

Chemical Equilibrium

A Chem1 Reference Text

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1 • Chemical change: how far, how fast?

Chemical change occurs when the atoms that make up one or more substances rearrange themselves in such a way that new substances are formed. These substances are the *components* of the *chemical reaction system*; those components which decrease in quantity are called *reactants*, while those that increase are *products*. A given chemical reaction system is defined by a balanced *net chemical equation* which is conventionally written as



Chemical change is one of the two central concepts of chemical science, the other being *structure*. The very origins of Chemistry itself are rooted in the observations of transformations such as the combustion of wood, the freezing of water, and the winning of metals from their ores that have always been a part of human experience. It was, after all, the quest for some kind of constancy underlying change that led the Greek thinkers of around 200 BC to the idea of elements and later to that of the atom. It would take almost 2000 years for the scientific study of matter to pick up these concepts and incorporate them into what would emerge, in the latter part of the 19th century, as a modern view of chemical change.

The first thing we need to know about a chemical reaction represented by a balanced equation is whether it can actually take place. If the reactants and products are all substances capable of an independent existence, then the answer is always “yes”, at least in principle. This answer must always be qualified, however, by the following two considerations:

- ***Does the reaction take place to a sufficient extent to produce useful (or even detectable) quantities of products?*** This refers to the *thermodynamics* (energetics) of the reaction, which controls its *tendency* to occur. The concept of chemical equilibrium which we treat in this chapter addresses this question directly. In a later chapter we will see that the tendency of a reaction to occur can be predicted entirely from the properties of the reactants and products through the law of thermodynamics. This is the *macroscopic* aspect of chemical change in that it makes no assumptions about the mechanistic details of how the atoms rearrange themselves as the reactants are transformed into products.
- ***What is the mechanism of the reaction?*** What happens, at the atomic or molecular level, when reactants are transformed into products? What *intermediate* species (those that are produced but later consumed so that they do not appear in the net reaction equation) are involved? This is the *microscopic*, or *kinetic* view of chemical change, and unlike the macroscopic aspects described in the preceding paragraph, cannot be predicted by theory as it is presently developed and must be inferred from the results of experiments. The variable we commonly observe that relates to the kinetics of a reaction is the *rate* at which it takes place. These rates can be extremely high (a mole per microsecond) or very low (a mole per year), and they are very frequently indistinguishable from zero. The rate of a given reaction can be highly influenced by factors such as particle size, the presence of a catalyst, or in some cases even the shape of the container.

A reaction that is thermodynamically possible but for which no reasonably rapid mechanism is available is said to be *kinetically limited*. Conversely, one that occurs rapidly but only to a small extent is *thermodynamically limited*. As you will see later, there are often ways of getting around both kinds of limitations, and their discovery and practical applications constitute an important area of industrial chemistry.

2 • What is equilibrium?

Basically, the term refers to what we might call a “balance of forces”. In the case of mechanical equilibrium, this is its literal definition. A book sitting on a table top remains at rest because the downward force exerted by the earth’s gravity acting on the book’s mass (this is what is meant by the “weight” of the book) is exactly balanced by the repulsive force between

atoms that prevents two objects from simultaneously occupying the same space, acting in this case between the table surface and the book. If you pick up the book and raise it above the table top, the additional upward force exerted by your arm destroys the state of equilibrium as the book moves upward. If you wish to hold the book at rest above the table, you adjust the upward force to exactly balance the weight of the book, thus restoring equilibrium. An object is in a state of mechanical equilibrium when it is either static (motionless) or in a state of unchanging motion. From the relation $f = ma$, it is apparent that if the net force on the object is zero, its acceleration must also be zero, so if we can see that an object is not undergoing a change in its motion, we know that it is in mechanical equilibrium.

Another kind of equilibrium we all experience is *thermal equilibrium*. When two objects are brought into contact, heat will flow from the warmer object to the cooler one until their temperatures become identical. Thermal equilibrium is a “balance of forces” in the sense that temperature is a measure of the tendency of an object to lose thermal energy. A metallic object at room temperature will feel cool to your hand when you first pick it up because the thermal sensors in your skin detect a flow of heat from your hand into the metal, but as the metal approaches the temperature of your hand, this sensation diminishes. The time it takes to achieve thermal equilibrium depends on how readily heat is conducted within and between the objects; thus a wooden object will feel warmer than a metallic object even if both are at room temperature because wood is a relatively poor thermal conductor. Thermal equilibrium is something we often want to avoid, or at least postpone; this is why we insulate buildings, perspire in the summer and wear heavier clothing in the winter.

3 • Chemical equilibrium

When a chemical reaction takes place in a container which prevents the entry or escape of any of the substances involved in the reaction, the quantities of these components change as some are consumed and others are formed. Eventually this change will come to an end, after which the composition will remain unchanged as long as the system remains undisturbed. The system is then said to be in its *equilibrium state*, or more simply, “at equilibrium”



A chemical reaction is in equilibrium when there is no tendency for the quantities of reactants and products to change.

The *direction* in which we write a chemical reaction (and thus which components are considered reactants and which are products) is arbitrary. Thus the equations



and

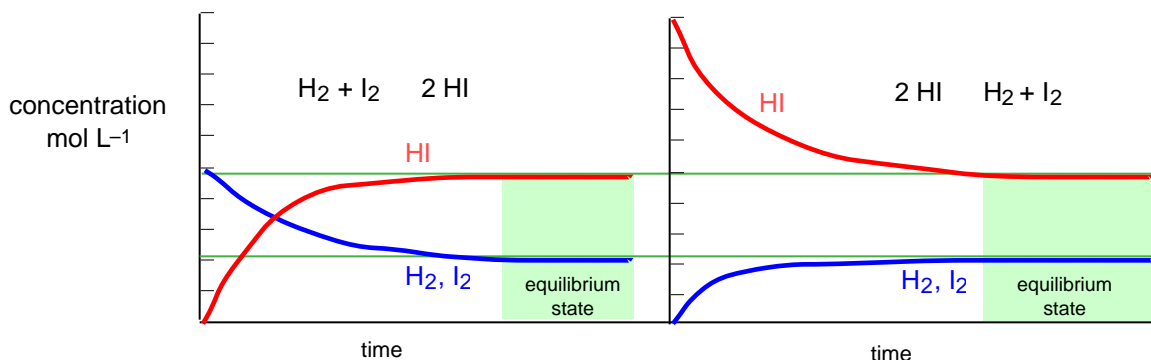


represent the same chemical reaction system in which the roles of the components are reversed, *and both yield the same mixture of components when the change is completed.*

This last point is central to the concept of chemical equilibrium. It makes no difference whether we start with two moles of HI or one mole each of H_2 and I_2 ; once the reaction has run to completion, the quantities of these two components will be the same. In general, then, we can say that the composition of a chemical reaction system will tend to change in a direction that brings it closer to its equilibrium composition. Once this equilibrium composition

has been attained, no further change in the quantities of the components will occur as long as the system remains undisturbed.

The two diagrams below show how the concentrations of the three components of a chemical reaction change with time (under the conditions in which this particular reaction is usually carried out, the time scale is typically 10 to 100 minutes.) Examine the two sets of plots carefully, noting which substances have zero initial concentrations, and are thus "reactants" in each case. Satisfy yourself that these two sets represent the same chemical reaction system, but with the reactions occurring in opposite directions. Most importantly, note how the concentrations of all the components are identical when the system reaches equilibrium.



The equilibrium state is independent of the direction from which it is approached. Whether we start with an equimolar mixture of H₂ and I₂ (left) or a pure sample of hydrogen iodide (shown on the right, using twice the initial concentration of HI to keep the number of atoms the same), the composition will be the same once equilibrium is attained (shaded regions on the right.) The time required to reach equilibrium is highly variable (from microseconds to centuries) and depends on the mechanism of the reaction and on the temperature.

4 • What is a reversible reaction?

A chemical equation of the form $A \rightarrow B$ represents the transformation of A into B, but it does not imply that *all* of the reactants will be converted into products, or that the reverse reaction $B \rightarrow A$ cannot also occur. In general, *both* processes can be expected to occur, resulting in an equilibrium mixture containing *all* of the components of the reaction system. (We use the word *components* when we do not wish to distinguish between reactants and products.) If the equilibrium state is one in which significant quantities of both reactants and products are present (as in the hydrogen iodide example given above), then the reaction is said to *incomplete* or *reversible*.

The latter term is preferable because it avoids confusion with "complete" in its other sense of being finished, implying that the reaction has run its course and is now at equilibrium.

- If it is desired to emphasize the reversibility of a reaction, the single arrow in the equation is replaced with a pair of hooked lines pointing in opposite directions, as in $A \rightleftharpoons B$. There is no fundamental difference between the meanings of $A \rightarrow B$ and $A \rightleftharpoons B$, however. Some older textbooks even use $A = B$.
- A reaction is said to be *complete* when the equilibrium composition contains no significant amount of the reactants. However, a reaction that is complete when written in one direction is said "not to occur" when written in the reverse direction.

In principle, *all* chemical reactions are reversible, but this reversibility may not be observable if the fraction of products in the equilibrium mixture is very small, or if the reverse reaction is kinetically inhibited.

5 • How did Napoleon Bonaparte help discover reversible reactions?



We can thank Napoleon for bringing the concept of reaction reversibility to Chemistry. Napoleon recruited the eminent French chemist Claude Louis Berthollet (1748-1822) to accompany him as scientific advisor on the most far-flung of his campaigns, the expedition into Egypt in 1798. Once in Egypt, Berthollet noticed deposits of sodium carbonate around the edges of some of the salt lakes found there. He was already familiar with the reaction



which was known to proceed to completion in the laboratory. He immediately realized that the Na_2CO_3 must have been formed by the reverse of this process brought about by the very high concentration of salt in the slowly-evaporating waters. This led Berthollet to question the belief of the time that a reaction could only proceed in a single direction. His famous textbook *Essai de statique chimique* (1803) presented his speculations on chemical affinity and his discovery that an excess of the product of a reaction could drive it in the reverse direction.

Unfortunately, Berthollet got a bit carried away by the idea that a reaction could be influenced by the amounts of substances present, and maintained that the same should be true for the compositions of individual compounds. This brought him into conflict with the recently accepted Law of Definite Proportions (that a compound is made up of fixed numbers of its constituent atoms), so his ideas (the good along with the bad) were promptly discredited and remained largely forgotten for 50 years. (Ironically, it is now known that certain classes of compounds do in fact exhibit variable composition of the kind that Berthollet envisioned.)

6 • What is the Law of Mass Action?

Berthollet's ideas about reversible reactions were finally vindicated by experiments carried out by others, most notably the Norwegian chemists (and brothers-in-law) Cato Guldberg and Peter Waage. During the period 1864-1879 they showed that an equilibrium can be approached from either direction (see the hydrogen iodide illustration above), implying that any reaction $aA + bB \rightleftharpoons cC + dD$ is really a competition between a "forward" and a "reverse" reaction. When a reaction is at equilibrium, the rates of these two reactions are identical, so no *net* (macroscopic) change is observed, although individual components are actively being transformed at the microscopic level.

Guldberg and Waage showed that the rate of the reaction in either direction is proportional to what they called the "active masses" of the various components:

$$\begin{aligned} \text{rate of forward reaction} &= k_f[A]^a[B]^b \\ \text{rate of reverse reaction} &= k_r[C]^c[D]^d \end{aligned}$$

in which the proportionality constants k are called *rate constants* and the quantities in square brackets represent concentrations. If we combine the two reactants A and B, the forward reaction starts immediately, but the formation of products allows the reverse process to get underway. As the reaction proceeds, the rate of the forward reaction diminishes while that of the reverse reaction increases. Eventually the two processes are proceeding at the same rate, and the reaction is at equilibrium:

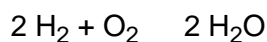
$$\begin{aligned} \text{rate of forward reaction} &= \text{rate of reverse reaction} \\ k_f[A]^a[B]^b &= k_r[C]^c[D]^d \end{aligned}$$

If we now change the composition of the system by adding some C or withdrawing some A (thus changing their “active masses”), the reverse rate will exceed the forward rate and a change in composition will occur until a new equilibrium composition is achieved.

The Law of Mass Action is thus essentially the statement that the equilibrium composition of a reaction mixture can vary according to the quantities of components that are present. This of course is just what Berthollet observed in his Egyptian salt ponds, but it was now seen to be a consequence of the dynamic nature of chemical equilibrium.

7 • How do we know when a reaction is at equilibrium?

Clearly, if we observe some change taking place-- a change in color, the emission of gas bubbles, the appearance of a precipitate, or the release of heat, we know the reaction is *not* at equilibrium. However, the *absence* of any sign of change does not by itself establish that the reaction is at equilibrium, which is defined above as the lack of any *tendency* for change to occur; “tendency” is not a property that is directly observable! Consider, for example, the reaction representing the synthesis of water from its elements:



You can store the two gaseous reactants in the same container indefinitely without any observable change occurring. But if you create an electrical spark in the container or introduce a flame, *bang!* After you pick yourself up off the floor and remove the shrapnel from what’s left of your body, you will know very well that the system was not initially at equilibrium! It happens that this particular reaction has a tremendous tendency to take place, but for reasons that we will discuss in a later chapter, nothing can happen until we “set it off” in some way— in this case by exposing the mixture to a flame, or (in a more gentle way) by introducing a platinum wire, which acts as a catalyst. *A reaction of this kind is said to be highly favored thermodynamically, but inhibited kinetically.* The hydrogen iodide reaction, by contrast, is only moderately favored thermodynamically (that’s why it is incomplete), but its kinetics are reasonably facile.

It is almost always the case, however, that once a reaction actually starts, it will continue on its own until it reaches equilibrium, so if we can observe the change as it occurs and see it slow down and stop, we can be reasonably certain that the system is in equilibrium. This is by far the chemist’s most common criterion.

There is one other experimental test for equilibrium in a chemical reaction, although it is really only applicable to the kind of reactions we described above as being reversible. As we shall see very soon, the equilibrium state of a system is always sensitive to the temperature, and often to the pressure, so any changes in these variables, however, small, will temporarily disrupt the equilibrium, resulting in an observable change in the composition of the system as it moves toward its new equilibrium state. Similarly, addition or removal of one component of the reaction will affect the amounts of all the others. If carrying out any of these operations fails to produce an observable change, then it is likely that the reaction is kinetically inhibited and that the system is not at equilibrium.

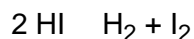
8 • What is the LeChâtelier principle?

If a reaction is at equilibrium and we alter the conditions so as to create a new equilibrium state, then the composition of the system will tend to change until that new equilibrium state is attained. (We say “tend to change” because if the reaction is kinetically inhibited, the change may be too slow to observe or it may never take place.) In 1884, the French chemical engineer and teacher Henri LeChâtelier (1850-1936) showed that in every such case, the new equilibrium state is one that partially reduces the effect of the change that brought it about. This law is known to every Chemistry student as the *LeChâtelier principle*. His original formulation was somewhat more complicated, but a reasonably useful paraphrase of it reads as follows:



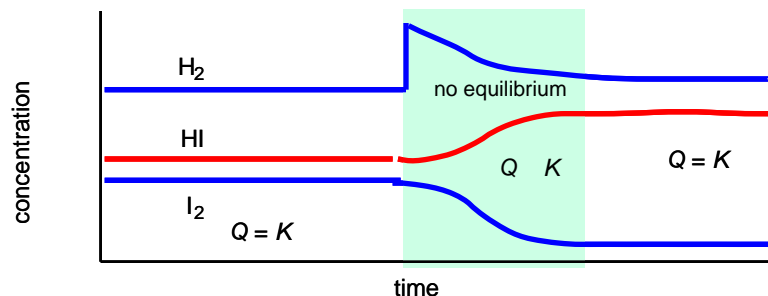
LeChâtelier principle: If a system at equilibrium is subjected to a change of pressure, temperature, or the number of moles of a substance, there will be a tendency for a net reaction in the direction that tends to reduce the effect of this change.

To see how this works (and you must do so, as this is of such fundamental importance that you simply cannot do any meaningful Chemistry without a thorough working understanding of this principle), look again the hydrogen iodide dissociation reaction



Consider an arbitrary mixture of these components at equilibrium, and assume that we inject more hydrogen gas into the container. Because the H_2 concentration now exceeds its new equilibrium value, the system is no longer in its equilibrium state, so a net reaction now ensues as the system moves to the new state. The LeChâtelier principle states that the net reaction will be in a direction that tends to reduce the effect of the added H_2 . This can occur if some of the H_2 is consumed by reacting with I_2 to form more HI ; in other words, a net reaction occurs in the reverse direction. Chemists usually simply say that “the equilibrium shifts to the left”.

To get a better idea of how this works, carefully examine the diagram below which follows the concentrations of the three components of this reaction as they might change in time (the time scale here will typically be about an hour). The following table contains several examples showing how changing the quantity of a reaction component can shift an established equilibrium

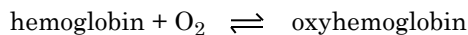


Disruption and restoration of equilibrium. At the left, the concentrations of the three components do not change with time because the system is at equilibrium. We then add more hydrogen to the system, disrupting the equilibrium. A net reaction then ensues that moves the system to a new equilibrium state (right) in which the quantity of hydrogen iodide has increased; in the process, some of the I_2 and H_2 are consumed. Notice that the new equilibrium state contains more hydrogen than did the initial state, but not as much as was added; as the LeChâtelier principle predicts, the change we made (addition of H_2) has been partially counteracted by the "shift to the right".

The following table contains several examples showing how changing the quantity of a reaction component can shift an established equilibrium.

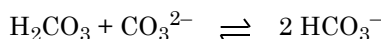
system	change	result
$CO_2 + H_2 \rightleftharpoons H_2O(g) + CO$	a drying agent is added to absorb H_2O	Shift to the right. Continuous removal of a product will force any reaction to the right.
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	Some nitrogen gas is added	No change; N_2 is not a component of this reaction system.
$NaCl(s) + H_2SO_4(l) \rightleftharpoons Na_2SO_4(s) + HCl(g)$	reaction is carried out in an open container	Because HCl is a gas that can escape from the system, the reaction is forced to the right. This is the basis for the commercial production of hydrochloric acid.
$H_2O(l) \rightleftharpoons H_2O(g)$	water evaporates from an open container	Continuous removal of water vapor forces the reaction to the right, so equilibrium is never achieved.
$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$	the solution is diluted	Shift to right; the product $[H^+][CN^-]$ diminishes more rapidly than does $[HCN]$.
$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$	some $NaCl$ is added to the solution	Shift to left due to increase in Cl^- concentration. This is known as the <i>common ion effect</i> on solubility.
$N_2 + 3 H_2 \rightleftharpoons 2 NH_3$	a catalyst is added to speed up this reaction	No change. Catalysts affect only the rate of a reaction; they have no effect at all on the composition of the equilibrium state.

The LeChâtelier principle in physiology: hemoglobin and oxygen transport. Many of the chemical reactions that occur in living organisms are regulated through the LeChâtelier principle. Few of these are more important to warm-blooded organisms than those that relate to aerobic respiration, in which oxygen is transported to the cells where it is combined with glucose and metabolized to carbon dioxide, which then moves back to the lungs from which it is expelled.



The partial pressure of O_2 in the air is 0.2 atm, sufficient to allow these molecules to be taken up by hemoglobin (the red pigment of blood) in which it becomes loosely bound in a complex known as oxyhemoglobin. At the ends of the capillaries which deliver the blood to the tissues, the O_2 concentration is reduced by about 50% owing to its consumption by the cells. This shifts the equilibrium to the left, releasing the oxygen so it can diffuse into the cells.

Carbon dioxide reacts with water to form the weak acid H_2CO_3 which would cause the blood acidity to become dangerously high if it were not promptly removed as it is excreted by the cells. This is accomplished by combining it with carbonate ion through the reaction



which is forced to the right by the high local CO_2 concentration within the tissues. Once the hydrogen carbonate (bicarbonate) ions reach the lung tissues where the CO_2 partial pressure is much smaller, the reaction reverses and the CO_2 is expelled.

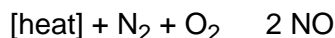
Carbon monoxide poisoning. Carbon monoxide, a product of incomplete combustion that is present in automotive exhaust and cigarette smoke, binds to hemoglobin 200 times more tightly than does O_2 . This blocks the uptake and transport of oxygen by setting up a competing equilibrium



Air that contains as little as 0.1 percent carbon monoxide can tie up about half of the hemoglobin binding sites, reducing the amount of O_2 reaching the tissues to fatal levels. Carbon monoxide poisoning is treated by administration of pure O_2 which promotes the shift of the above equilibrium to the left. This can be made even more effective by placing the victim in a hyperbaric chamber in which the pressure of O_2 can be made greater than 1 atm.

9 • How do changes in temperature affect equilibria?

Virtually all chemical reactions are accompanied by the liberation or uptake of heat. If we regard heat as a “reactant” or “product” in an endothermic or exothermic reaction respectively, we can use the LeChâtelier principle to predict the direction in which an increase or decrease in temperature will shift the equilibrium state. Thus for the oxidation of nitrogen, an endothermic process, we can write



Suppose this reaction is at equilibrium at some temperature T_1 and we raise the temperature to T_2 . The LeChâtelier principle tells us that a net reaction will occur in the direction that will partially counteract this change, meaning that the system must absorb some of this additional heat, and the equilibrium will shift to the right.

Nitric oxide, the product of this reaction, is a major air pollutant which initiates a sequence of steps leading to the formation of atmospheric smog. Its formation is an unwanted side reaction which occurs when the air (which is introduced into the combustion chamber of an engine to supply oxygen) gets heated to a high temperature. Designers of internal combustion engines now try, by various means, to limit the temperature in the

combustion region, or to restrict its highest-temperature part to a small volume within the combustion chamber.

10 • How do changes in pressure affect equilibria?

You will recall that if the pressure of a gas is reduced, its volume will increase; pressure and volume are inversely proportional. With this in mind, suppose that the reaction



is in equilibrium at some arbitrary temperature and pressure, and that we double the pressure, perhaps by compressing the mixture to a smaller volume. From the LeChâtelier principle we know that the equilibrium state will change to one that tends to counteract the increase in pressure. This can occur if some of the NO_2 reacts to form more of the dinitrogen tetroxide, since two moles of gas is being removed from the system for every mole of N_2O_4 formed, thereby decreasing the total volume of the system. Thus increasing the pressure will shift this equilibrium to the right.

It is important to understand that the changing the pressure will have a significant effect only on reactions in which there is a change in the number of moles of gas. For the above reaction, this change $n_g = (n_{\text{products}} - n_{\text{reactants}}) = 1 - 2 = -1$. In the case of the nitrogen oxidation reaction described previously, $n_g = 0$ and pressure will have no effect.

The volumes of solids and liquids are hardly affected by the pressure at all, so for reactions that do not involve gaseous substances, the effects of pressure changes are ordinarily negligible. Exceptions arise under conditions of very high pressure such as exist in the interior of the Earth or near the bottom of the ocean. A good example is the dissolution of calcium carbonate $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$. There is a slight decrease in the volume when this reaction takes place, so an increase in the pressure will shift the equilibrium to the right, so that calcium carbonate becomes more soluble at higher pressures. The skeletons of several varieties of microscopic organisms that inhabit the top of the ocean are made of CaCO_3 , so there is a continual rain of this substance toward the bottom of the ocean as these organisms die. As a consequence, the floor of the Atlantic ocean is covered with a blanket of calcium carbonate. This is not true for the Pacific ocean, which is deeper; once the skeletons fall below a certain depth, the higher pressure causes them to dissolve. Some of the seamounts (undersea mountains) in the Pacific extend above the solubility boundary so that their upper parts are covered with CaCO_3 sediments.

The effect of pressure on a reaction involving substances whose boiling points fall within the range of commonly encountered temperature will be sensitive to the states of these substances at the temperature of interest.



The commercial production of hydrogen is carried out by treating natural gas with steam at high temperatures and in the presence of a catalyst (“steam reforming of methane”):



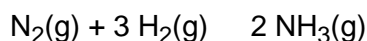
Given the following boiling points: CH_4 (methane) = -161°C , H_2O = 100°C , CH_3OH = 65°C , H_2 = -253°C , predict the effects of an increase in the total pressure on this equilibrium at 50° , 75° and 120°C .

temp	equation	n_g	shift
50°	$\text{CH}_4(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{OH}(l) + \text{H}_2(g)$	0	none
75°	$\text{CH}_4(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{OH}(g) + \text{H}_2(g)$	+1	to left
120°	$\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CH}_3\text{OH}(g) + \text{H}_2(g)$	0	none

For reactions involving gases, only changes in the partial pressures of those gases directly involved in the reaction are important; the presence of other gases has no effect.

11 • What is the Haber process and why is it important?

The Haber process for the synthesis of ammonia is based on the exothermic reaction



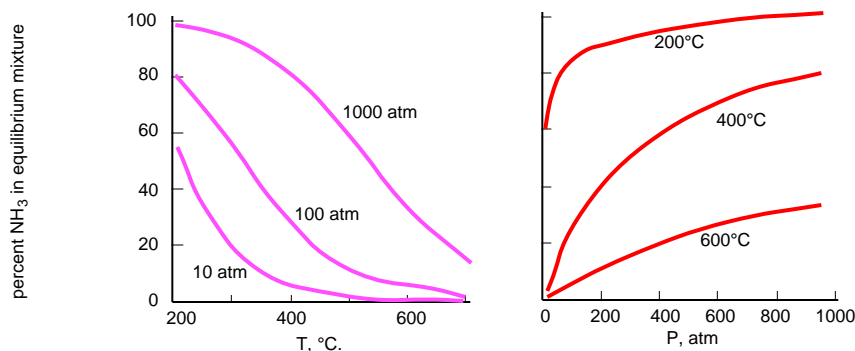
The LeChâtelier principle tells us that in order to maximize the amount of product in the reaction mixture, it should be carried out at high pressure and low temperature. However, the lower the temperature, the slower the reaction (this is true of virtually all chemical reactions.) As long as the choice had to be made between a low yield of ammonia quickly or a high yield over a long period of time, this reaction was infeasible economically.

Although nitrogen is a major component of air, the strong triple bond in N_2 makes it extremely difficult to incorporate this element into species such as NO_3^- and NH_4^+ which serve as the starting points for the wide variety of nitrogen-containing compounds that are essential for modern industry. This conversion is known as *nitrogen fixation*, and because nitrogen is an essential plant nutrient, modern intensive agriculture is utterly dependent on huge amounts of fixed nitrogen in the form of fertilizer. Until around 1900, the major source of fixed nitrogen was the NaNO_3 (Chile saltpeter) found in extensive deposits in South America. Several chemical processes for obtaining nitrogen compounds were developed in the early 1900's, but they proved too inefficient to meet the increasing demand.

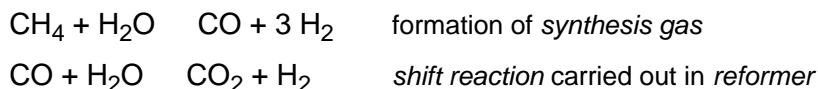


Although the direct synthesis of ammonia from its elements had been known for some time, the yield of product was found to be negligible. In 1905, Fritz Haber (1868-1934) began to study this reaction, employing the thinking initiated by LeChâtelier and others, and the newly-developing field of thermodynamics that served as the basis of these principles. From the LeChâtelier law alone, it is apparent that this exothermic reaction is favored by low temperature and high pressure. However, it was not as simple as that: the rate of any reaction increases with the temperature, so working with temperature alone, one has the choice between a high product yield achieved only very slowly, or a very low yield quickly. Further, the equipment, and the high-strength alloy steels need to build it, did not exist at the time. Haber solved the first problem by developing a catalyst that would greatly speed up the reaction at lower temperatures. The second problem, and the development of an efficient way of producing hydrogen,

would delay the practical implementation of the process until 1913, when the first plant based on the Haber-Bosch process (as it is more properly known, Bosch being the person who solved the major engineering problems) came into operation. The timing could not have been better for Germany, since this country was about to enter the First World War, and the Allies had established a naval blockade of South America, cutting off the supply of nitrate for the the German munitions industry.



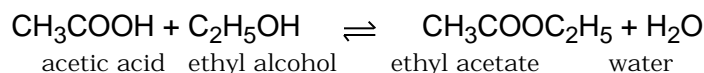
Bosch's plant operated the ammonia reactor at 200 atm and 550°C. Later, when stronger alloy steels had been developed, pressures of 800-1000 atm became common. The source of hydrogen in modern plants is usually natural gas, which is mostly methane:



The Haber-Bosch process is considered the most important chemical synthesis developed in the 20th century. Besides its scientific importance as the first large-scale application of the laws of chemical equilibrium, it has had tremendous economic and social impact; without an inexpensive source of fixed nitrogen, the intensive crop production required to feed the world's growing population would have been impossible. In 1918, Haber was awarded the Nobel Prize in Chemistry in recognition of his work.

12 • How can we characterize a chemical equilibrium?

If the position of an equilibrium (that is, the composition of a chemical reaction system at equilibrium) can depend on the amounts of substances brought together (the "active masses" as defined by Guldberg and Waage's Law of Mass Action), an important question arises: is there a single, measurable property that is unique to any chemical reaction system that can be used to predict its equilibrium composition for all possible initial amounts of the substances involved in the reaction? The answer, which of course is "yes", first became evident through a careful examination of a reaction studied by Berthollet:



The product, ethyl acetate, is called an *ester*, so the reaction as a whole is known as an *esterification* reaction. By combining various amounts of acetic acid and ethanol, different amounts of products were obtained once the reaction came to equilibrium (it takes about an hour of boiling in the presence of HCl, which acts as a catalyst.)

The equilibrium concentrations that we might observe in each experiment are shown in the shaded region of the table. Although you can detect some pattern to these numbers if you examine them carefully, they don't tell us very much about the reaction itself. If, however,

expt	initial concentration, mol L ⁻¹		concentration at equilibrium, mol L ⁻¹				equilibrium constant
	CH ₃ COOH	C ₂ H ₅ OH	CH ₃ COOH	C ₂ H ₅ OH	CH ₃ COOC ₂ H ₅	H ₂ O	
1	1.00	0.18	0.829	0.009	0.171	0.171	3.9
2	1.00	1.0	0.333	0.333	0.667	0.667	4.0
3	1.00	2.0	0.142	1.142	0.888	0.858	4.5
4	1.00	8.0	0.034	2.034	0.966	0.966	3.9

we substitute them into the expression

$$\frac{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]} = K_c$$

we find that the results (shown in the rightmost column of the table) are about the same for each set of initial concentrations, the differences being due to experimental error. Their average value, $K_c = 4.1$, is a *property* of this particular reaction under the conditions of pressure and temperature at which it is being observed.

We call K_c the *equilibrium constant in terms of concentrations*. We use the term “constant” here with some reservation; equilibrium constants are highly dependent on the temperature, sometimes increasing with temperature and sometimes decreasing, depending on the particular reaction.

More generally, for a reaction having the form $aA + bB \rightleftharpoons cC + dD$, the equilibrium expression (the formula that defines K) is given by



$$\frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

in which the bracketed terms represent the concentrations of the various components. This can be generalized further by considering the coefficients of the reactants (a and b) as negative numbers, reflecting the fact that these components are consumed in the reaction. Denoting these *stoichiometric coefficients* by ν_i , the expression becomes

$$\prod_i C_i^{\nu_i}$$

in which C_i represents the concentration of the i th component, or some function proportional to the concentration, such as the pressure for a gaseous substance. The main reason for showing this here is to introduce you to the \prod notation for denoting a product of an indefinite number of terms; you will also find that writing it this is a good way to impress your teachers, parents and friends.

13 • What is the equilibrium quotient?

In the previous section we defined the *equilibrium expression* for the reaction $aA + bB \rightleftharpoons cC + dD$ as

$$\frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

In the general case in which the concentrations can have any arbitrary values (including

zero), this expression is called the equilibrium quotient and its value is denoted by Q (or Q_c if we wish to emphasize that the terms represent molar concentrations.) If the terms correspond to *equilibrium* concentrations, then the above expression is called the *equilibrium constant* and its value is denoted by K (or K_c .) **K is thus the special value that Q has when the reaction is at equilibrium.**

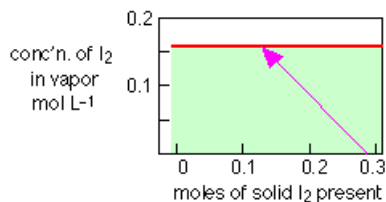
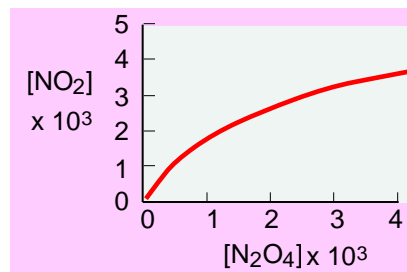
The value of Q in relation to K serves as an index how the composition of the reaction system compares to that of the equilibrium state, and thus it indicates the direction in which any net reaction must proceed. For example, if we combine the two reactants A and B at concentrations of 1 mol L^{-1} each, the value of Q will indeterminate large($1/0$). If instead our mixture consists only of the two products C and D, $Q = 0/1 = 0$. It is easy to see (by simply application of the LeChâtelier principle) that the ratio of Q/K immediately tells us whether, and in which direction, a net reaction will occur as the system moves toward its equilibrium state:

Q/K	net reaction to reach equilibrium
>1	Product concentration too high; net reaction proceeds to left
1	System is at equilibrium; no net change will occur.
<1	Product concentration too low; net reaction proceeds to right.

14 • A visual way of thinking about Q and K

The formal definitions of Q and K are quite simple, but they are of limited usefulness unless you are able to relate them to real chemical situations. The following diagrams illustrate the relation between Q and K from various standpoints. Take some time to study each one carefully, making sure that you are able to relate the printed description to the illustration.

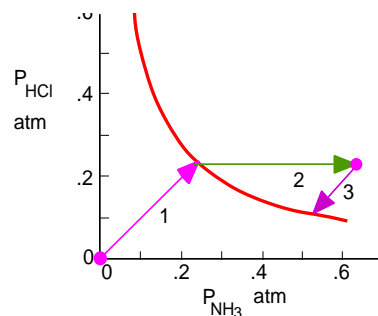
Each tiny dot on the graph represents a possible combination of NO_2 and N_2O_4 concentrations, each of which corresponds to a certain value of Q for the chemical reaction system $\text{N}_2\text{O}_4 \rightleftharpoons 2 \text{NO}_2$. (There are of course an infinite number of possible states of this system within the concentration boundaries shown on the plot.) Only those dots that fall on the red line correspond to equilibrium states of this system (those for which $Q=K$). The line itself is a plot of $[\text{NO}_2] = ([\text{N}_2\text{O}_4]K)^{0.5}$. If the system is initially in a non-equilibrium state, its composition will change in a direction that moves it to one on the line.



One of the simplest equilibria we can write is that between a solid and its vapor. Using the sublimation of iodine $\text{I}_2(s) \rightleftharpoons \text{I}_2(g)$ as an example, we see that the possible equilibrium states of the system (shaded area in the diagram) are limited to those in which at least some solid is present, but that within this region, the quantity of iodine vapor is constant (as long as the temperature is unchanged.) The arrow shows the succession of states the system passes through when 0.29 mole of solid iodine is placed in a 1-L sealed container; the unit slope of this line reflects the fact that each mole of I_2 removed from the solid ends up in the vapor.

reflects the fact that each mole of I_2 removed from the solid ends up in the vapor.

The decomposition of ammonium chloride $\text{NH}_4\text{Cl}(s) \rightleftharpoons \text{NH}_3(g) + \text{HCl}(g)$ is another example of a solid-gas equilibrium. Arrow 1 traces the states the system passes through when solid NH_4Cl is placed in a closed container. Arrow 2 represents the addition of ammonia to the equilibrium mixture; the system responds by following the path 3 back to a new equilibrium state which, as the LeChâtelier principle predicts, contains a smaller quantity of ammonia than was added. Lines 1 and 3 have unit slopes because changes in the quantities of HCl and NH_3 are identical when the system undergoes any spontaneous change as it returns to an equilibrium state.



15 • Does everything stop when equilibrium is reached?

When a reaction system is not at equilibrium, the quantities of reactants or products will change until $Q = K$, at which point no further change will occur as long as the system remains at the same temperature and pressure. So all *net change* does come to an end when equilibrium is reached.

But the absence of any net change does not mean that nothing is happening. Since all reactions are reversible at least in principal, we can regard an equilibrium $A \rightleftharpoons B$ as the sum of two processes

A	B	forward reaction	$\text{rate}_f = k_f[A]$
B	A	reverse reaction	$\text{rate}_r = k_r[B]$

The expressions given in the rightmost column above simply reflect the fact that the rate at which a substance undergoes change should be proportional to its concentration; this is just another statement of the Law of Mass Action. The proportionality constants k_f and k_r are the *forward and reverse rate constants*. If we start with substance A alone, the absence of B means that the forward reaction alone is proceeding. Then, as the concentration of B begins to build up, the reverse reaction comes into operation, the rate of the forward reaction diminishes due to the reduction in the concentration of B. At some point these two processes will come into exact balance so that the forward and reverse rates are the same, at which point we can write

$$k_f[A] = k_r[B]$$

and combine the k 's to obtain

$$\frac{k_f}{k_r} = \frac{[B]}{[A]} = K$$

thus showing that the equilibrium constant can in a sense be regarded as the resultant of the two opposing rate constants. If the rate constant of the forward reaction exceeds that of the reverse step, then the equilibrium state will be one in which the product dominates. (Note carefully that although the two rate *constants* will generally be different, the forward and reverse *rates* themselves will always be identical at equilibrium.)

The preceding paragraph shows how the concept of the equilibrium constant follows from the Law of Mass Action, but it is not a proper derivation of the formula for equilibrium constants in general.

The single most important idea for you to carry along with you from this section is that *equilibrium is a dynamic process* in which the forward and reverse reactions are continually opposing each other in a dead heat.

To see if you really understand this, try explaining to yourself how the LeChâtelier Principle as it applies to concentrations of reaction components follows from the idea of opposing reaction steps.

Although it is the *ratio* of k_f/k_r , that determines K , the magnitudes of these rate constants also make a difference; if they are small (or as is often the case, zero) then the reaction is *kinetically inhibited* and equilibrium will be achieved slowly or not at all. When their values are large, equilibrium is achieved quickly; the equilibrium is said to be *facile* and the reaction is *fast*. Sometimes a very slow equilibrium can be made more facile by addition of a suitable *catalyst*.

16 • What other ways are there of writing equilibrium expressions?

Although we commonly write equilibrium quotients and equilibrium constants in terms of molar concentrations, any concentration-like term can be used, including mole fraction and molality. Sometimes the symbols K_c , K_x , and K_m are used to denote these forms of the equilibrium constant. We will not make use of the latter two in this course, but there is one other formulation that is important for you to know, and is commonly preferred when the reaction components are gases. The concentration of a gaseous substance in moles (n) per liter varies directly with its partial pressure:

$$c = \frac{n}{V} = \frac{PV}{RTV} = \frac{P}{RT}$$

so for a reaction $A(g) \rightleftharpoons B(g)$ we can write the equilibrium constant as

$$K_p = \frac{P_B}{P_A}$$

It is important to point out that the numerical values of K 's and Q 's expressed in these different ways will not generally be the same.

All of these forms of the equilibrium constant are only approximately correct, working best at low concentrations or pressures. The only equilibrium constant that is truly "constant" (except that it still varies with the temperature!) is expressed in terms of *activities*, which you can think of as "effective concentrations" that allow for interactions between molecules. In practice, this distinction only becomes important for equilibria involving gases at very high pressures (such as are sometimes encountered in chemical engineering) and ionic solutions more concentrated than about 0.001 M . We will not deal much with activities in this course.

For a reaction such as $CO_2(g) + OH^-(aq) \rightleftharpoons HCO_3^-(aq)$ that involves both gaseous and dissolved components, a "hybrid" equilibrium constant is commonly used:

$$K = \frac{[HCO_3^-]}{P_{CO_2}[OH^-]}$$

17 • Unchanging concentrations in equilibrium expressions

Substances whose concentrations undergo no significant change in a chemical reaction do not appear in equilibrium constant expressions. How can the concentration of a reactant or product not change when a reaction involving that substance takes place? There are two general cases to consider.

The substance is also the solvent.

This happens all the time in acid-base chemistry. Thus for the hydrolysis of the cyanide ion $\text{CN}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCN} + \text{OH}^-$, we write

$$\frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]}$$

in which no $[\text{H}_2\text{O}]$ term appears. The justification for this omission is that water is both the solvent and reactant, and the amount of water consumed in the reaction is so minute (because K is so small) that any change in the concentration of H_2O from that of pure water (55.6 mol L^{-1}) will be negligible.

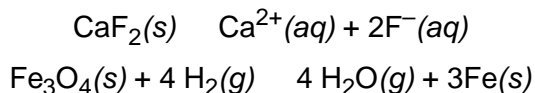
Be careful about throwing away H_2O whenever you see it. In the esterification reaction



that we discussed in a previous section, a $[\text{H}_2\text{O}]$ term must be present in the equilibrium expression if the reaction is assumed to be between the two liquids acetic acid and ethanol. If, on the other hand, the reaction takes place between a dilute aqueous solution of the acid and the alcohol, then the $[\text{H}_2\text{O}]$ term would not be used.

The substance is a solid or a pure liquid phase.

This is most frequently seen in solubility equilibria, but there are many other reactions in which solids are directly involved:



These are heterogeneous reactions (meaning reactions in which some components are in different phases), and the argument here is that concentration is only meaningful when applied to a substance within a single phase. Thus the term $[\text{CaF}_2]$ would refer to the “concentration of calcium fluoride within the solid CaF_2 ”, which is a constant depending on the molar mass of CaF_2 and the density of that solid. The concentrations of the two ions will be independent of the quantity of solid CaF_2 in contact with the water; in other words, the system can be in equilibrium as long as any CaF_2 at all is present.

Throwing out the constant-concentration terms can lead to some rather sparse-looking equilibrium expressions. For example, the equilibrium constant for each of the processes shown in the following table consists solely of the partial pressure of a gas:

$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$	$K_p = P_{\text{CO}_2}$	Thermal decomposition of limestone, a first step in the manufacture of cement.
$\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{Na}_2\text{SO}_4(\text{s}) + 10 \text{H}_2\text{O}(\text{g})$	$K_p = P_{\text{H}_2\text{O}}^{10}$	Sodium sulfate decahydrate is a solid in which H_2O molecules (“waters of hydration”) are incorporated into the crystal structure.)
$\text{I}_2(\text{s}) \rightleftharpoons \text{I}_2(\text{g})$	$K_p = P_{\text{I}_2}$	Sublimation of solid iodine; this is the source of the purple vapor you can see above solid iodine in a closed container.

$\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g)$	$K_p = P_{\text{H}_2\text{O}}$	Vaporization of water. When the partial pressure of water vapor in the air is equal to K , the relative humidity is 100%.
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The last two processes represent changes of state, or phase equilibria, which can be treated exactly the same as chemical reactions. In each of the heterogeneous processes shown in the table, the reactants and products can be in equilibrium (that is, permanently coexist) only when the partial pressure of the gaseous product has the value consistent with the indicated K_p . Bear in mind also that these K_p s all increase with the temperature.



What are the values of K_p for the equilibrium between liquid water and its vapor at 25°C, 100°C, and 120°C? The vapor pressure of water at these three temperatures is 23.8 torr, 1 atm, and 1489 torr, respectively.

These “vapor pressures” are the partial pressures of water vapor in equilibrium with the liquid, so they are the same as the K_p s when expressed in units of atmospheres.

25°C	100°C	120°C
$K_p = \frac{23.8 \text{ torr}}{760 \text{ torr/atm}} = 0.031 \text{ atm}$ <p>The partial pressure of H_2O above liquid water in a closed container at 25°C will build up to this value. If the cover is removed so that this pressure cannot be maintained, the system will cease to be at equilibrium and the water will evaporate.</p>	$K_p = 1.00 \text{ atm}$ <p>This temperature corresponds of course to the boiling point of water. The <i>normal boiling point</i> of a liquid is the temperature at which the partial pressure of its vapor is 1 atm.</p>	$K_p = \frac{1489 \text{ torr}}{760 \text{ torr/atm}} = 1.96 \text{ atm}$ <p>The only way to heat water above its normal boiling point is to do so in a closed container that can withstand the increased vapor pressure. Thus a pressure cooker that operates at 120°C must be designed to withstand an internal pressure of at least 2 atm.</p>

18 • Significance of the numerical value of an equilibrium constant

Your ability to interpret the numerical value of a quantity in terms of what it means in a practical sense is an essential part of developing a working understanding of Chemistry. This is particularly the case for equilibrium constants, whose values span the entire range of the positive numbers. Although there is no explicit rule, for most practical purposes you can say that equilibrium constants within the range of roughly 0.01 to 100 indicate that a chemically significant amount of all components of the reaction system will be present in an equilibrium mixture and that the reaction will be incomplete or “reversible”. As an equilibrium constant approaches the limits of zero or infinity, the reaction can be increasingly characterized as a one-way process; we say it is “complete” or “irreversible”. The latter term must of course not be taken literally; the LeChâtelier principle still applies (especially insofar as temperature is concerned), but addition or removal of reactants or products will have less effect. Although it is by no means a general rule, it frequently happens that reactions having very large or very small equilibrium constants are kinetically hindered, often to the extent that the reaction essentially does not take place.

reaction	eq. constant	remarks
$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}(\text{g})$	5×10^{-31} at 25°C 0.0013 at 2100°C	These two very different values of K illustrate very nicely why reducing combustion-chamber temperatures is environmentally friendly.
$3 \text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$	7×10^5 at 25°C, 56 at 1300°C	See the discussion of this reaction in the section on the Haber process.
$\text{H}_2(\text{g}) \rightleftharpoons 2 \text{H}(\text{g})$	10^{-36} at 25°C 6×10^{-5} at 5000°C	Dissociation of any stable molecule into its atoms is endothermic. This means that <i>all</i> molecule will decompose at sufficiently high temperatures.
$\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g})$	8×10^{-41} at 25°C	You won't find water a very good source of oxygen gas at ordinary temperatures!
$\text{CH}_3\text{COOH}(\text{l}) \rightleftharpoons 2 \text{H}_2\text{O}(\text{l}) + 2 \text{C}(\text{s})$	$K_c = 10^{13}$ at 25°C	This tells us that acetic acid should decompose to carbon, but nobody has ever found graphite (or diamonds) forming in a bottle of vinegar. A good example of a kinetically super-hindered reaction!

19 • Do equilibrium constants have units?

The equilibrium expression for the synthesis of ammonia $3 \text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$ is

$$K_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3}$$

so K_p and Q_p for this process would appear to have units of atm^{-1} , and K_c and Q_c would be expressed in $\text{mol}^{-2} \text{L}^2$. And yet these quantities are often represented as being dimensionless. Which is correct? The answer is that both forms are acceptable. There are some situations (which you will encounter later) in which K 's *must* be considered dimensionless, but in simply quoting the value of an equilibrium constant it is permissible to include the units, and this may even be useful in order to remove any doubt about the units of the individual terms that make up the equilibrium expression. In carrying out your own calculations, however, there is rarely any real need to show the units.

Strictly speaking, equilibrium expressions do not have units because the concentration or pressure terms that go into them are really *ratios* having the forms $(n \text{ mol L}^{-1})/(1 \text{ mol L}^{-1})$ or $(n \text{ atm})/(1 \text{ atm})$ in which the unit quantity in the denominator refers to the *standard state* of the substance; thus the units always cancel out. For substances that are liquids or solids, the standard state is just the concentration of the substance within the liquid or solid, so for something like $\text{CaF}_2(\text{s})$, the term going into the equilibrium expression is $[\text{CaF}_2]/[\text{CaF}_2]$ which cancels to unity; this is the reason we don't need to include terms for solid or liquid phases in equilibrium expressions. The subject of standard states would take us somewhat beyond where we need to be at this point in the course, so we will simply say that the concept is made necessary by the fact that energy, which ultimately governs chemical change, is always relative to some arbitrarily defined zero value which, for chemical substances, is the standard state.

20 • Equilibrium expressions and the reaction equation

It is important to remember that an equilibrium quotient or constant is always tied to a specific chemical equation, and if we write the equation in reverse or multiply its coefficients by a common factor, the value of Q or K will be different.

The rules are very simple:

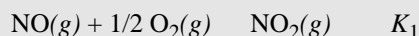
- Writing the equation in reverse will invert the equilibrium expression;
- Multiplying the coefficients by a common factor will raise Q or K to the corresponding power.

Here are some of the possibilities for the reaction involving the equilibrium between gaseous water and its elements:

$2 \text{H}_2 + \text{O}_2 \rightleftharpoons 2 \text{H}_2\text{O}(g)$	$10 \text{H}_2 + 5 \text{O}_2 \rightleftharpoons 5 \text{H}_2\text{O}(g)$	$\text{H}_2 + 1/2 \text{O}_2 \rightleftharpoons \text{H}_2\text{O}(g)$	$\text{H}_2\text{O}(g) \rightleftharpoons \text{H}_2 + 1/2 \text{O}_2$
$K_p = \frac{P_{\text{H}_2\text{O}}^2}{P_{\text{H}_2}^2 P_{\text{O}_2}}$	$K_p = \frac{P_{\text{H}_2\text{O}}^5}{P_{\text{H}_2}^{10} P_{\text{O}_2}}$	$K_p = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2} P_{\text{O}_2}^{0.5}}$	$K_p = \frac{P_{\text{H}_2} P_{\text{O}_2}^{0.5}}{P_{\text{H}_2\text{O}}}$



Show the relationship between the equilibrium constants for the following two reactions:



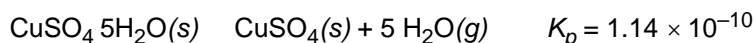
Solution: reaction (2) is the reverse of (1), multiplied by two, so $K_1 = 1/K_2^2$.

21 • Heterogeneous reactions: the vapor pressure of solid hydrates

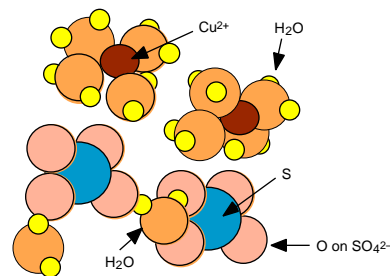
Many common inorganic salts form solids which incorporate water molecules into their crystal structures. These water molecules are usually held rather loosely and can escape as water vapor. Copper(II) sulfate, for example forms a pentahydrate in which four of the water molecules are coordinated to the Cu^{2+} ion while the fifth is hydrogen-bonded to SO_4^{2-} . This latter water is more tightly bound, so that the pentahydrate loses water in two stages on heating:



These dehydration steps are carried out at the temperatures indicated above, but at any temperature, some moisture can escape from a hydrate. For the complete dehydration of the pentahydrate we can define an equilibrium constant



The vapor pressure of the hydrate (for this reaction) is the partial pressure of water vapor at which the two solids can coexist indefinitely; its value is $K_p^{1/5}$ atm. If a hydrate is exposed to air in which the partial pressure of water vapor is less than its vapor pressure, the reaction will proceed to the right and the hydrate will lose moisture. Vapor pressures always increase



with temperature, so any of these compounds can be dehydrated by heating.

Loss of water usually causes a breakdown in the structure of the crystal; this is commonly seen with sodium sulfate, whose vapor pressure is sufficiently large that it can exceed the partial pressure of water vapor in the air when the relative humidity is low. What one sees is that the well-formed crystals of the decahydrate undergo deterioration into a powdery form, a phenomenon known as *efflorescence*. When a solid is able to take up moisture from the air, it is described as *hygroscopic*. A small number of anhydrous solids that have low vapor pressures not only take up atmospheric moisture on even the driest of days, but will become wet as water molecules are adsorbed onto their surfaces; this is most commonly observed with sodium hydroxide and calcium chloride. With these solids, the concentrated solution that results continues to draw in water from the air so that the entire crystal eventually dissolves into a puddle of its own making; solids exhibiting this behavior are said to be *deliquescent*.

name	formula	vapor pressure, torr	
		25°C	30°C
sodium sulfate decahydrate	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	19.2	25.3
copper sulfate pentahydrate	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	7.8	12.5
calcium chloride monohydrate	$\text{CaCl}_2 \cdot \text{H}_2\text{O}$	3.1	5.1
(water)	H_2O	23.5	31.6



At what relative humidity will copper sulfate pentahydrate lose its waters of hydration when the air temperature is 30°C? What is K_p for this process at this temperature?

Solution: From the table, we see that the vapor pressure of the hydrate is 12.5 torr, which corresponds to a relative humidity (you remember what this is, don't you?) of $12.5/31.6 = 0.40$ or 40%. This is the humidity that will be maintained if the hydrate is placed in a closed container of dry air.

For this hydrate, $K_p = P_{(\text{H}_2\text{O})}^5$, so the partial pressure of water vapor that will be in equilibrium with the hydrate and the dehydrated solid (remember that *both* solids must be present to have equilibrium!), expressed in atmospheres, will be $(12.5/760)^5 = 1.20 \times 10^{-9}$.

One of the first hydrates to be investigated in detail was calcium sulfate hemihydrate ($\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$) which LeChâtelier (he of the "principle") showed to be what forms when the form of CaSO_4 known as *plaster of Paris* hardens; the elongated crystals of the hydrate bind themselves into a cement-like mass.

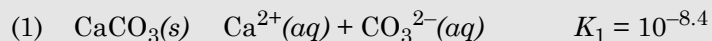
22 • How can we find the equilibrium constant for a series of reactions?

Many chemical changes can be regarded as the sum or difference of two or more other reactions. If we know the equilibrium constants of the individual processes, we can easily calculate that for the overall reaction according to this rule:

The equilibrium constant for the sum of two or more reactions is the product of the equilibrium constants for each of the steps.

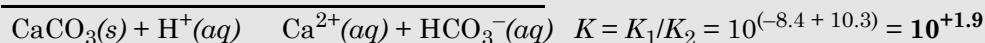
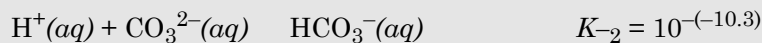
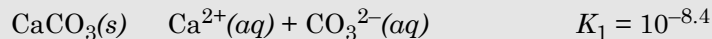


Given the following equilibrium constants:



Calculate the value of K for the reaction $\text{CaCO}_3(s) + \text{H}^+(aq) = \text{Ca}^{2+}(aq) + \text{HCO}_3^-(aq)$

Solution: The net reaction is the sum of reaction 1 and the reverse of reaction 2:



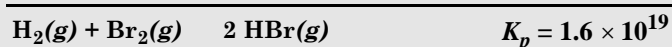
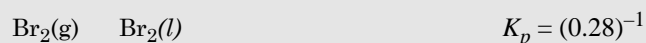
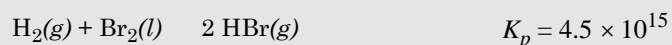
Comment: This net reaction describes the dissolution of limestone by acid; it is responsible for the eroding effect of acid rain on buildings and statues. This is an example of a reaction that has practically no tendency to take place by itself (the dissolution of calcium carbonate) begin “driven” by a second reaction having a large equilibrium constant. From the standpoint of the LeChâtelier principle, the first reaction is “pulled to the right” by the removal of carbonate by the hydrogen ion. “Coupled” reactions of this type are widely encountered in all areas of chemistry, and especially in biochemistry, in which a dozen or so reactions may be linked in this way.

The individual reactions do not need to actually take place in the overall process; very frequently we use their equilibrium constants in order to calculate the equilibrium constant of another reaction.



The synthesis of HBr from hydrogen and liquid bromine has an equilibrium constant $K_p = 4.5 \times 10^{15}$ at 25°C. Given that the vapor pressure of liquid bromine is 0.28 atm, find K_p for the homogeneous gas-phase reaction at the same temperature.

Solution: The net reaction we seek is the sum of the heterogeneous synthesis and the reverse of the vaporization of liquid bromine:



23 • Measuring and calculating equilibrium constants

Clearly, if the concentrations or pressures of all the components of a reaction are known, then the value of K can be found by simple substitution. Observing individual concentrations or partial pressures directly may not always be practical, however. If one of the components is colored, the extent to which it absorbs light of an appropriate wavelength may serve as an index of its concentration. Pressure measurements are ordinarily able to measure only the total pressure of a gaseous mixture, so if two or more gaseous products are present in the equilibrium mixture, the partial pressure of one may need to be inferred from that of the other, taking into account the stoichiometry of the reaction.



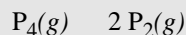
In an experiment carried out by Taylor and Krist (J. Am. Chem. Soc. 1941: 1377), hydrogen iodide was found to be 22.3% dissociated at 730.8°K. Calculate K_c for $2 \text{ HI}(g) = \text{H}_2(g) + \text{I}_2(g)$.

No explicit molar concentrations are given, but we do know that for every n moles of HI, 0.223 n moles of each product is formed and $(1-0.223)n = 0.777n$ moles of HI remains. For simplicity, we assume that $n=1$ and that the reaction is carried out in a 1.00-L vessel, so that we can substitute the required concentration terms directly into the equilibrium expression.

$$K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = \frac{(0.223)^2}{(0.777)^2} = 0.12$$



Ordinary white phosphorus, P_4 , forms a vapor which dissociates into diatomic molecules at high temperatures:



A sample of white phosphorus, when heated to 1000°C , formed a vapor having a total pressure of 0.20 atm and a density of 0.152 gL^{-1} . Use this information to evaluate the equilibrium constant K_p for this reaction.

Solution: Before worrying about what the density of the gas mixture has to do with K_p , start out in the usual way by laying out the information required to express K_p in terms of an unknown x .

	P4	2 P2	
initial moles:	1	0	Since K is independent of the number of moles, assume the simplest case.
moles at equilibrium:	$1-x$	$2x$	x is the fraction of P_4 that dissociates.
eq. mole fractions:	$\frac{1-x}{1+x}$	$\frac{2x}{1+x}$	The denominator is the total number of moles: $1-x+2x = 1+x$
eq. partial pressures:	$\frac{1-x}{1+x} \times 2 \text{ atm}$	$\frac{2x}{1+x} \times 2 \text{ atm}$	Partial pressure is the mole fraction times the total pressure.

Expressing the equilibrium constant in terms of x gives

$$K_p = \frac{\frac{1-x}{1+x}}{\frac{2x}{1-x}} = \frac{(1-x)^2}{2x}$$

Now we need to find the dissociation fraction x of P_4 , and at this point we hope you remember those gas laws that you were told you would be needing later in the course! The density of a gas is directly proportional to its molecular weight, so you need to calculate the densities of pure P_4 and pure P_2 vapors under the conditions of the experiment. One of these densities will be greater than 0.152 gL^{-1} and the other will be smaller; all you need to do is to find where the measured density falls in between the two limits, and you will have the dissociation fraction.

The atomic weight of phosphorus is 31.97, giving a molar mass of 127.9 g for P_4 . This mass must be divided by the volume to find the density; assuming ideal gas behavior, the volume of 127.9 g (1 mole) of P_4 is given by RT/P , which works out to 522 L (remember to use the absolute temperature here.) The density of pure P_4 vapor under the conditions of the experiment is then $d = m/v = (128 \text{ g mol}^{-1}) \div (522 \text{ L mol}^{-1}) = 0.245 \text{ g L}^{-1}$. The density of pure P_2 would be half this, or 0.122 g L^{-1} . The difference between these two limiting densities is 0.123 g L^{-1} , and the difference between the density of pure P_4 and that of the equilibrium mixture is $(.245 - .152) \text{ g L}^{-1}$ or 0.093 g L^{-1} . The ratio $0.093 \div 0.123 = 0.76$ is therefore the fraction of P_4 that remains and its fractional dissociation is $x = (1 - 0.76) = 0.24$. Substituting this into the expression above yields $K_p = 1.2$.

24 • How can we predict equilibrium compositions?

This is by far the most common kind of equilibrium problem you will encounter: starting with an arbitrary number of moles of each component, how many moles of each will be

present when the system comes to equilibrium? The principal source of confusion and error for beginners at this relates to the need to determine the values of several unknowns (a concentration or pressure for each component) from a single equation, the equilibrium expression. The key to this is to make use of the stoichiometric relationships between the various components, which usually allow us to express the equilibrium composition in terms of a single variable. The easiest and most error-free way of doing this is adopt a systematic approach in which you create and fill in a small table as shown in the following problem example. You then substitute the equilibrium values into the equilibrium constant expression, and solve it for the unknown. This very often involves solving a quadratic or higher-order equation. Quadratics can of course be solved by using the familiar quadratic formula, but it is often easier to use an algebraic or graphical approximation, and for higher-order equations this is the only practical approach. There is almost never any need to get an exact answer, since the equilibrium constants you start with are rarely known all that precisely.



Phosgene is a poisonous gas that dissociates at high temperature into two other poisonous gases, carbon monoxide and chlorine. The equilibrium constant $K_p = 0.0041$ at 600°K . Find the equilibrium composition of the system after 0.124 atm of COCl_2 is allowed to reach equilibrium at this temperature.

	$\text{COCl}_2(g)$	$\text{CO}(g)$	$\text{Cl}_2(g)$
initial pressures	0.124 atm	0	0
change	$-x$	$+x$	$+x$
equilibrium pressures	$0.124 - x$	x	x

Substitution of the equilibrium pressures into the equilibrium expression gives

$$\frac{x^2}{0.124 - x} = 0.0041$$

This expression can be rearranged into standard polynomial form $x^2 + 0.0041x - 0.00054 = 0$ and solved by the quadratic formula, but we will simply obtain an approximate solution by iteration. Because the equilibrium constant is small, we know that x will be rather small compared to 0.124 , so the above relation can be approximated by

$$\frac{x^2}{0.124} = 0.0041$$

which gives $x = 0.0225$. To see how good this is, substitute this value of x into the denominator of the original equation and solve again:

$$\frac{x^2}{0.124 - 0.0225} = \frac{x^2}{0.102} = 0.0041$$

This time, solving for x gives 0.0204 . Iterating once more, we get

$$\frac{x^2}{0.124 - 0.0204} = \frac{x^2}{0.104} = 0.0041$$

and $x = 0.0206$ which is sufficiently close to the previous to be considered the final result. The final partial pressures are then 0.104 atm for COCl_2 , and 0.0206 atm each for CO and Cl_2 . Note: using the quadratic formula to find the exact solution yields the two roots -0.0247 (which we ignore) and 0.0206 , which show that our approximation is quite good. Note: using the quadratic formula to find the exact solution yields the two roots -0.0247 (which we ignore) and 0.0206 , which show that our approximation is quite good.



The gas-phase dissociation of phosphorus pentachloride to the trichloride has $K_p = 3.60$ at 540°C :



What will be the partial pressures of all three components if 0.200 mole of PCl_5 and 3.00 moles of PCl_3 are combined and brought to equilibrium at this temperature and at a total pressure of 1.00 atm?

	$\text{PCl}_5(g)$	$\text{PCl}_3(g)$	$\text{Cl}_2(g)$
initial moles	0.200	3.00	0
change	$-x$	$+x$	$+x$
equilibrium moles	$0.200 - x$	$3.00 + x$	x
eq. partial pressures	$\frac{0.200 - x}{3.20 + x}(1.00 \text{ atm})$	$\frac{3.00 + x}{3.20 + x}(1.00 \text{ atm})$	$\frac{x}{3.20 + x}(1.00 \text{ atm})$

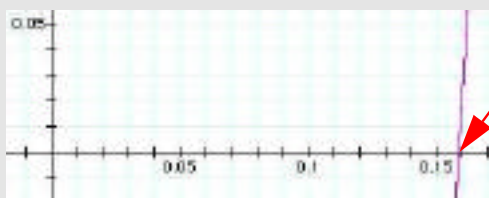
The partial pressures in the bottom row were found by multiplying the mole fraction of each gas by the total pressure: $P_i = X_i P_t$. The term in the denominator of each mole fraction is the total number of moles of gas present at equilibrium: $(0.200 - x) + (3.00 + x) + x = 3.20 + x$.

Substituting the equilibrium partial pressures into the equilibrium expression, we have

$$\frac{(3.00 + x)(x)}{(0.200 - x)(3.20 + x)} = 3.60$$

whose polynomial form is $4.60x^2 + 13.80x - 2.304 = 0$.

Plotting this (on the Macintosh Graphical Calculator) yields $x = 0.159$ as the positive root:



Substitution of this root into the expressions for the equilibrium partial pressures in the table yields the following values: $P(\text{PCl}_5) = 0.012 \text{ atm}$, $P(\text{PCl}_3) = 0.94 \text{ atm}$, $P(\text{Cl}_2) = 0.047 \text{ atm}$.

25 • Effects of dilution on an equilibrium

In the section that introduced the LeChâtelier principle, it was mentioned that diluting a weak acid such as acetic acid CH_3COOH ("HAc") will shift the dissociation equilibrium to the right:



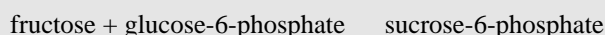
Thus a $0.10M$ solution of acetic acid is 1.3% ionized, while in a $0.01M$ solution, 4.3% of the HAc molecules will be dissociated. This comes about because as the solution becomes more dilute, the product $[\text{H}_3\text{O}^+][\text{Ac}^-]$ decreases more rapidly than does the $[\text{HAc}]$ term. At the

same time the concentration of H_2O becomes greater, but because it is so large to start with (about 55.5M), any effect this might have is negligible, which is why no $[\text{H}_2\text{O}]$ term appears in the equilibrium expression.

For a reaction such as $\text{CH}_3\text{COOH}(l) + \text{C}_2\text{H}_5\text{OH}(l) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(l) + \text{H}_2\text{O}(l)$ (in which the water concentration does change), dilution will have no effect on the equilibrium; the situation is analogous to the way the pressure dependence of a gas-phase reaction depends on the number of moles of gaseous components on either side of the equation.



The biochemical formation of a disaccharide sugar from two monosaccharides is exemplified by the reaction



(Sucrose is ordinary table sugar.) To what volume should a solution containing 0.050 mol of each monosaccharide be diluted in order to bring about 5% conversion to sucrose phosphate?

Solution: The initial and final numbers of moles are as follows:

	fructose	glucose-6-P	sucrose-6-P
initial moles	0.05	0.05	0
final moles	0.0485	0.0485	0.0015

Substituting into the expression for K_c in which the solution volume is the unknown, we have

$$\frac{[\text{suc6P}]}{[\text{Fruc}][\text{gluc6P}]} = \frac{\frac{.0485}{V}}{\frac{.0485}{V}^2} = 0.05$$

Solving for V gives a final solution volume of 78 mL.

26 • Phase distribution equilibria

It often happens that two immiscible liquid phases are in contact, one of which contains a solute. How will the solute tend to distribute itself between the two phases? One's first thought might be that some of the solute will migrate from one phase into the other until it is distributed equally between the two phases, since this would correspond to the maximum dispersion (randomness) of the solute. This, however, does not take into account the differing solubilities the solute might have in the two liquids; if such a difference does exist, the solute will preferentially migrate into the phase in which it is more soluble. For a solute S distributed between two phases and the process $S = S$ is defined by the distribution law

$$K_d = \frac{[S]}{[S]}$$

in which K_d is the *distribution ratio* (also called the distribution coefficient.)

The transport of substances between different phases is of immense importance in such diverse fields as pharmacology and environmental science. For example, if a drug is to pass from the aqueous phase with the stomach into the bloodstream, it must pass through the lipid (oil-like) phase of the epithelial cells that line the digestive tract. Similarly, a pollutant such as a pesticide residue that is more soluble in oil than in water will be preferentially taken up and retained by marine organism, especially fish, whose bodies contain more oil-

like substances; this is basically the mechanism whereby such residues as DDT can undergo *biomagnification* as they become more concentrated at higher levels within the food chain. For this reason, environmental regulations now require that oil-water distribution ratios be established for any new chemical likely to find its way into natural waters. The standard “oil” phase that is almost universally used is octanol, $C_8H_{17}OH$.

In preparative chemistry it is frequently necessary to recover a desired product present in a reaction mixture by extracting it into another liquid in which it is more soluble than the unwanted substances. On the laboratory scale this operation is carried out in a separatory funnel in which the two phases are brought into intimate contact by shaking. After the two liquids have separated into layers, the bottom layer is drawn off. If the distribution ratio is too low to achieve efficient separation in a single step, it can be repeated; there are automated devices that can carry out hundreds of successive extractions, each yielding a product of higher purity. In these applications our goal is to exploit the LeChâtelier principle by repeatedly upsetting the phase distribution equilibrium that would result if two phases were to remain in permanent contact.



The distribution ratio for iodine between carbon disulfide and water is 650. Calculate the concentration of I_2 remaining in the aqueous phase if after 5.0 mL of 0.10M I_2 in water is shaken with 1.0 mL of CS_2 .

Solution: The equilibrium constant is

$$K_d = \frac{C_{CS_2}}{C_{H_2O}} = 650$$

and conservation of mass requires that

$$0.1M \times 5 \text{ ml} = (C_{CS_2} \times 1 \text{ mL}) + (C_{H_2O} \times 5 \text{ mL})$$

The concentration of the iodine in the CS_2 phase works out to 0.5M, while that in the water phase is 0.0008M indicating that this is an efficient process.