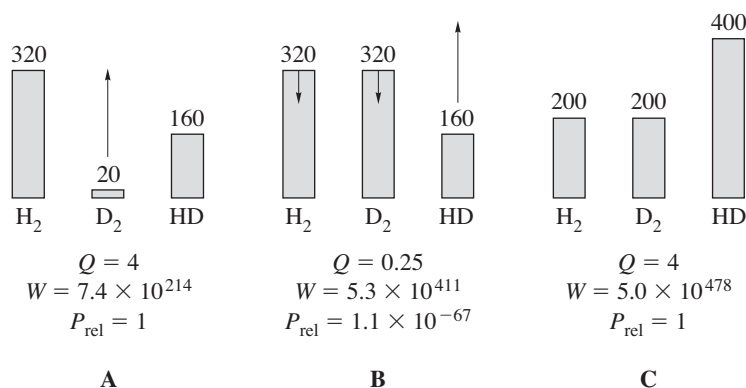
Figure 1.4
Three distributions illustrating Le Châtelier's principle. In each case, the reaction quotient, Q, the number of ways of that distribution being found, W, and the relative probability of this distribution relative to the most probable for that number of H and D atoms, P_{rel}, are indicated. Distribution A is the most probable distribution before the disturbance. Adding 300 D_2 molecules creates Distribution B, which, though having more ways of being found relative to A is still incredibly less probable to be found with continued shuffling *relative to Distribution C*. It is inconceivable that with scrambling the system will ever be found again in Distribution B.
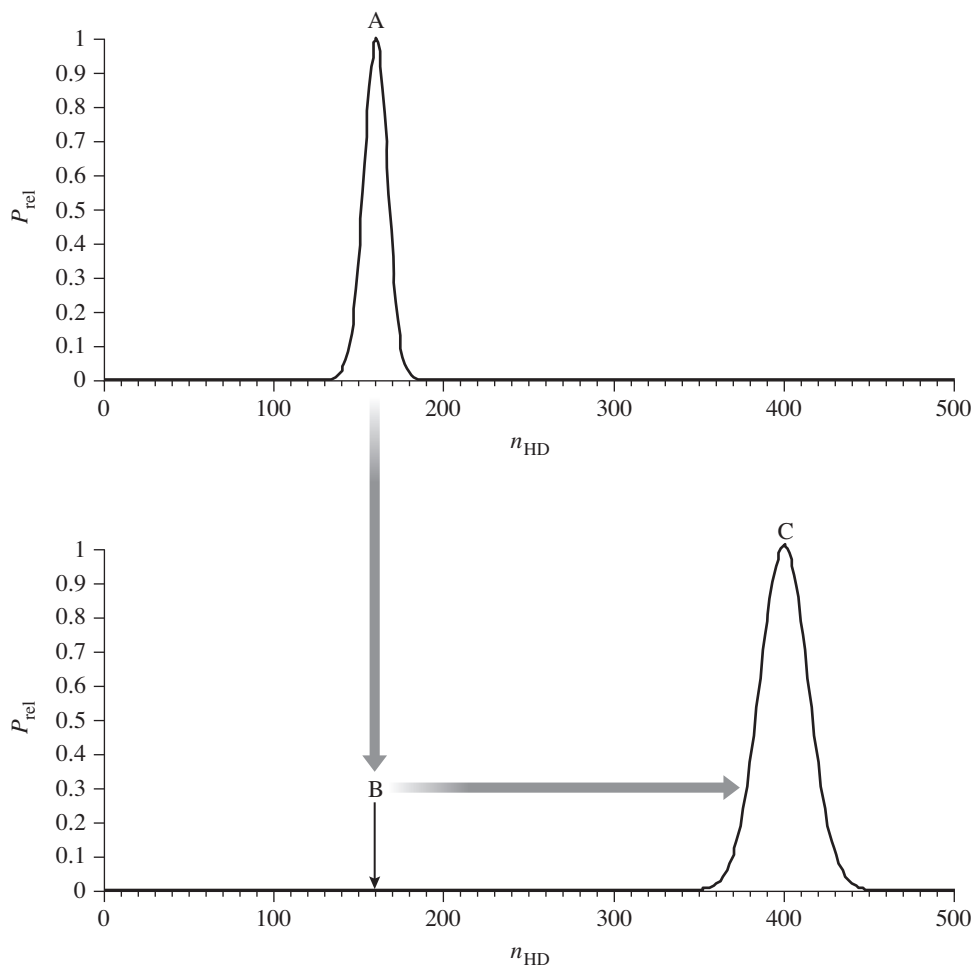
$Q = 4$
$W = 7.4 \times 10^{214}$
$P_{rel} = 1$
A

$Q = 0.25$
$W = 5.3 \times 10^{411}$
$P_{rel} = 1.1 \times 10^{-67}$
B

$Q = 4$
$W = 5.0 \times 10^{478}$
$P_{rel} = 1$
C

Figure 1.5
Relative probabilities vs. number of HD molecules in the mixture of 800 H and 200 D atoms before (above) and after (below) adding an additional 300 D_2 molecules. The equilibrium "shifts to the right," producing more HD, illustrating Le Châtelier's principle. Distribution A from Figure 1.4 is at the center of the curve on the top; Distribution C is at the center of the curve on the bottom. Distribution B is at the same place as Distribution A (160 HD), but its probability *relative to Distribution C* is essentially 0.

The reaction that occurs in response to the disturbance is the forward reaction

$$120\,H_2 + 120\,D_2 \longrightarrow 240\,HD$$

which gets rid of some of that added D_2 and ends up with 200 H_2 + 200 D_2 + 400 HD. The resultant most probable distribution still has $Q = 4$, but we say that the equilibrium has *shifted* to the right. The shift is easily seen on a graph of relative probability vs. number of HD molecules (Figure 1.5). As another example, let us now add 400 HD molecules to our new equilibrium mix, giving 200 H_2 + 200 D_2 + 800 HD initially (Figure 1.6). The system responds to the added HD product with the reverse reaction

$$100\,H_2 + 100\,D_2 \longleftarrow 200\,HD$$

shifting the equilibrium to the left and re-establishing $Q = 4$ and a much more probable distribution, 300 H_2 + 300 D_2 + 600 HD.

　　Note that there is no magic here. The shift in the equilibrium is simply the establishment of a new most probable distribution based entirely on the idea that *that* distribution has *soooo*
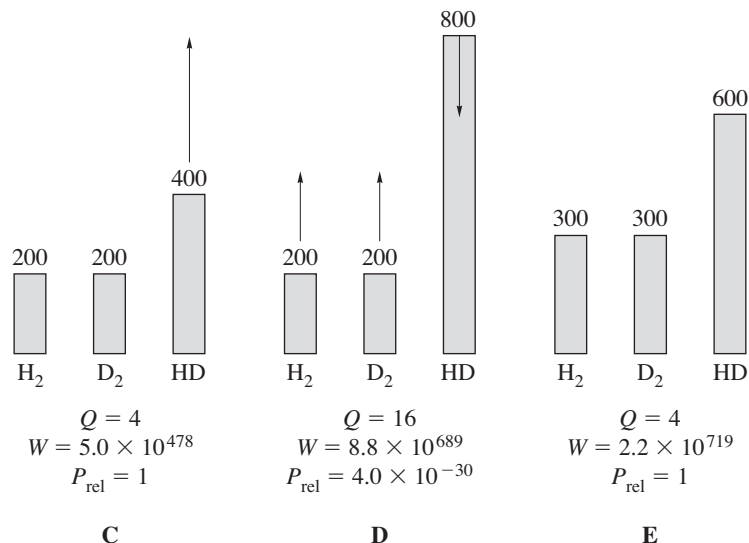
Figure 1.6
Adding 400 HD molecules to Distribution C (the third distribution in Figure 1.4) results in Distribution D. With continued scrambling, this distribution is not expected to last long, because it has a probability of only 4.0×10^{-30} relative to Distribution E. Random exchange will lead ultimately to a new most probable distribution, Distribution E, or something very close to it.

many more ways of being found. Each individual way is just as likely as another, but this final most probable distribution constitutes a whopping 2.2×10^{719} ways. With a few thousand atoms it might be possible to observe slightly different distributions now and then, but with mole quantities, we don't have to worry about them. (The curves in Figure 1.5 collapse to sharp spikes.) It's just too unlikely that the system will be found in any significantly different distribution. Again, there will be fluctuations around this distribution. We just won't be able to detect them.

1.15 Determining Equilibrium Amounts and Constants Based on Probability

Given the following information:

$$\mathrm{H_2 + D_2 \rightleftharpoons 2\,HD} \qquad K = 4$$
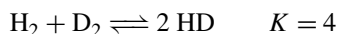
and specific initial concentrations, you may already have learned how to determine the equilibrium concentrations of H_2, D_2, and HD. For example, say you had 4.0 mol of H_2 and 1.0 mol of D_2 in a 1-L flask to start with. The technique involves setting up a table something like the following, where $2x$ is the number of moles of HD formed at equilibrium:

	H_2	D_2	HD
[ ]$_0$	4.0	1.0	0
Δ	$-x$	$-x$	$+2x$
[ ]$_{eq}$	$4.0-x$	$1.0-x$	$2x$

and substituting these values into the equilibrium expression:

$$4 = K_c = \frac{[\mathrm{HD}]^2}{[\mathrm{H_2}][\mathrm{D_2}]} = \frac{(2x)^2}{(4.0 - x)(1.0 - x)}$$

Solving this equation using either algebra or an equation-solving calculator gives $x = 0.8$. Substituting in on the bottom line, we get $[\mathrm{H_2}]_{eq} = 3.2\ M$, $[\mathrm{D_2}]_{eq} = 0.2\ M$, and $[\mathrm{HD}]_{eq} = 1.6\ M$.

This method works just fine when there is only one equilibrium equation and we know the value of its equilibrium constant. However, as we have seen, there is another way, based on probability, which does NOT depend upon knowing the value of K initially and works for all isotope exchanges. In summary, the method goes like this:

1. Determine the number of moles of each of the exchanging atom types ($N_H = 8.0$ mol, $N_D = 2.0$ mol, for example).
2. Add these to get the total number of exchanging atoms ($N_{atoms} = 10.0$ mol).
3. Determine the probability of a randomly selected atom being of each type:

$$P_H = \frac{N_H}{N_{atoms}} = \frac{(8.0 \text{ mol})}{(10.0 \text{ mol})} = 0.80$$

$$P_D = \frac{N_D}{N_{atoms}} = \frac{(2.0 \text{ mol})}{(10.0 \text{ moles})} = 0.20$$

Note that probabilities properly have no units, and the sum of these atomic probabilities is 1.

4. From this information, determine the approximate probability of each *molecule* type:

$$P_{H_2} = P_H \times P_H = (0.80)(0.80) = 0.64$$

$$P_{D_2} = P_D \times P_D = (0.20)(0.20) = 0.04$$

$$P_{HD} = P_H \times P_D + P_D \times P_H = (0.80)(0.20) + (0.20)(0.80) = 0.32$$

Note that, here too, the values are unitless, and the sum of the probabilities is 1.

5. Determine the total number of *molecules*. In this case we are starting with 4.0 mol of H_2 and 1.0 mol of D_2, for a total of 5.0 mol of molecules. Note that in isotope exchange reactions the total number of molecules does not change, so in the end we still have 5.0 mol of molecules.
6. Finally, using the idea that $N_x = P_x \times N_{molecules}$, determine the number of each type of molecule at equilibrium:

$$N_{H_2} = P_{H_2} \times N_{molecules} = (0.64)(5.0 \text{ mol}) = 3.2 \text{ mol } H_2$$

$$N_{D_2} = P_{D_2} \times N_{molecules} = (0.04)(5.0 \text{ mol}) = 0.2 \text{ mol } D_2$$

$$N_{HD} = P_{HD} \times N_{molecules} = (0.32)(5.0 \text{ mol}) = 1.6 \text{ mol HD}$$

So we have that the most probable distribution in this case is characterized by 3.2 mol H_2, 0.2 mol D_2, and 1.6 mol of HD. Now, from *this* result we can actually calculate the value of the equilibrium constant, K:

$$K = \frac{[HD]^2}{[H_2][D_2]} = \frac{(N_{HD}/V)^2}{(N_{H_2}/V)(N_{D_2}/V)} = \frac{(1.6/1)^2}{(3.2/1)(0.2/1)} = 4$$

Note that we could have ignored the volume, V, altogether here, as it drops out from the equation in this and all isotope exchange reactions. In fact, we can easily show that Q is always 4 for this system regardless of how much H_2, D_2, or HD we start with. Based on the idea that $N_x = P_x N_{molecules}$, we have:

$$K = \frac{N_{HD}^2}{N_{H_2} N_{D_2}} = \frac{(P_{HD} N_{molecules})^2}{P_{H_2} N_{molecules} P_{D_2} N_{molecules}} = \frac{(P_{HD})^2}{P_{H_2} P_{D_2}}$$

(Here P stands for probability, not pressure!) So we can use P_x just as we could use n_x or [X] in these isotope exchange reactions. Substituting in the equivalent *atomic* probabilities

we calculated in Step 4, all the probabilities cancel, and we get the value 4:

$$K = \frac{(P_{\text{H}}P_{\text{D}} + P_{\text{D}}P_{\text{H}})^2}{(P_{\text{H}}P_{\text{H}})(P_{\text{D}}P_{\text{D}})} = \frac{(2P_{\text{H}}P_{\text{D}})^2}{P_{\text{H}}^2 P_{\text{D}}^2} = 4$$

Thus, the reaction quotient, Q, is a constant at equilibrium, regardless of the initial number of H or D atoms in the system. We say that at equilibrium, $Q = K$, which is 4 in this case.

One of the main objectives of this book is to convince you that not only in simple isotope exchange reactions but in *all* reactions equilibrium amounts, equilibrium expressions, and the whole concept of an equilibrium constant are all based solely on probability. You may not be convinced yet that this method is easier than the tabular method of determining equilibrium concentrations involving setting up and solving an equation involving x, but remember that here we do not have to worry about there being more than one equilibrium at work, and we didn't even have the value of K to start with. Using probability not only gives us the equilibrium amounts of all reactants and products, it also gives us the *value* of the equilibrium constant itself.

1.16 Summary

Applying just the very basics of probability theory, namely

$$P_x = \frac{\text{ways of getting } x}{\text{ways total}}$$

we have derived four basic ideas useful for calculating the probability of various outcomes:

- AND probability multiplies
- OR probability adds
- AND and OR probability can be combined
- $P_{\text{not } x} = 1 - P_x$

With small systems we have to be careful about dependencies and count our cards carefully. However, as the number of cards or atoms in a system increases, we can make some very good approximations that remove the effect of these dependencies. In particular, when we want to know the *most probable distribution* of atoms, we can base our entire calculation on simple atom probabilities calculated as $P_x = N_x/N_{\text{atoms}}$.

For simple isotope exchange reactions, even with relatively few atoms, the idea of an equilibrium constant is justified. The equilibrium state in such an atom-scrambling reaction is characterized by the most probable distribution of atoms. Just as for flips of a coin, we cannot guarantee a result, but due to the incredible number of atoms involved in real chemical reactions, the *fluctuations* we might imagine observing are just too small to detect.

In reality, of course, things aren't quite so simple. The big difference between what we have been doing and real chemical reactions is that in real chemical systems there is something else besides atoms that is being distributed, namely energy. In Chapter 2 we will start to look at the rules relating to how energy is distributed in real chemical systems.

Problems

The symbol Ⓐ indicates that the answer to the problem can be found in the "Answers to Selected Exercises" section at the back of the book.

Basic Probability

1.1 Ⓐ A jar contains one blue ball, one green ball, one red ball, and three orange balls. What is the probability that a ball drawn at random (a) will be green? (b) will be orange? (c) will not be blue?

1.2 A CD player holds three CDs. The first disk by U2 has 10 tracks, the second disk by Pink Floyd has 9 tracks, and the final disk by Yo-Yo Ma has 16 tracks. If the CD player is set to pick a track at random from any CD, but will not repeat any one track until all tracks have played on all CDs, what is the probability that (a) the first track played will be by U2? (b) the first three tracks will be by U2? (c) the first song will be my favorite Pink Floyd song? (d) none of the first 5 tracks played will be by Yo-Yo Ma?

1.3 Your dresser has three shirts, one black, one blue, and one green; three pairs of pants, also one black, one blue, and one green; and three pairs of socks, also one black, one blue, and one green. You randomly pick out one shirt, one pair of pants, and one pair of socks. What is the probability (a) that your shirt will be green? (b) that you won't have to wear the green pants? (c) that your outfit will be monochromatic—that is, that the shirt, pants, and socks will be the same color? (d) that you will look like Johnny Cash—that is, that the shirt, pants, and socks will all be black?

1.4 Ⓐ A four-sided die (shown below) is a tetrahedron rather than a cube. All of the sides of the die are regular equilateral triangles rather than squares as in a six-sided die. The faces of the four-sided die are labeled 1, 2, 3, and 4. (a) Assuming there is an equal probability of landing on any side, what is the probability of rolling a 2 with this die? If a pair of four-sided dice is rolled, what is the probability that the sum of the two dice (b) will be 4? (c) will be 4 or 6?
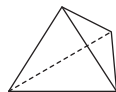
1.5 An eight-sided die is a regular octagon rather than a cube. All sides of the die are labeled 1 to 8. A ten-sided die is a regular decahedron rather than a cube. All sides of this die are labeled 1 to 10. For both of these dice there is an equal probability of landing on any side. For each die (a) what is the probability of rolling an 8? Why is there a greater probability of rolling an 8 with one die? (b) what is the probability of not rolling a 2? (c) what is the probability of rolling an 8 or a 9?

1.6 (a) For the single roll of a normal six-sided die, show that the sum of the probabilities of all possible outcomes adds up to 1. (b) Show that this is true also for the roll of two four-sided dice. (c) Provide a simple nonmathematical explanation of why

the sum of all the probabilities of all of the outcomes of an event *has* to add up to 1.

1.7 Ⓐ What is the probability that the first card drawn from a well-shuffled standard deck of cards (a) is a diamond? (b) is the jack of diamonds? (c) will not be a face card—a jack, queen, or king? (d) What is the probability that the first two cards drawn will be diamonds?

1.8 Powerball™ is a lottery game played in many states. To win the jackpot you need to match 5 numbers, in any order, to the numbers drawn from a field of 49 and match one number, the powerball, to a number drawn from a field of 42. You can think of it as drawing five numbered balls from a jar with 49 balls numbered 1–49 and then drawing one ball from a second jar that has 42 balls numbered 1–42. (a) What is the probability of winning the jackpot? (b) What is the probability of not winning the jackpot?

Chemical Distributions

1.9 Simple probability governs the equilibrium positions of chemical systems and the number of heads and tails you can toss with a coin. Why does a "normal" chemical system never seem to fluctuate from its equilibrium position, but if you flip a coin 100 times you expect that you might not get exactly 50 heads and 50 tails?

1.10 A system initially containing 2.0 mol of H_2 and 1.0 mol of D_2 is allowed to equilibrate, forming HD. Determine the amounts of H_2, D_2, and HD expected at equilibrium.

1.11 A system initially containing 2.0 mol of H_2O, 1.0 mol of D_2O, and 2.0 mol of HDO is allowed to exchange hydrogen for deuterium. Determine the amounts of H_2O, D_2O, and HDO expected at equilibrium. (Note that the oxygen atom should be ignored because it is not exchanging.)

1.12 Ⓐ Chlorine naturally occurs with two major isotopes ^{35}Cl and ^{37}Cl. On earth, approximately 76% of all chlorine atoms are ^{35}Cl and 24% are ^{37}Cl. Given 1.5 mol of chlorine atoms in their natural abundances, what is the most probable distribution of $^{35}Cl_2$, $^{37}Cl_2$, and $^{35}Cl^{37}Cl$?

1.13 Ⓐ Starting with the system in the previous problem, what is the new most probable distribution if (a) 0.5 mol of $^{35}Cl_2$ is added? (b) if 0.25 mol of $^{35}Cl^{37}Cl$ is added? (c) if 0.50 mol of $^{37}Cl_2$ and 0.25 mol of $^{35}Cl^{37}Cl$ are added?

1.14 The three natural isotopes of oxygen and their natural abundances are ^{16}O (99.757%), ^{17}O (0.038%), and ^{18}O (0.205%). What is the most probable distribution of O_2 molecules among the six different possibilities in a sample containing 2 mol of natural O_2?

1.15 Copper naturally occurs in two major isotopes, ^{65}Cu and ^{63}Cu. What is the number of moles of $^{63}Cu^{65}Cu$ you expect to have at equilibrium if you start with 1.75 mol of $^{65}Cu_2$ and 0.50 mol of $^{63}Cu_2$?

1.16 Starting with the system in the previous problem, what is the new most probable distribution if (a) 0.75 mol of $^{63}Cu_2$ is added? (b) 1.75 mol of $^{63}Cu^{65}Cu$ is added? (c) 0.25 mol of $^{63}Cu_2$ and 0.25 mol of $^{63}Cu^{65}Cu$ are added?

1.17 Ⓐ Iridium occurs naturally in two isotopes ^{191}Ir and ^{193}Ir with natural abundances of 37.3% and 62.7% respectively. A 1.345-mol sample of natural Ir_2O_3 is analyzed. (a) What would be the expected amounts of $^{191}Ir^{193}IrO_3$, $^{193}Ir_2O_3$ and $^{191}Ir_2O_3$? (Note that the oxygen atom should be ignored since it is not exchanging.) (b) Using your answers from (a), calculate the equilibrium constant for the isotope exchange reaction between $^{191}Ir^{193}IrO_3$, $^{193}Ir_2O_3$, and $^{191}Ir_2O_3$ as written:

$$2\ ^{191}Ir^{193}IrO_3 \rightleftharpoons\ ^{191}Ir_2O_3 +\ ^{193}Ir_2O_3$$
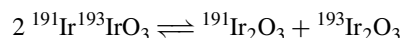
**1.18** A sample of 1.75 mol of N_2 is created by mixing 1 mol of $^{14}N_2$ and 0.75 mol of $^{15}N_2$. The molecules are allowed to react, and equilibrium is established. What is the most probable distribution of $^{14}N_2$, $^{15}N_2$, and $^{14}N^{15}N$ at equilibrium?

1.19 Ⓐ Silver naturally occurs in two major isotopes, ^{107}Ag and ^{109}Ag. A 1.75-mol sample of natural silver atoms is allowed to react to form Ag_2. After equilibrium is achieved, the most probable distribution of Ag_2 molecules is found to be 0.235 mol $^{107}Ag_2$, 0.203 mol $^{109}Ag_2$, and 0.437 mol $^{107}Ag^{109}Ag$. Using this information and a bit of algebra, determine the natural abundance of ^{107}Ag, expressed in percent (%).

Brain Teasers

1.20 A normal six-sided die has been *loaded* so that the probability of rolling a 6 is twice as much as that of rolling any other number. What is the probability (a) of rolling a 6 with this die? (b) of rolling a 4? (c) How much more likely are you to roll two of these loaded dice and have the sum of the two dice be 8 than you are with the roll of two normal dice?

1.21 A mixture of ammonia isotopes containing 2.0 mol of NH_3 and 1.0 mol of ND_3 is allowed to equilibrate, producing a mixture of NH_3, ND_3, NH_2D, and NHD_2. (a) Ignoring the N atoms (because they are not exchanging), determine the most probable distribution once equilibrium is achieved. (b) Use this information to predict the value of the equilibrium constants for each of the following two isotope exchange reactions:

$$NH_3 + ND_3 \rightleftharpoons NH_2D + NHD_2$$
$$NH_3 + NHD_2 \rightleftharpoons 2\ NH_2D$$
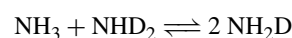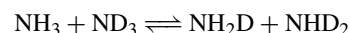
1.22 Methane, CH_4, can undergo two types of isotope exchanges. The carbon atom can exchange ^{12}C for ^{13}C, and the hydrogens can exchange H for D. For example, one possibility would be:

$$^{13}CH_2D_2 +\ ^{12}CH_2D_2 \rightleftharpoons\ ^{13}CH_3D +\ ^{12}CHD_3$$
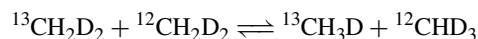
(a) List all possible isotope exchange reactions in this case (including simple switches of reactants for products). (b) Determine the value of K for each possibility based on probability.