# chemical principles revisited

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Chemical Equilibrium

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Many chemical reactions do not proceed to completion; instead, they establish a dynamic equilibrium in which *two opposing reactions occur at the same rate.*[1] For example, mixing solutions containing cerium(IV) and iodide ions gives rise to the reaction

$$2Ce^{4+}_{(aq)} + 3I^-_{(aq)} \rightleftharpoons 2Ce^{3+}_{(aq)} + I^-_{3(aq)}$$
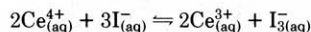
On the other hand, when cerium(III) is added to a solution of triiodide ion, significant quantities of cerium(IV) and iodide ions are produced. The extent of either reaction is easily gauged by the intensity of the orange-red color of the triiodide ion. The concentration of this colored ion rapidly reaches a constant level that is independent of the route by which it is formed. It makes no difference whether Ce^{4+} and I^- or Ce^{3+} and I^-_3 are selected as the original reactants; the same condition of equilibrium will result. In the beginning, if Ce^{4+} and I^- are the original reactants, the concentrations of Ce^{4+} and I^- will be high, and consequently the forward reaction will proceed rapidly. No reverse reaction is possible at the start, since Ce^{3+} and I^-_3 are not yet present. As Ce^{3+} and I^-_3 are formed, the reverse reaction will begin slowly and gradually increase in rate as Ce^{3+} and I^-_3 accumulate. Meanwhile the forward reaction is slowing down as Ce^{4+} and I^- are being used up, as shown in Figure 1.

Conditions of chemical equilibrium that most chemical reactions can attain may be compared to a person running on a treadmill, which moves faster as the runner increases his speed. When the runner and the treadmill are in equilibrium, the runner is apparently stationary to an observer. If the runner increases his speed, he advances a short distance. However, as the treadmill also moves faster, the runner again appears to be stationary; although, his position is in advance of his previous stationary position.

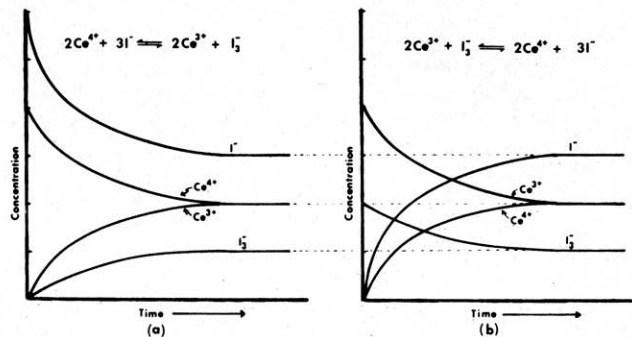In a reversible reaction, such as

$$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$$
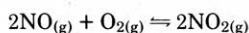
the equilibrium amounts of NO, O_2, and NO_2 remain constant; yet like the runner and the treadmill, the reactions proceed in opposite directions at the same rate.

The Law of Mass Action

In 1864, the Norwegian chemists Cato M. Guldberg and Peter Waage proposed that the rate of a chemical reaction is proportional to the *active masses* of the reacting substances; the molecular concentration of a substance in solution or in the gas phase is used as a measure of its *active mass.*[2] The significance of this statement, which is called the *Law of Mass Action* (the rate law in kinetics) is more apparent as the quantitative notions of chemical equilibrium are developed. For example, consider the general reversible reaction in which an equilibrium exists between four substances A, B, D, and E

$$A + B \rightleftharpoons D + E$$

Two reactions are proceeding, one to the right (called the forward reaction), in which A and B react to form D and E and

[1] Mickey, C. D., J. CHEM. EDUC., **57**, 659 (1980)
[2] Glasstone, S., "Textbook of Physical Chemistry," D. Van Nostrand Company, Inc., New York, **1946**, p. 817.

The variation in concentration of reactants and products as a function of time. (a) Initially, stoichiometric amounts of Ce^{4+} and I^- are mixed and allowed to reach equilibrium. (b) Stoichiometric amounts of Ce^{3+} and I^-_3 are allowed to react at the same temperature. In both instances, the final equilibrium concentrations of all species are the same.

the other to the left (called the reverse reaction), in which D and E react to form A and B. According to the Law of Mass Action, *the rate of the forward reaction is proportional to the concentrations of the reactants A and B, while the rate of the reverse reaction is proportional to the concentration of D and E.* Thus, the forward reaction has the rate

$$Rate_f = k_f[A][B]$$

and the reverse reaction has the rate

$$Rate_r = k_r[D][E]$$

where brackets, [ ], represent the molar concentrations of the enclosed substances, and k_f and k_r are proportionality constants called *specific rate constants.*

Guldberg and Waage assumed that equilibrium results when the rates of the forward and reverse reactions are equal, *i.e.,*

$$Rate_f = Rate_r$$

Therefore, at equilibrium,

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

Writing this equation in a more useful form gives

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

Inasmuch as k_f and k_r are both constants, their ratio k_f/k_r is also a constant, hence

$$\frac{k_f}{k_r} = K_{eq} = \frac{[D]}{[A]}\frac{[E]}{[B]}$$

in which K_{eq} is called the *equilibrium constant.* Although the kinetic arguments used for the derivation of this equilibrium constant are not applicable to complex multistep reactions, they are valid for simple one-step bimolecular reactions.

> This feature is aimed as a review of basic chemical principles and as a reappraisal of the state of the art. Comments, suggestions for topics, and contributions should be sent to the feature editor.

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The Equilibrium Constant and Ideal Behavior

The expression

$$k_{eq} = \frac{[D][E]}{[A][B]}$$

is only rigorously valid in situations where all reactants and products behave like ideal gases or are components of an ideal solution. For example, just as conductivity in concentrated solutions of strong electrolytes fails to indicate complete ionization, because of the interference of ions with the motions of other ions, the presence of high concentrations of ions interferes with the reactions of any ion. If the rates of reactions in concentrated solutions of strong electrolytes are calculated and compared with the measured rates of these same reactions, there are discrepancies which increase with the increase in concentration. Moreover, these discrepancies will be reflected in the equilibrium constant. If the *activity* of the reacting particle is substitued for its concentration or partial pressure a correct rate of reaction is found and the equilibrium constant will be rigorously valid. The correction factor used as a multiplier of the actual pressure or concentration to produce the *activity* is called the *activity coefficient* (γ). The experimentally determined value of the *activity coefficient* varies, not only from one substance to another, but also with pressure, concentration, and temperature. The magnitude of the *activity coefficient* is always less than one and approaches unity as the partial pressure or concentration decreases. The *activity* (a) of a reaction component is its molar concentration or partial pressure times an *activity coefficient* (γ), or $a = \gamma M$ for solutions and $a = \gamma P$ for gases. The *activity* of a pure liquid or a pure solid, at constant temperature, is defined as unity.

One of the great theoretical outcomes of chemical thermodynamics was the rigorous derivation of equilibrium constants using *activities*, rather than molarities or partial pressures. Although it is not possible within the scope of this article, it can be shown that the thermodynamic analog of the preceding equilibrium-constant expression is

$$K_{eq} = \frac{a_D a_E}{a_A a_B}$$

Frequently, as in this discussion, equilibrium constants are based on molarities or partial pressures instead of the more exact *activities*, for three reasons: (1) the measurement of reagents are usually made in grams and put into solutions in terms of grams or moles per liter; (2) the activity coefficient of any ion changes not only with its own concentration, but with that of other ions in the solution; (3) all substances for which equilibria are calculated are either in dilute solutions of their kinds of ions and molecules or are weak electrolytes, so the approximations secured by the use of molarities or partial pressures instead of activities are sufficiently accurate.

General Form of the Equilibrium Constant

Fortunately, it is not necessary to know the mechanism or rate laws for a reversible reaction to be able to write the equilibrium-constant expression. Even if a reversible reaction proceeds through a series of complicated steps, each individual step is reversible and, at equilibrium, the reversible reactions proceed at the same rate in both directions. Thus, the equilibrium-constant expression can be derived from the balanced equation for the overall reaction. Consider the reaction

$$CO_{2(aq)} + 3H_2O_{(l)} \rightleftharpoons 2H_3O^+_{(aq)} + CO^{2-}_{3(aq)}$$
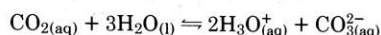
If the forward reaction is a single-step termolecular reaction, its rate will be expressed as:

$$Rate_f = k_f[CO_2][H_2O]^3$$

Likewise, if the reverse reaction is a single-step trimolecular reaction, its rate will be given by the equation:

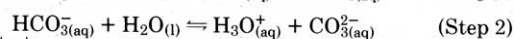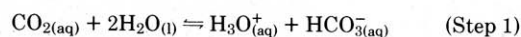$$Rate_r = k_r[H_3O^+]^2[CO^{2-}_3]$$

and at equilibrium,

$$R_f = R_r$$

therefore,

$$k_f[CO_2][H_2O]^3 = k_r[H_3O^+]^2[CO^{2-}_3]$$

hence

$$\frac{k_f}{k_r} = K_{eq} = \frac{[H_3O^+]^2[CO^{2-}_3]}{[CO_2][H_2O]^3}$$

Alternately, assume that the reaction proceeds by the following two-step mechanism:

$$CO_{2(aq)} + 2H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HCO^-_{3(aq)} \quad \text{(Step 1)}$$

$$HCO^-_{3(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CO^{2-}_{3(aq)} \quad \text{(Step 2)}$$

For the first step

$$R_f = k_f[CO_2][H_2O]^2$$

$$R_r = k_r[H_3O^+][HCO_3^-]$$

At equilibrium, $R_f = R_r$, and since the ratio of two constants is a third constant

$$\frac{k_f}{k_r} = K_1 = \frac{[H_3O^+][HCO_3^-]}{[CO_2][H_2O]^2}$$

Similarly, for the second step:

$$R'_f = k'_f[HCO_3^-][H_2O]$$

$$R'_r = k'_r[H_3O^+][CO^{2-}_3]$$

At equilibrium, $R_f' = R_r'$ and

$$\frac{k'_f}{k'_r} = K_2 = \frac{[H_3O^+][CO^{2-}_3]}{[HCO_3^-][H_2O]}$$

The product of two constants is a third constant; therefore, the product

$$K_1 \times K_2 = K_{eq} = \frac{[H_3O^+][HCO_3^-]}{[CO_2][H_2O]^2}$$
$$\times \frac{[H_3O^+][CO^{2-}_3]}{[HCO_3^-][H_2O]} = \frac{[H_3O^+]^2[CO^{2-}_3]}{[CO_2][H_2O]^3}$$

Consequently, the equilibrium-constant expression turns out to be the same; whether based on kinetic arguments or the balanced equation. Thus, for the general reaction:

$$rA + sB \rightleftharpoons xD + zE$$
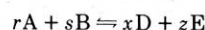
in which r, s, x, and z represent the coefficients of A, B, D, and E, respectively, in the balanced equation, the formulation of K_{eq} is

$$K_{eq} = \frac{[D]^x[E]^z}{[A]^r[B]^s}$$

There are several different but interrelated types of equilibrium constants, with the symbol K_{eq} generally used to represent any of the various kinds. However, special designations for equilibrium constants are frequently used to characterize a particular equilibrium system. The symbol K_p, for example, indicates a particular equilibrium constant in which the quantities of gaseous reactants and products are expressed in terms of their partial pressures. Concentrations can be related to partial pressures through the *ideal gas law* ($PV = nRT$); therefore, the partial pressure for any gaseous reactant or product, that behaves ideally, is proportional to its concentration. Hence, for the gas phase equilibrium:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$
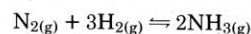
the equilibrium-constant expression is

$$K_p = \frac{P^2_{NH_3}}{P_{N_2}P^3_{H_2}} = 3.52 \times 10^{-7} \qquad \text{at } 1000°K$$

The symbol K_c represents a particular equilibrium constant in which the quantities of reactants and products are expressed in terms of their molarities. The K_c value for the previous reaction is

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = 2.37 \times 10^{-3} \qquad \text{at } 1000°K$$

Two different reactions will generally have different equilibrium constants. At 1000°K the reaction involving carbon monoxide, oxygen, and carbon dioxide

$$2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$$
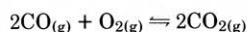
has the equilibrium constant value

$$K_c = \frac{[CO_2]^2}{[CO]^2[O_2]} = 2.24 \times 10^{22} \qquad \text{at } 1000°K$$

The fact that in the latter reaction K_c is greater than K_c in the former reaction means that at 1000°K carbon monoxide and oxygen are more completely converted to carbon dioxide than nitrogen and hydrogen are to ammonia. Thus, the magnitude of the equilibrium constant may be used to gauge the extent to which a given reaction progresses toward completion. If all other factors are equal, a value of $K_{eq} > 1$ indicates a high degree of conversion of reactants to products and a value of $K_{eq} < 1$ indicates a low degree of conversion.

The Forward and Reverse Reactions

Since equations for chemical reactions may be written in a variety of different but equivalent ways, each value for an equilibrium must always be accompanied by the specific equation which it represents. For example, in the reaction

$$Cu^0_{(s)} + 2Ag^+_{(aq)} \rightleftharpoons Cu^{2+}_{(aq)} + 2Ag^0_{(s)}$$
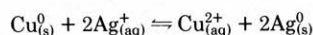
The equilibrium constant is

$$K_c = \frac{[Cu^{2+}]}{[Ag^+]^2} = 2 \times 10^{15} \qquad \text{at } 298°K$$

Suppose the reaction is written as

$$Cu^{2+}_{(aq)} + 2Ag^0_{(s)} \rightleftharpoons Cu^0_{(s)} + 2Ag^+_{(aq)}$$
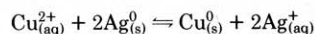
consistency is maintained and ambiguity avoided, if the equilibrium constant is written as

$$K_c = \frac{[Ag^+]^2}{[Cu^{2+}]} = 5 \times 10^{-16} \qquad \text{at } 298°K$$

Quantitatively, for any reversible reaction the value of the equilibrium constant for the reverse reaction is the reciprocal of the equilibrium constant for the forward reaction. In other words,

$$K_{(reverse)} = \frac{1}{K_{(forward)}}$$

As illustrated in the last two equations, it is customary to exclude the concentration terms for solids from the equilibrium expression. The concentrations of the silver and copper solids are constant, hence the respective equilibrium-constant expressions are simplified by combining the constants. Similarly, the concentration of a pure liquid is constant, hence its concentration term is also excluded from the equilibrium-constant expression. For example, consider the reaction

$$NH_4^+{}_{(aq)} + HNO_{2(aq)} \rightleftharpoons N_{2(aq)} + 2H_2O_{(l)} + H^+{}_{(aq)}$$
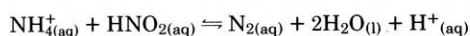
the equilibrium constant is expressed by

$$K_{eq} = \frac{[N_2][H_2O]^2[H^+]}{[NH_4^+][HNO_2]}$$

Combining the two constants in this equation gives

$$\frac{K_{eq}}{[H_2O]^2} = K_c = \frac{[N_2][H^+]}{[NH_4^+][HNO_2]}$$

Factors Influencing Equilibrium

At equilibrium a chemical reaction is proceeding in the forward and reverse directions with equal velocities, thus it is expected that the parameters, such as temperature and concentration, which affect the rate of any reaction will also affect the equilibrium; that is, these same parameters can change the balance between the two opposing reactions. To understand the problem more clearly, again consider the analogy between a chemical system in equilibrium and a person running on a treadmill which increases its speed as the person advances. If the person while running and apparently remaining stationary with respect to some fixed point, increases his speed he advances; but as he does so the speed of treadmill also increases and again the runner comes to an apparent stationary position. For the second time, the runner and the treadmill are in a state of equilibrium, but the runner has now occupied a position farther forward. If, on the other hand, the runner tires he runs slower. Momentarily he shifts his position backward; but since the treadmill is readjusted to a slower rate, the runner will soon assume a new position of equilibrium. During the short interval that the runner advances or falls back, the position of equilibrium is *shifted*.

In a analogous manner, the equilibrium position of a chemical reaction may be shifted; and it is customary to speak of a *shift in equilibrium* to the right or to the left with reference to the chemical equation for the reaction taking place. Thus, in the equilibrium between nitrogen, hydrogen, and ammonia as represented by the equation

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$
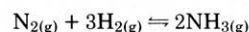
all these substances are present in definite amounts and the reaction is proceeding in both directions. If now, by some influence, the equilibrium is affected so that more ammonia is formed; the equilibrium is *shifted* to the right. During the change from one equilibrium position to another, the reaction proceeds momentarily faster from left to right than from right to left. This situation is analogous to the momentary shift in the position of the runner on the treadmill when he is inspired to run faster.

Le Chatelier's Principle and Chemical Equilibrium

Extensive studies of reversible reactions and the equilibria associated with them led the French chemist, Henri Louis Le Chatelier (1888), to make a simple generalization, commonly referred to as Le Chatelier's Principle:

A system at equilibrium, when subjected to any stress (such as change in temperature, pressure, or concentration of matter) so that equilibrium is disturbed, will tend to adjust itself so as to remove the stress and re-establish equilibrium.

Of the three stresses, only a change in temperature will affect the magnitude of the equilibrium constant. For example,

Reaction	Temp (°K)	K
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$	623	2.66×10^{-2}
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$	723	6.59×10^{-3}
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$	1000	2.37×10^{-3}

The Effect of Temperature on an Equilibrium

All chemical reactions are accompanied by energy changes. Some reactions are exothermic—produce heat during the reaction; others are endothermic—absorb heat from the surroundings. In the reaction

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_3 + 22.08 \text{ kcal}$$
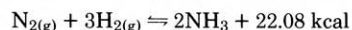
nitrogen and hydrogen, in combining to from ammonia, produce heat. When ammonia decomposes into nitrogen and hydrogen (the reverse reaction), an equivalent amount of heat must be absorbed. When this system is at equilibrium, no heat change occurs.

A quantitative relationship between the equilibrium constant and temperature can be derived from the Arrhenius equation for the *specific rate constant*, since the equilibrium constant, K_{eq}, is equal to the ratio k_f/k_r. The *specific rate constant* for the forward reaction is

$$k_f = A_f e^{-Ea/RT}$$

while the corresponding expression for the reverse reaction is

$$k_r = A_r e^{-Ea/RT}$$

Substitution shows the temperature dependence of K_{eq},

$$K_{eq} = \frac{k_f}{k_r} = \frac{A_f e^{-Ea/RT}}{A_r e^{-Ea/RT}} = \frac{A_f}{A_r} e^{-(Ea)_f - (Ea)_r/RT}$$

and

$$K_{eq} = Z e^{-\Delta Ea/RT}$$

(where Z, a constant, is the ratio of A_f/A_r). Thus, for exothermic reactions K_{eq} decreases as temperature increases, and for endothermic reactions K_{eq} increases as temperature increases. In other words, increasing the temperature will shift the position of equilibrium to the left for an exothermic reaction; whereas, increasing the temperature will shift the position of equilibrium to the right for an endothermic reaction. This simplified derivation supports the generalization of Le Chatelier.

According to Le Chatelier's principle, if heat is added to the nitrogen, hydrogen, ammonia system (increase of temperature), the system will change in such a way as to minimize the stress. To relieve the stress (increase of temperature), the system will absorb heat, *i.e.*, the formation of nitrogen and hydrogen from ammonia will be favored since this reaction absorbs heat. In reality, part of the heat is used to increase the temperature of the system and part is used to *shift the equilibrium.*

The Effect of Changing Concentration on the Position of Equilibrium

Another way to put a stress on a system is to alter the concentration of one or more of the components. This can be accomplished by adding or removing one or more of the equilibrium species. For example, consider the equilibrium

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$
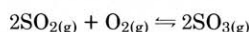
where

$$K_{eq} = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

A stress can be placed on this system by adding sulfur dioxide, oxygen, or both. In either event, the product of the molar concentrations in the denominator of the equilibrium-constant expression exceeds the *equilibrium value,* and the ratio of the molar concentrations is now less than K_{eq}. If the molar concentration of sulfur dioxide is increased, the reaction rate to the right will increase, and the change which tends to use up sulfur dioxide and oxygen and thus remove the stress will be favored. This conforms to Le Chatelier's principle which indicates that the equilibrium system will shift so as to minimize the stress. Sulfur dioxide and oxygen will be used up faster than they are formed, and the molar concentration of sulfur trioxide will increase. However, as the molarity of sulfur trioxide increases, the rate of its dissociation into sulfur dioxide and oxygen will also increase. Eventually, the forward and reverse reactions will attain equal rates and equilibrium will be re-established. The stress placed on the system, when the concentration of sulfur dioxide was increased, will have been removed by changes in the molarites of all the substances such that the value of K_{eq} is restored. Note that when the concentration of sulfur dioxide is increased, the net changes which occur in the system are such that the concentration of oxygen is decreased while the concentration of sulfur trioxide is increased. In other words, oxygen can be used up more completely and sulfur trioxide can be produced more efficiently by increasing the concentration of sulfur dioxide. On the other hand, the introduction of more sulfur trioxide into the system favors the reverse reaction, more sulfur dioxide and oxygen are formed while some sulfur trioxide is consumed, i.e.,

the position of the equilibrium shifts to the left.

Conversely, removal of a component from an equilibrium system favors the reaction which replaces it. For example, the removal of sulfur trioxide from the equilibrium system shifts the position of equilibrium to the right. The forward rate will momentarily be greater than the reverse rate; the system is temporarily out of equilibrium and sulfur trioxide molecules will be produced faster than they are used up in the reverse reaction. Similarly, if part of the sulfur dioxide or oxygen is removed, the reverse reaction, forming more sulfur dioxide and oxygen, will be favored.

The Effect of Pressure on Equilibrium: A Special Case of Changing Concentration

Change of pressure is insignificant for liquids and solids because of their low compressibility, but it is extremely important for gases because the molarity of a gas, at constant temperature, is directly proportional to its partial pressure ($PV = nRT$). Therefore, as the external pressure on a gaseous system increases, the substances undergo compression and the molarity increases. Le Chatelier's principle indicates that, if a *stress* is placed on a reversible system by increasing the pressure, that chemical change will be favored which will tend to reduce the pressure. For a gaseous system, the increase in pressure is achieved by increasing the total number of molecules per unit volume. This process will favor the net chemical change that will reduce the total number of molecules per unit volume.

Consider the reversible reaction

$$2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$$
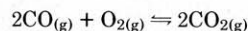
A total of three moles of carbon monoxide and oxygen form only two moles of carbon dioxide. The formation of carbon dioxide will therefore decrease the total number of molecules in the system, and the total gaseous pressure will therefore be reduced. Thus, increasing the total external pressure on the system will favor the conversion of carbon monoxide and oxygen to carbon dioxide. Conversely, a decrease in the total external pressure will favor the dissociation of carbon dioxide to carbon monoxide and oxygen.

If PCl_5 is injected into a closed system at $523°K$, it dissociates to an equilibrium state:

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

Since there are two moles of gaseous product compared to only one mole of gaseous reactant, an increase in the external pressure will cause a shift in the equilibrium to the left, i.e., less PCl_5 dissociates; whereas a decrease in the external pressure will favor the dissociation of PCl_5. In other words, there is a shift in the equilibrium to the right.

Certain gaseous reactions are not affected by changes in pressure, for example:

$$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$$
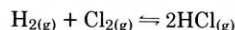
In this case there are two moles of reactants and two moles of product. Changes in the external pressure have no effect on this system because there are equal numbers of molecules on both sides of the equation.

Catalysts and Equilibrium

While catalysts are used to increase the rate of a reaction, they cannot change the numerical value of the equilibrium constant and hence cannot change the relative amounts of reactants and products present at equilibrium. However, the catalyst may greatly reduce the time necessary for the establishment of equilibrium. This is extremely important from an industrial viewpoint, since the rate at which a product can be produced is a primary consideration. Catalysts may be used effectively in many reactions which allow conversion of only a small percentage of reactants into products (position of equilibrium shifted far to the left) because, from a production standpoint, it is far more important to obtain a small yield in a few minutes than to obtain a large yield in several days.