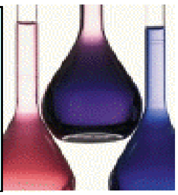
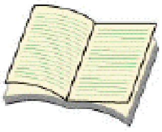
all about
Chemical equilibrium
how to understand reactions
that can go in either direction





Chem 1
Virtual Textbook
reference text

Q and K: what's the difference?

home | Introduction | Le Châtelier | about Q and K | Expressions | Calculations

Contents of this page

What is the equilibrium quotient?

In the previous section we defined the ***equilibrium expression*** for the reaction

$$aA + bB \rightarrow cC + dD \quad \text{as} \quad \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

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

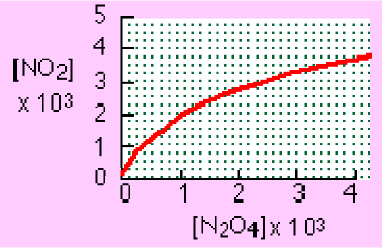
The value of Q in relation to K serves as an index how the composition of the reaction system compares to that of the equilibrium state, and thus it indicates the direction in which any net reaction must proceed. For example, if we combine the two reactants A and B at concentrations of 1 mol L^{-1} each, the value of Q will be 0÷1=0. If instead our mixture consists only of the two products C and D, Q will be indeterminately large (1÷0). It is easy to see (by simple application of the Le Châtelier 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. The three possibilities are shown in the table below.

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

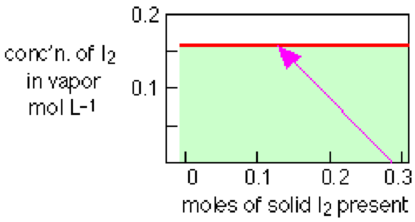
It is very important that you be able to work out these relations for yourself, not by memorizing them, but from the definitions of *Q* and *K*.

A visual way of thinking about Q and K

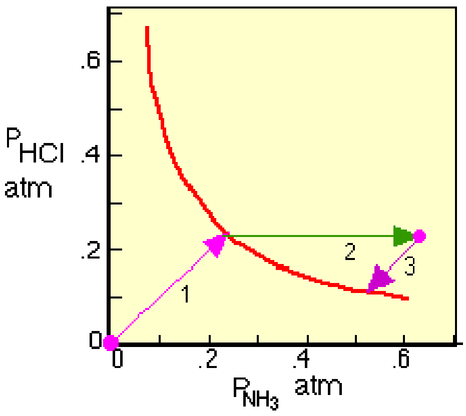
The formal definitions of *Q* and *K* are quite simple, but they are of limited usefulness unless you are able to relate them to real chemical situations. The following diagrams illustrate the relation between *Q* and *K* from various standpoints. Take some time to study each one carefully, making sure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



Each tiny dot on the graph represents a possible combination of NO_2 and N_2O_4 concentrations that produce a certain value of *Q* for the chemical reaction system $N_2O_4 \rightarrow 2\ NO_2$. (There are of course an infinite number of possible *Q*'s 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 $[NO_2] = ([N_2O_4]K)^{0.5}$. 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 $I_2(s) \rightarrow I_2\ (g)$ 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 (red line) 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.



The decomposition of ammonium chloride

$NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$ 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 Le Châtelier 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.

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

$A \rightarrow B$	forward reaction	$rate_f = k_f\,[A]$
$B \rightarrow A$	reverse reaction	$rate_r = k_r\,[B]$

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, which must be done through the laws of thermodynamics.

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 Le Châtelier Principle as it applies to concentrations of reaction components follows directly 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 in the presence of a suitable ***catalyst***.

Summary

Make sure you thoroughly understand the following essential ideas which have been presented above. It is especially imortant that you know the precise meanings of all the highlighted terms in the context of this topic.

- When arbitrary quantities of the different ***components*** of a ***chemical reaction system*** are combined, the overall system composition will not likely correspond to the equilibrium composition. As a result, a net change in composition ("a shift to the right or left") will tend to take place until the ***equilibrium state*** is attained.
- The equilibrium state is characterised by the value of the ***equilibrium expression***, whose formulation is defined by the coefficients in the balanced reaction equation; it may be expressed in terms of concentrations, or in the case of gaseous components, as partial pressures.
- The various terms in the equilibrium expression can have any arbitrary value (including zero); the value of the equilibrium expression itself is called the equilibrium quotient ***Q.***
- If the concentration or pressure terms in the equilibrium expression correspond to the equilibrium state of the system, then ***Q*** has the special value ***K***, which we call the ***equilibrium constant***.
- The ratio of Q/K thus serves as an index of how far the system is from its equilibrium composition, and its sign indicates the direction in which the net reaction must proceed in order to reach its equilibrium state.

- When this ratio is unity (Q = K), then the equilibrium state has been reached, and no further net change will take place as long as the system remains undisturbed.

top of page Next

home | Introduction | Le Châtelier | about Q and K | Expressions | Calculations

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