

Chemical Equilibrium

1) The concept of Equilibrium

A dynamic equilibrium exists when the rates of the forward and reverse reactions are equal. No further net change in reactant or product concentration occurs. The double arrow. implies that the process is dynamic.

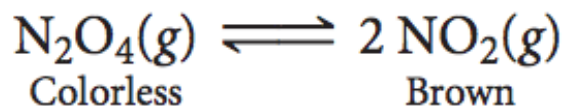


When the reactants and products are all in solution, , the equilibrium constant is expressed in terms of molarities.

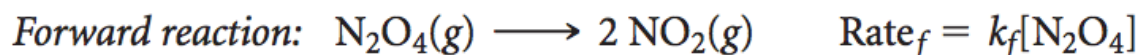
$$K_c = \frac{[D]^d [E]^e}{[A]^a [B]^b} \quad \begin{array}{l} \longleftarrow \text{products} \\ \longleftarrow \text{reactants} \end{array}$$

- At equilibrium, the concentrations of reactants and products no longer change with time.
- For equilibrium to occur, neither reactants nor products can escape from the system.
- At equilibrium, a particular ratio of concentration terms equals a constant.

Example: Consider the colorless frozen N_2O_4 . At room temperature, it decomposes to brown NO_2 .



At some point, the color stops changing and we have a mixture of N_2O_4 and NO_2 . The rate laws for elementary reactions can be written from their chemical equations:



At equilibrium, the rate at which NO_2 forms in the forward reaction equals the rate at which N_2O_4 forms in the reverse reaction:

$$\begin{array}{ccc} k_f[\text{N}_2\text{O}_4] & = & k_r[\text{NO}_2]^2 \\ \text{Forward reaction} & & \text{Reverse reaction} \end{array}$$

Rearranging this equation gives

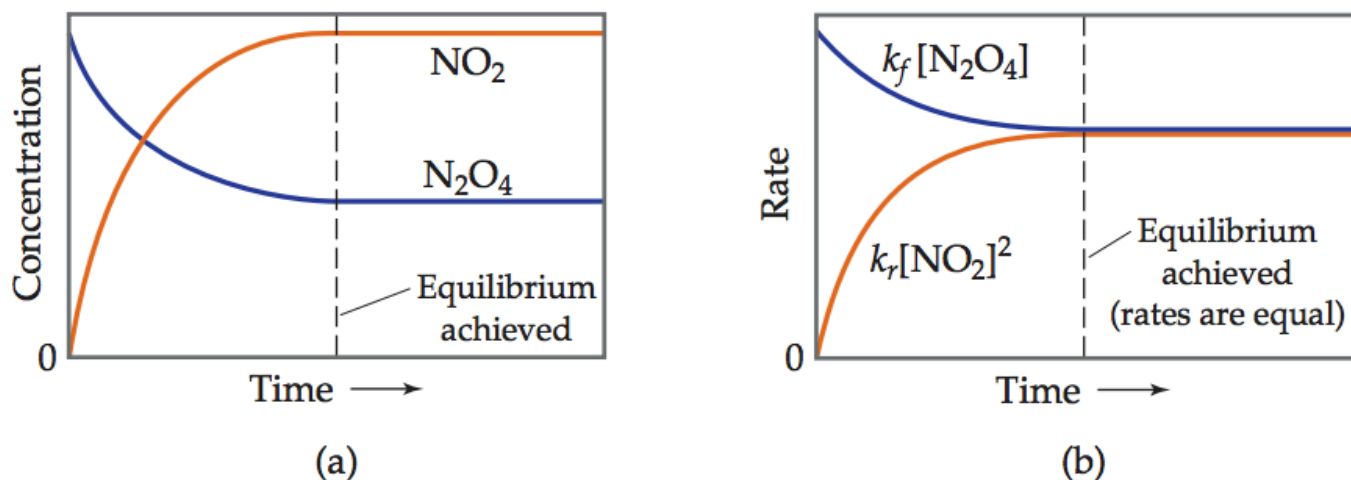
$$\frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{k_f}{k_r} = \text{a constant}$$

The figure below shows that equilibrium occurs when the rate of the forward reaction equals the rate of the reverse reaction

The equilibrium expression depends on stoichiometry.

It does not depend on the reaction mechanism

The value for K_c varies with temperature.



We generally omit the units of the equilibrium constant.

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{[0.0172]^2}{0.00140} = 0.211$$

TABLE 15.1 • Initial and Equilibrium Concentrations of $\text{N}_2\text{O}_4(\text{g})$ and $\text{NO}_2(\text{g})$ at $100\text{ }^\circ\text{C}$

Experiment	Initial $[\text{N}_2\text{O}_4]$ (M)	Initial $[\text{NO}_2]$ (M)	Equilibrium $[\text{N}_2\text{O}_4]$ (M)	Equilibrium $[\text{NO}_2]$ (M)	K_c
1	0.0	0.0200	0.00140	0.0172	0.211
2	0.0	0.0300	0.00280	0.0243	0.211
3	0.0	0.0400	0.00452	0.0310	0.213
4	0.0200	0.0	0.00452	0.0310	0.213

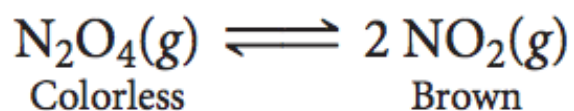
2) Equilibrium Constants in Terms of Pressure, K_p

When the reactants and products in a chemical reaction are gases, we can formulate the equilibrium-constant expression in terms of partial pressures.



$$K_p = \frac{(P_D)^d (P_E)^e}{(P_A)^a (P_B)^b}$$

Example: For the reaction:



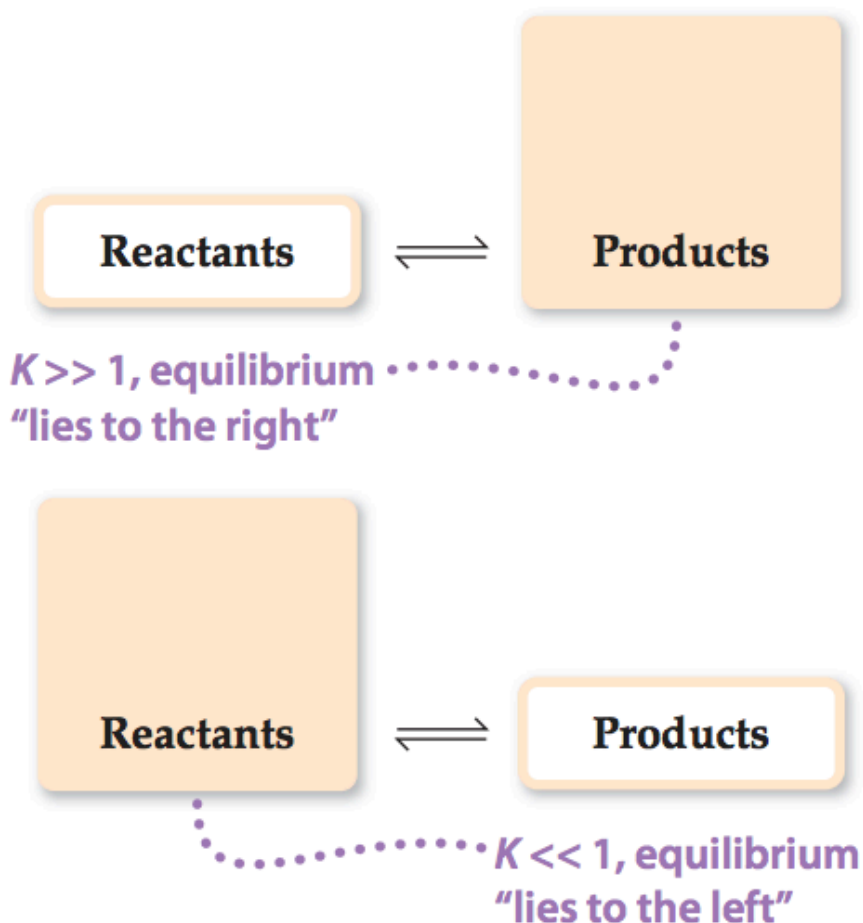
$$K_p = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}}$$

3) The Magnitude of Equilibrium Constants

The equilibrium constant K_c is the ratio of products to reactants. Therefore, the larger the K_c , the more products are present at equilibrium. Conversely, the smaller the K_c , the more reactants are present at equilibrium.

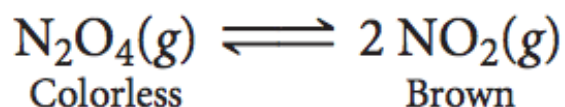
If $K \gg 1$: (large K): Equilibrium lies to right, products predominate.

If $K \ll 1$: (small K): Equilibrium lies to left, reactants predominate



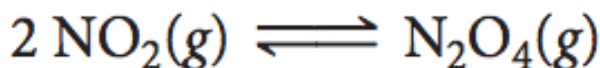
4) The Direction of the Chemical Equation and K

The equilibrium-constant expression for a reaction written in one direction is the reciprocal of the expression for the reaction written in the reverse direction. Consequently, the numerical value of the equilibrium constant for the reaction written in one direction is the reciprocal of that for the reverse reaction.



$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{[0.0172]^2}{0.00140} = 0.211$$

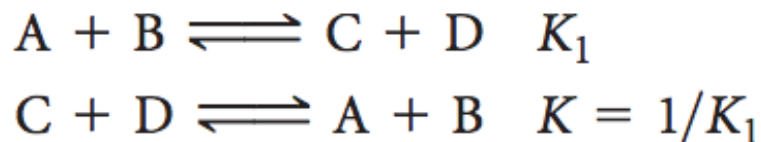
For the reverse reaction:



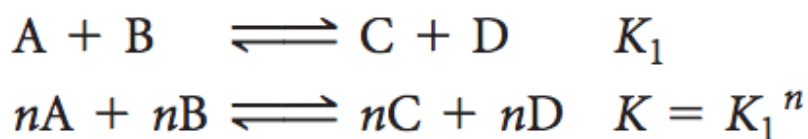
$$K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = \frac{1}{0.212} = 4.72 \quad (\text{at } 100 \text{ }^\circ\text{C})$$

Summary:

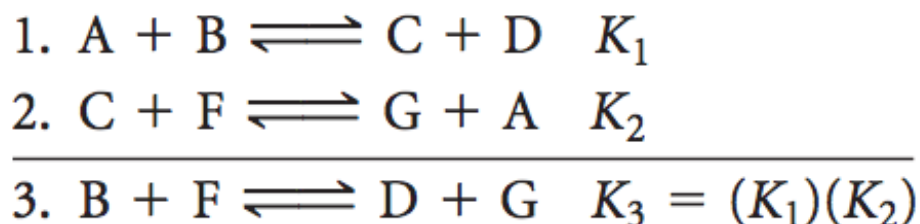
1. The equilibrium constant of a reaction in the reverse direction is the inverse (or reciprocal) of the equilibrium constant of the reaction in the forward direction:



2. The equilibrium constant of a reaction that has been multiplied by a number is equal to the original equilibrium constant raised to a power equal to that number:



3. The equilibrium constant for a net reaction made up of two or more reactions is the product of the equilibrium constants for the individual reactions:



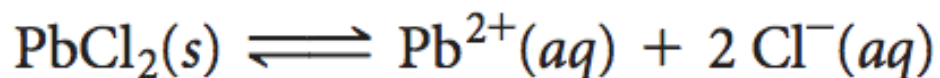
5) Heterogeneous Equilibria

Equilibria in which all reactants and products are present in the same phase (usually gas or liquid) are called homogeneous equilibria.

Equilibria in which one or more reactants and products are present in a different phase are called heterogeneous equilibria.

Because equilibrium-constant expressions include terms only for reactants and products whose concentrations can change during a chemical reaction, the **concentrations of pure solids and pure liquids are omitted**. In other words, whenever a pure solid or pure liquid is involved in a heterogeneous equilibrium, its concentration is not included in the equilibrium constant expression.

Example 1: Consider the equilibrium that occurs when solid lead(II) chloride dissolves in water to form a saturated solution:



$$K_c = [\text{Pb}^{2+}][\text{Cl}^{-}]^2$$

Example 2: Decomposition of calcium carbonate is another example of a heterogeneous reaction. Omitting the concentrations of the solids from the equilibrium-constant expression gives



$$K_c = [\text{CO}_2] \quad \text{and} \quad K_p = P_{\text{CO}_2}$$

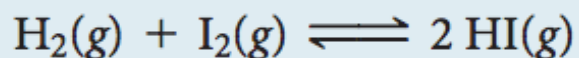
6) Calculating equilibrium constant

Often we do not know the equilibrium concentrations of all species in an equilibrium mixture. If we know the equilibrium concentration of at least one species, however, we can generally use the stoichiometry of the reaction to deduce the equilibrium concentrations of the others.

The following steps outline the procedure:

1. Tabulate all known initial and equilibrium concentrations (or pressures) of the species that appear in the equilibrium-constant expression.
2. For those species for which initial and equilibrium concentrations are known, calculate the change in concentration that occurs as the system reaches equilibrium.
3. Use the stoichiometry of the reaction (that is, the coefficients in the balanced chemical equation) to calculate the changes in concentration for all other species in the equilibrium-constant expression.
4. Use initial concentrations from step 1 and changes in concentration from step 3 to calculate any equilibrium concentrations not tabulated in step 1.
5. Determine the value of the equilibrium constant.

Example:



	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	\rightleftharpoons	$2 \text{HI}(\text{g})$
Initial concentration (M)	1.000×10^{-3}		2.000×10^{-3}		0
Change in concentration (M)					
Equilibrium concentration (M)					1.87×10^{-3}

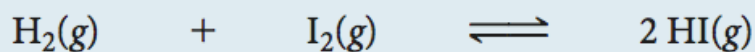
$$\text{Change in } [\text{HI}] = 1.87 \times 10^{-3} \text{ M} - 0 = 1.87 \times 10^{-3} \text{ M}$$

$$\left(1.87 \times 10^{-3} \frac{\text{mol HI}}{\text{L}} \right) \left(\frac{1 \text{ mol H}_2}{2 \text{ mol HI}} \right) = 0.935 \times 10^{-3} \frac{\text{mol H}_2}{\text{L}}$$

$$\left(1.87 \times 10^{-3} \frac{\text{mol HI}}{\text{L}} \right) \left(\frac{1 \text{ mol I}_2}{2 \text{ mol HI}} \right) = 0.935 \times 10^{-3} \frac{\text{mol I}_2}{\text{L}}$$

$$[\text{H}_2] = 1.000 \times 10^{-3} \text{ M} - 0.935 \times 10^{-3} \text{ M} = 0.065 \times 10^{-3} \text{ M}$$

$$[\text{I}_2] = 2.000 \times 10^{-3} \text{ M} - 0.935 \times 10^{-3} \text{ M} = 1.065 \times 10^{-3} \text{ M}$$



Initial concentration (M)	1.000×10^{-3}		2.000×10^{-3}		0
Change in concentration (M)	-0.935×10^{-3}		-0.935×10^{-3}		$+1.87 \times 10^{-3}$
Equilibrium concentration (M)	0.065×10^{-3}		1.065×10^{-3}		1.87×10^{-3}

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(1.87 \times 10^{-3})^2}{(0.065 \times 10^{-3})(1.065 \times 10^{-3})} = 51$$

7) APPLICATIONS OF EQUILIBRIUM CONSTANTS

Predicting the Direction of Reaction

For a general reaction:



We define the reaction quotient, Q , as

$$Q_c = \frac{[D]^d [E]^e}{[A]^a [B]^b}$$

Where $[A]$, $[B]$, $[D]$, and $[E]$ are molarities (for substances in solution) or partial pressure (for gases) at any given time.

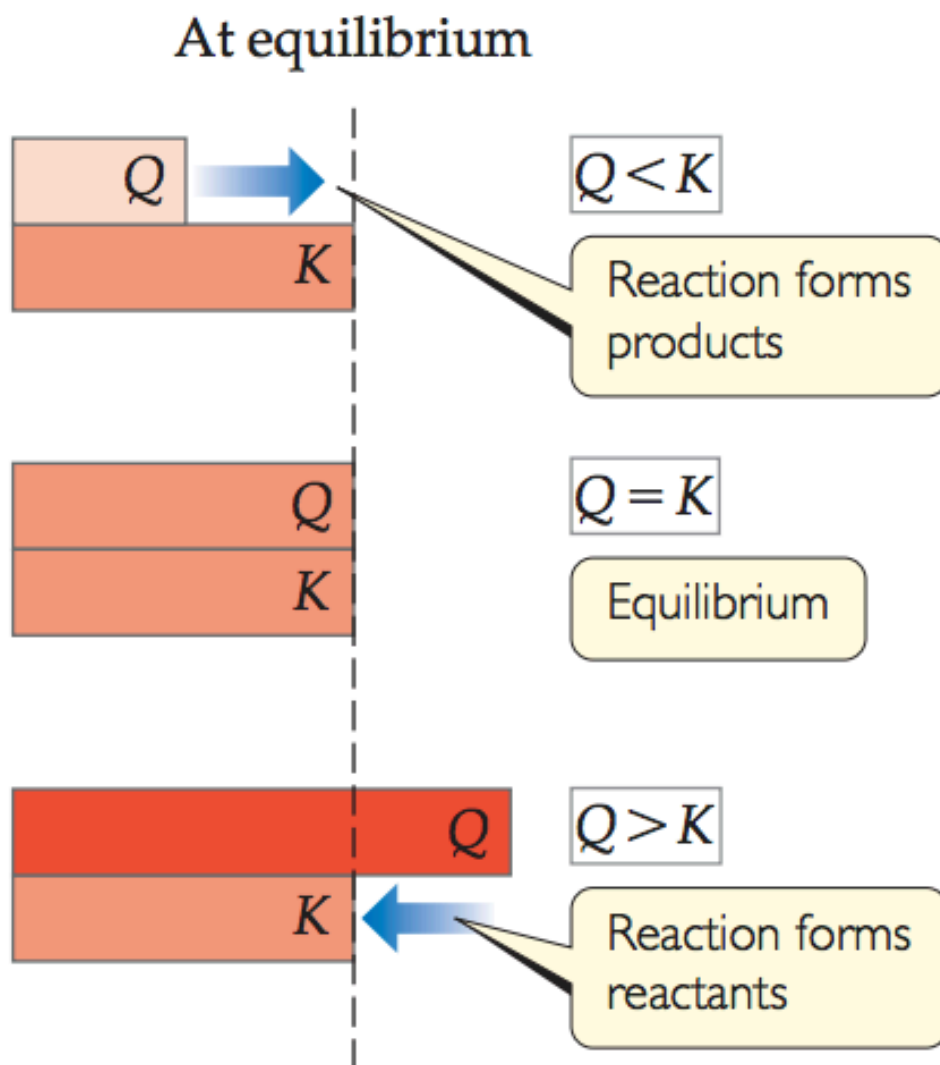
The reaction quotient Q_c quotient is obtained by applying the law of mass action using initial concentrations instead of equilibrium concentration. It is used to determine the direction a system will shift to reach equilibrium.

We compare the values of Q_c and K_c or Q_p and K_p . Three possible situations arise:

$Q_c = K$ only at equilibrium

$Q_c < K$: The concentration of products is too small and that of reactants too large. Then the forward reaction must occur to reach equilibrium.

$Q_c > K$: The concentration of products is too large and that of reactants too small. Then the reverse reaction must occur to reach equilibrium.



8) Le Chatelier's Principle

HenriLouis Le Châtelier* (1850–1936) is a French industrial chemist:

If a system at equilibrium is disturbed by a change in temperature, pressure, or a component concentration, the system will shift its equilibrium position so as to counteract the effect of the disturbance.

a) Change the Reactant or Product Concentration: If a chemical system is already at equilibrium and the concentration of any substance in the mixture is increased (either reactant or product), the system reacts to consume some of that substance.

Conversely, if the concentration of a substance is decreased, the system reacts to produce some of that substance.

b) Effects of Volume and Pressure Changes: At constant temperature, **reducing the volume** of a gaseous equilibrium mixture causes the system to **shift in the direction that reduces the number of moles of gas**.

In a reaction with the same number of moles of gas in the products and reactants, changing the pressure has no effect on the equilibrium.

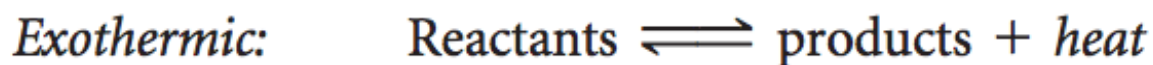
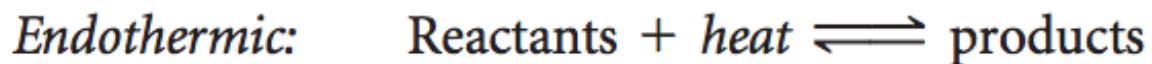
In addition, no change will occur if we increase the total gas pressure by the addition of a gas that is not involved in the reaction.

Changes in concentrations or partial pressures shift equilibria without changing the value of the equilibrium constant.

In contrast, almost every equilibrium constant changes as the temperature changes.

c) Effect of Temperature Changes: The equilibrium constant is temperature dependent.

Relationship between K and temperature: We do this by treating heat as a chemical reagent. In an endothermic (heat-absorbing) reaction, we consider heat a reactant, and in an exothermic (heat-releasing) reaction, we consider heat a product:



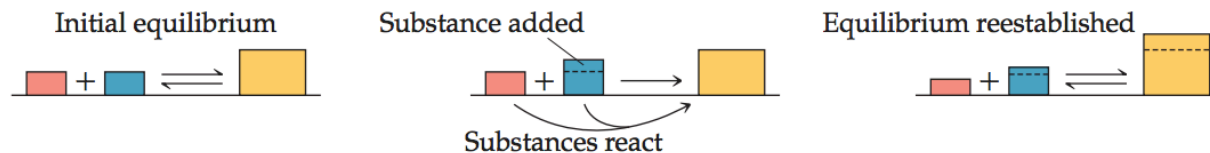
When the temperature of a system at equilibrium is increased, the system reacts as if we added a reactant to an endothermic reaction or a product to an exothermic reaction. The equilibrium shifts in the direction that consumes the excess reactant (or product), namely heat.

Le Chatelier's Principle

If a system at equilibrium is disturbed by a change in **concentration, pressure, or temperature**, the system will shift its equilibrium position so as to counter the effect of the disturbance.

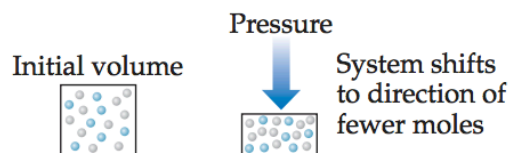
Concentration: adding or removing a reactant or product

If a substance is added to a system at equilibrium, the system reacts to consume some of the substance. If a substance is removed from a system, the system reacts to produce more of substance.



Pressure: changing the pressure by changing the volume

At constant temperature, reducing the volume of a gaseous equilibrium mixture causes the system to shift in the direction that reduces the number of moles of gas.



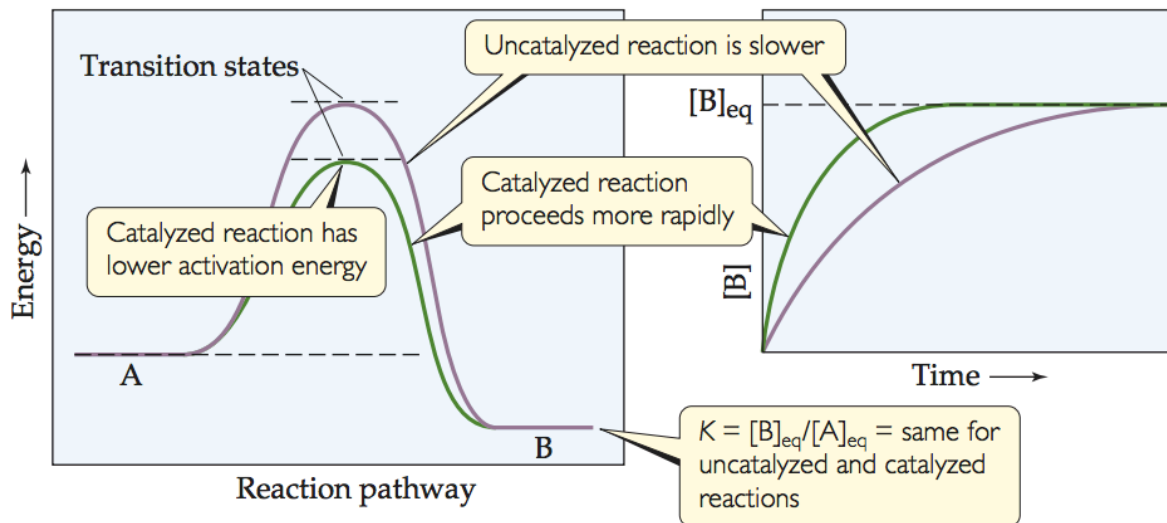
Temperature:

If the temperature of a system at equilibrium is increased, the system reacts as if we added a reactant to an endothermic reaction or a product to an exothermic reaction. The equilibrium shifts in the direction that consumes the "excess reactant," namely heat.



9) The Effect of a Catalyst:

A catalyst lowers the activation energy barrier for the reaction. Therefore, a catalyst will decrease the time taken to reach equilibrium (increases the rate at which equilibrium is achieved). A catalyst does not affect the composition of the equilibrium mixture.



10) Relating the equilibrium constant based on pressures to the equilibrium constant based on concentration:

The quantity Δn is the change in the number of moles of gas in the balanced chemical equation. It equals the sum of the coefficients of the gaseous products minus the sum of the coefficients of the gaseous reactants:

$$\Delta n = (\text{moles of gaseous product}) - (\text{moles of gaseous reactant})$$

$$K_p = K_c(RT)^{\Delta n}$$