Chemistry, The Central Science, 11th edition
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Chapter 15
Chemical Equilibrium

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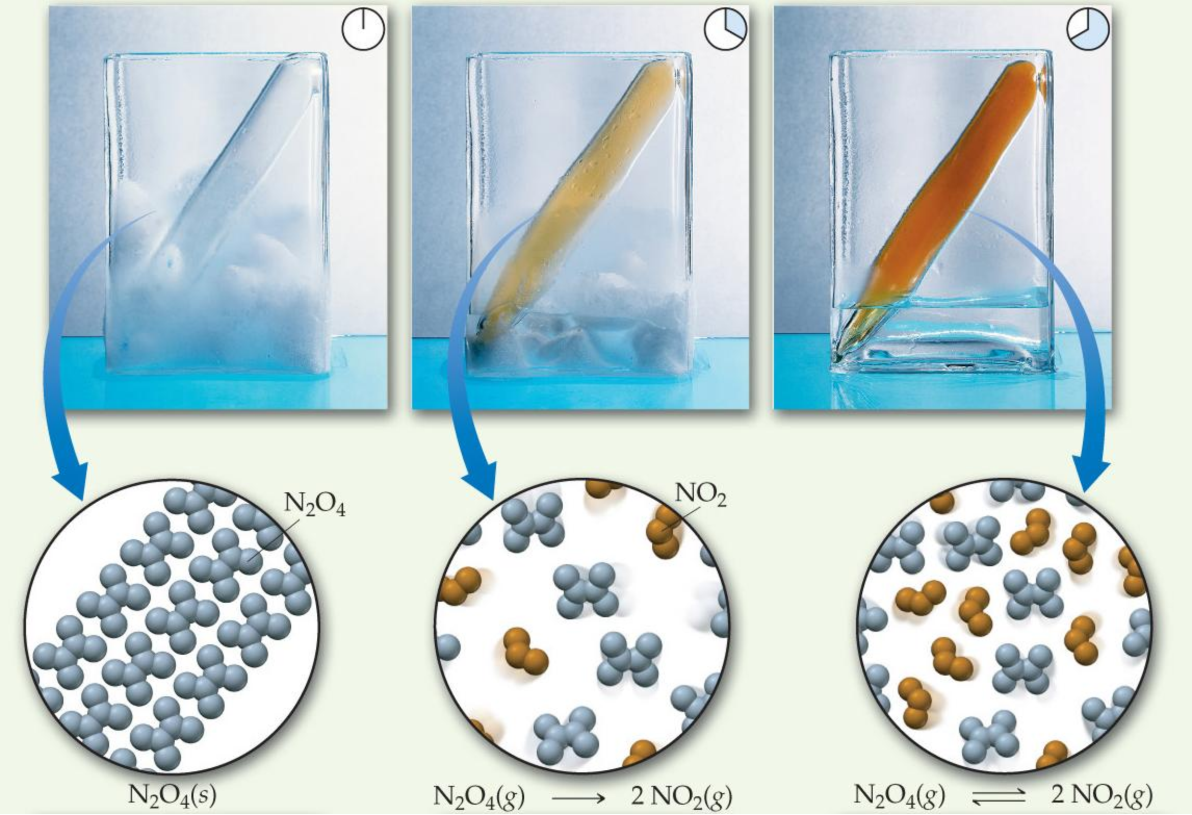
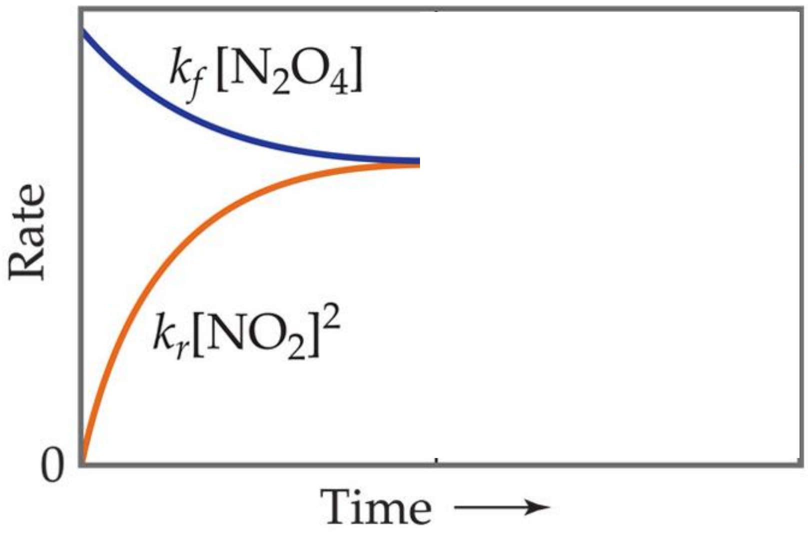
The Concept of Equilibrium



Chemical equilibrium occurs when a reaction and its reverse reaction proceed at the same rate.

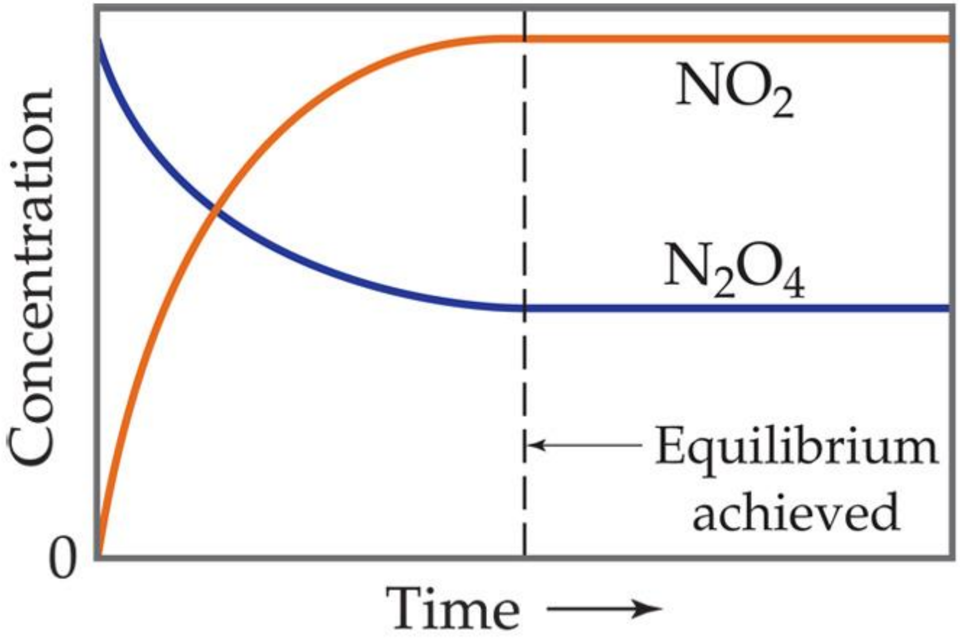
The Concept of Equilibrium



- As a system approaches equilibrium, both the forward and reverse reactions are occurring.
- At equilibrium, the forward and reverse reactions are proceeding *at the same rate*.

A System at Equilibrium

Once equilibrium is achieved, the *amount* of each reactant and product remains constant.



Depicting Equilibrium

Since, in a system at equilibrium, both the forward and reverse reactions are being carried out, we write its equation with a double arrow.

$$N_2O_{4\,(g)} \rightleftharpoons 2\ NO_{2\,(g)}$$

The Equilibrium Constant

Equilibrium

The Equilibrium Constant

- Forward reaction:

$$N_2O_{4\,(g)} \longrightarrow 2\ NO_{2\,(g)}$$

- Rate Law:

$$\text{Rate} = k_f\,[N_2O_4]$$

The Equilibrium Constant

- Reverse reaction:

$$2\ NO_{2\ (g)} \longrightarrow N_2O_{4\ (g)}$$

- Rate Law:

$$\text{Rate} = k_r\,[NO_2]^2$$

The Equilibrium Constant

- Therefore, at equilibrium

$$\text{Rate}_f = \text{Rate}_r$$

$$k_f\,[N_2O_4] = k_r\,[NO_2]^2$$

- Rewriting this, it becomes

$$\frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]}$$

The Equilibrium Constant

The ratio of the rate constants is a constant at that temperature, and the expression becomes

$$K_{eq} = \frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]}$$

The Equilibrium Constant

- Consider the generalized reaction

$$aA + bB \rightleftharpoons cC + dD$$

- The equilibrium expression for this reaction would be

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

The Equilibrium Constant

Since pressure is proportional to concentration for gases in a closed system, the equilibrium expression can also be written

$$K_p = \frac{(P_C{}^c)\,(P_D{}^d)}{(P_A{}^a)\,(P_B{}^b)}$$

Relationship Between K_c and K_p

- From the Ideal Gas Law we know that

$$PV = nRT$$

- Rearranging it, we get

$$P = \frac{n}{V} RT$$

Relationship Between K_c and K_p

Plugging this into the expression for K_p for each substance, the relationship between K_c and K_p becomes

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

where

Δn = (moles of gaseous product) - (moles of gaseous reactant)

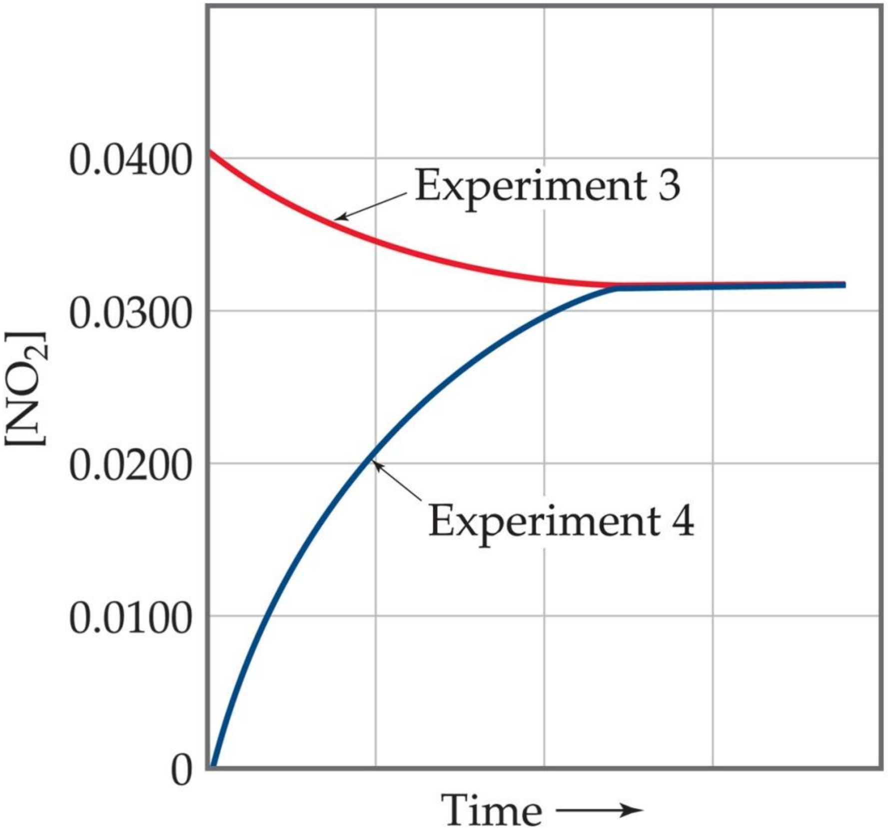
Equilibrium

Equilibrium Can Be Reached from Either Direction

Initial and Equilibrium Concentrations of N_2O_4 and NO_2 in the Gas Phase at 100 °C					
Experiment	Initial $[N_2O_4]$ (M)	Initial $[NO_2]$ (M)	Equilibrium $[N_2O_4]$ (M)	Equilibrium $[NO_2]$ (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

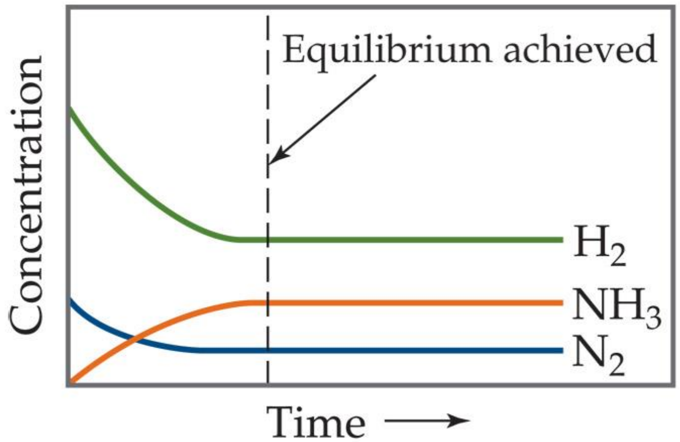
As you can see, the ratio of $[NO_2]^2$ to $[N_2O_4]$ remains constant at this temperature no matter what the initial concentrations of NO_2 and N_2O_4 are.

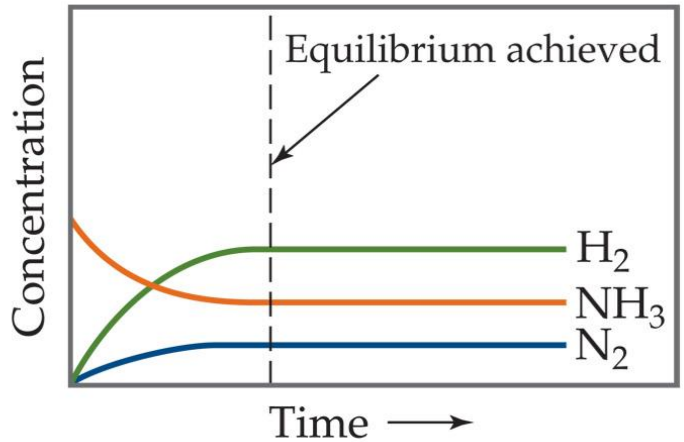
Equilibrium Can Be Reached from Either Direction



This is the data from the last two trials from the table on the previous slide.

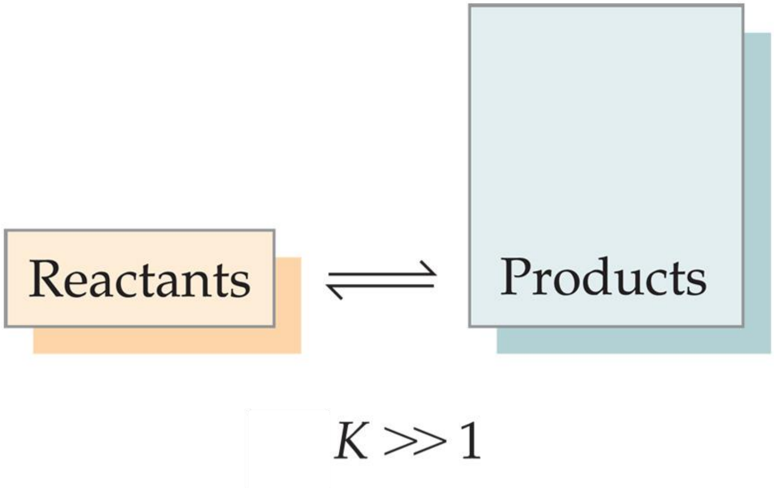
Equilibrium Can Be Reached from Either Direction



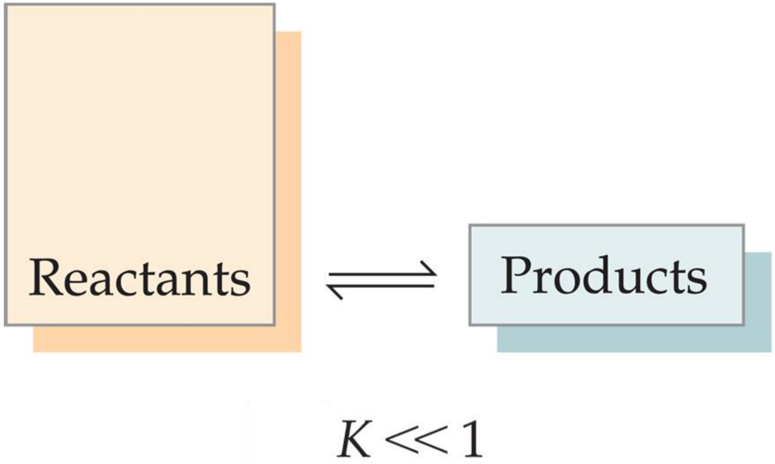


It doesn't matter whether we start with N_2 and H_2 or whether we start with NH_3: we will have the same proportions of all three substances at equilibrium.

What Does the Value of *K* Mean?



- If *K*>>1, the reaction is *product-favored*; product predominates at equilibrium.



- If *K*<<1, the reaction is *reactant-favored*; reactant predominates at equilibrium.

Manipulating Equilibrium Constants

The equilibrium constant of a reaction in the reverse reaction is the reciprocal of the equilibrium constant of the forward reaction.

$$N_2O_{4\,(g)} \longrightarrow 2\ NO_{2\,(g)} \quad K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.212 \text{ at } 100\ °C$$

$$2\ NO_{2\,(g)} \longrightarrow N_2O_{4\,(g)} \quad K_c = \frac{[N_2O_4]}{[NO_2]^2} = 4.72 \text{ at } 100\ °C$$

Manipulating Equilibrium Constants

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

$$N_2O_{4(g)} \longrightarrow 2\ NO_{2(g)} \quad K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.212 \text{ at } 100\ °C$$

$$2\ N_2O_{4(g)} \longrightarrow 4\ NO_{2(g)} \quad K_c = \frac{[NO_2]^4}{[N_2O_4]^2} = (0.212)^2 \text{ at } 100\ °C$$

Manipulating Equilibrium Constants

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

Sample Exercise 15.1 Writing Equilibrium-Constant Expressions

Write the equilibrium expression for K_c for the following reactions:

(a) $2\,O_3(g) \rightleftharpoons 3\,O_2(g)$
(b) $2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g)$
(c) $Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2{}^+(aq)$

Solution

Solve: (a) $K_c = \dfrac{[O_2]^3}{[O_3]^2}$, (b) $K_c = \dfrac{[NOCl]^2}{[NO]^2[Cl_2]}$, (c) $K_c = \dfrac{[Ag(NH_3)_2{}^+]}{[Ag^+][NH_3]^2}$

Practice Exercise

Write the equilibrium-constant expression K_c, for **(a)** $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$, **(b)** $Cd^{2+}(aq) + 4\,Br^-(aq) \rightleftharpoons CdBr_4{}^{2-}(aq)$

Answers: (a) $K_c = \dfrac{[HI]^2}{[H_2][I_2]}$; (b) $K_c = \dfrac{[CdBr_4{}^{2-}]}{[Cd^{2+}][Br^-]^4}$

Sample Exercise 15.2 Converting between K_c and K_p

In the synthesis of ammonia from nitrogen and hydrogen,

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

K_c = 9.60 at 300 ° C. Calculate K_p for this reaction at this temperature.

Solution

Analyze: We are given K_c for a reaction and asked to calculate K_p.
Plan: The relationship between K_c and K_p is given by Equation 15.14. To apply that equation, we must determine Δn by comparing the number of moles of product with the number of moles of reactants (Equation 15.15).

Solve: There are two moles of gaseous products (2 NH_3) and four moles of gaseous reactants (1 N_2 + 3 H_2). Therefore, $\Delta n = 2 - 4 = -2$. (Remember that Δ functions are always based on products minus reactants.) The temperature, T, is 273 + 300 = 573 K. The value for the ideal-gas constant, R, is 0.0821 L-atm/mol-K. Using $K_c = 9.60$, we therefore have

$$K_p = K_c(RT)^{\Delta n} = (9.60)(0.0821 \times 573)^{-2} = \frac{(9.60)}{(0.0821 \times 573)^2} = 4.34 \times 10^{-3}$$

Heterogeneous Equilibrium

The Concentrations of Solids and Liquids Are Essentially Constant

Both can be obtained by multiplying the density of the substance by its molar mass — and both of these are constants at constant temperature.

The Concentrations of Solids and Liquids Are Essentially Constant

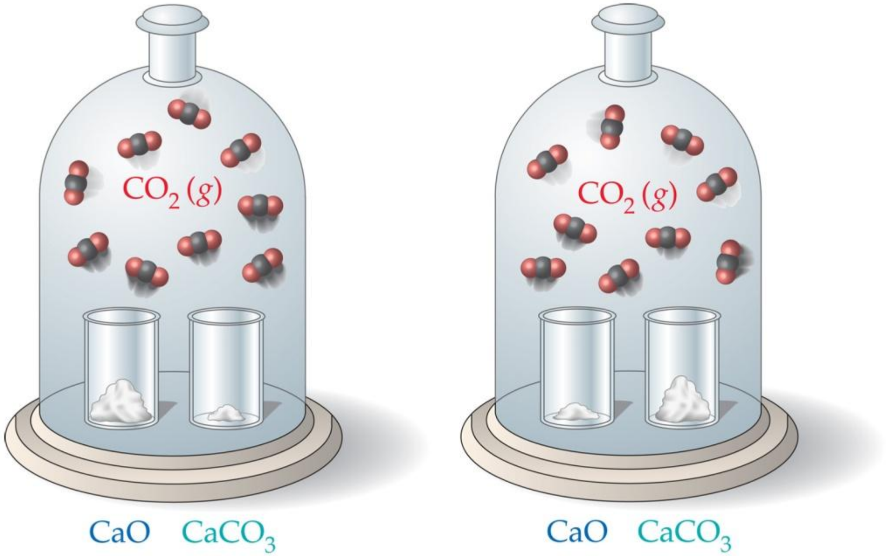
Therefore, the concentrations of solids and liquids do not appear in the equilibrium expression.

$$PbCl_{2\,(s)} \rightleftharpoons Pb^{2+}{}_{(aq)} + 2\,Cl^{-}{}_{(aq)}$$

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

$$CaCO_{3\,(s)} \rightleftharpoons CO_{2\,(g)} + CaO_{(s)}$$

As long as *some* $CaCO_3$ or CaO remain in the system, the amount of CO_2 above the solid will remain the same.



Equilibrium Calculations

An Equilibrium Problem

A closed system initially containing 1.000×10^{-3} *M* H_2 and 2.000×10^{-3} *M* I_2 at 448 °C is allowed to reach equilibrium. Analysis of the equilibrium mixture shows that the concentration of HI is 1.87×10^{-3} *M*. Calculate K_c at 448 °C for the reaction taking place, which is

$$H_{2\,(g)} + I_{2\,(s)} \longrightarrow 2\,HI_{\,(g)}$$

What Do We Know?

	$[H_2]$, M	$[I_2]$, M	$[HI]$, M
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change			
At equilibrium			1.87×10^{-3}

[HI] Increases by 1.87×10^{-3} *M*

	$[H_2]$, *M*	$[I_2]$, *M*	[HI], *M*
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change			$+1.87 \times 10^{-3}$
At equilibrium			1.87×10^{-3}

Stoichiometry tells us $[H_2]$ and $[I_2]$ decrease by half as much.

	$[H_2]$, *M*	$[I_2]$, *M*	[HI], *M*
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change	-9.35×10^{-4}	-9.35×10^{-4}	$+1.87 \times 10^{-3}$
At equilibrium			1.87×10^{-3}

We can now calculate the equilibrium concentrations of all three compounds…

	$[H_2]$, M	$[I_2]$, M	$[HI]$, M
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change	-9.35×10^{-4}	-9.35×10^{-4}	$+1.87 \times 10^{-3}$
At equilibrium	6.5×10^{-5}	1.065×10^{-3}	1.87×10^{-3}

…and, therefore, the equilibrium constant.

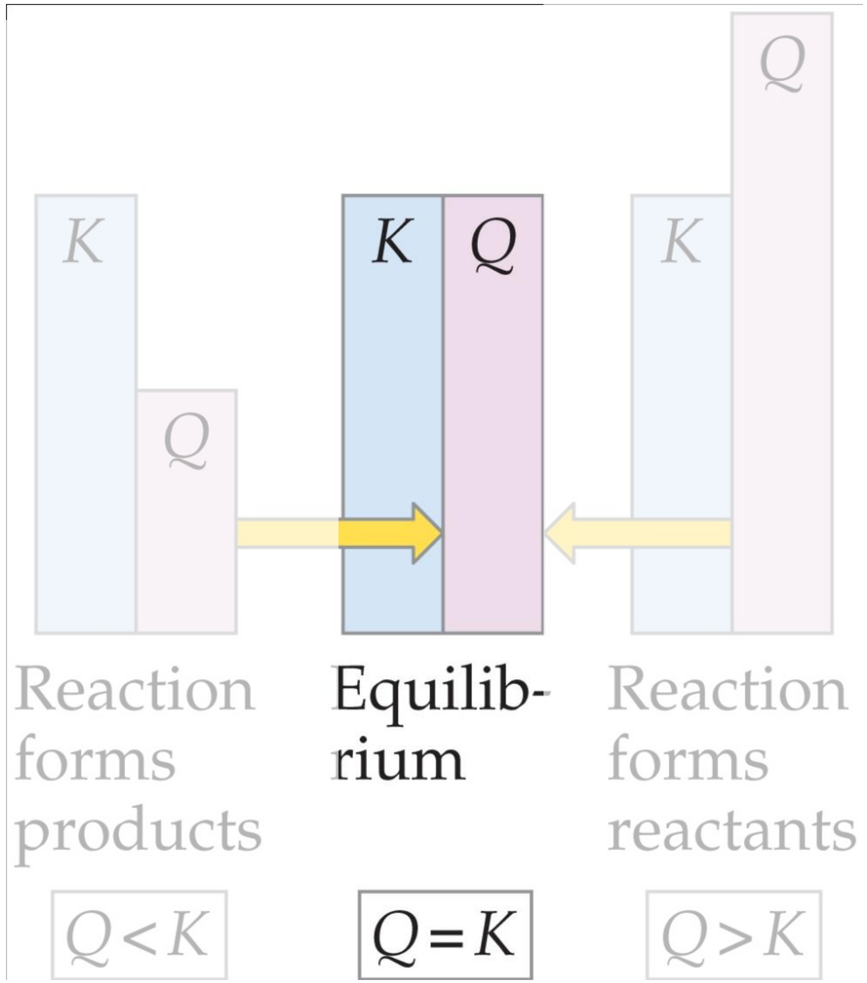
$$K_c = \frac{[HI]^2}{[H_2]\,[I_2]}$$

The Reaction Quotient (*Q*)

- *Q* gives the same ratio the equilibrium expression gives, but for a system that is *not* at equilibrium.
- To calculate *Q*, one substitutes the initial concentrations on reactants and products into the equilibrium expression.

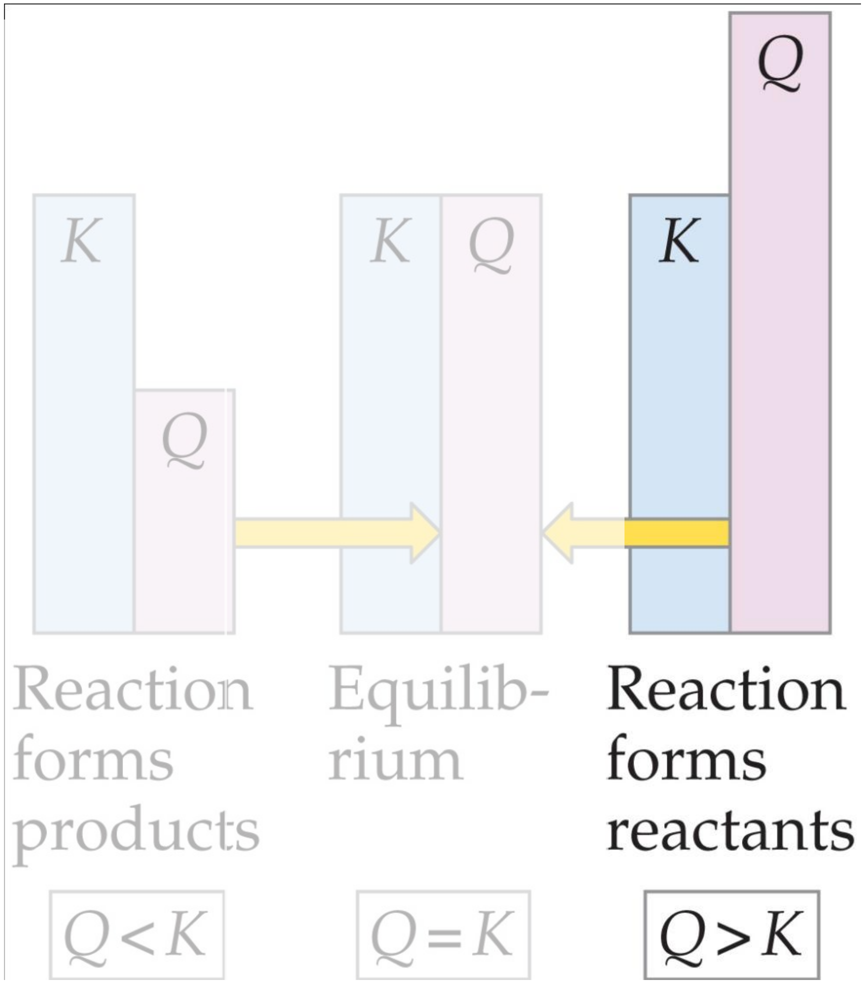
If $Q = K$,

the system is at equilibrium.

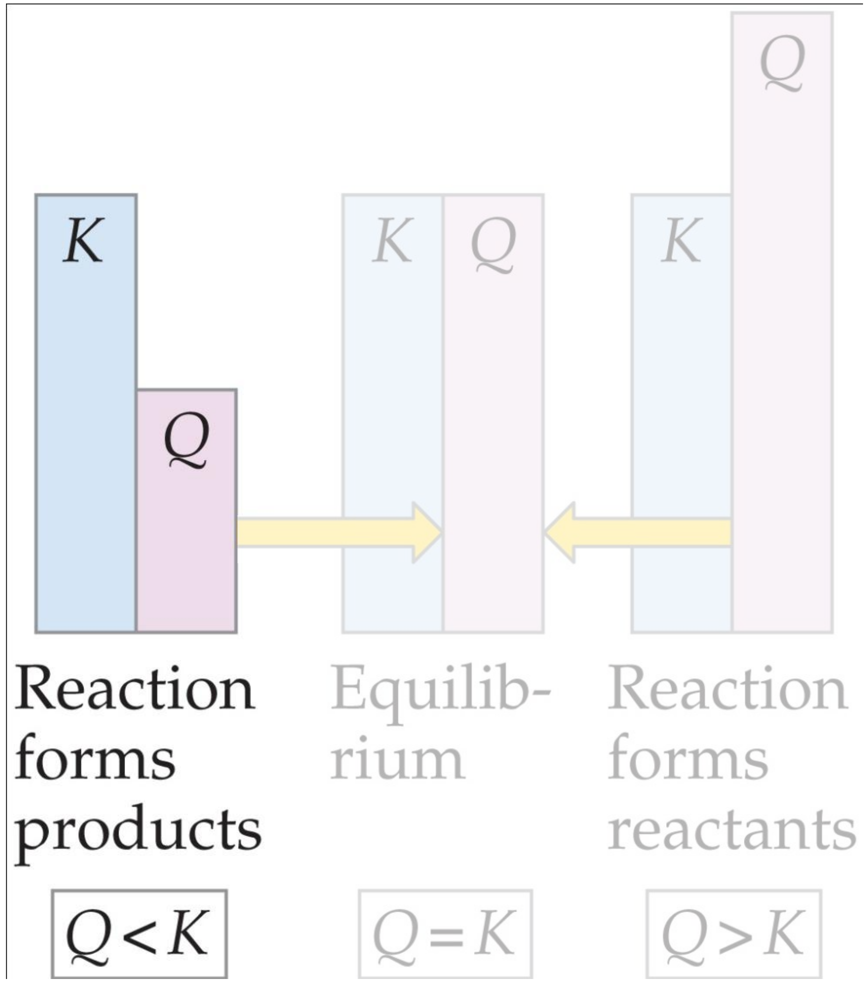


Equilibrium

If $Q > K$, there is too much product, and the equilibrium shifts to the left.



If $Q < K$, there is too much reactant, and the equilibrium shifts to the right.



Equilibrium

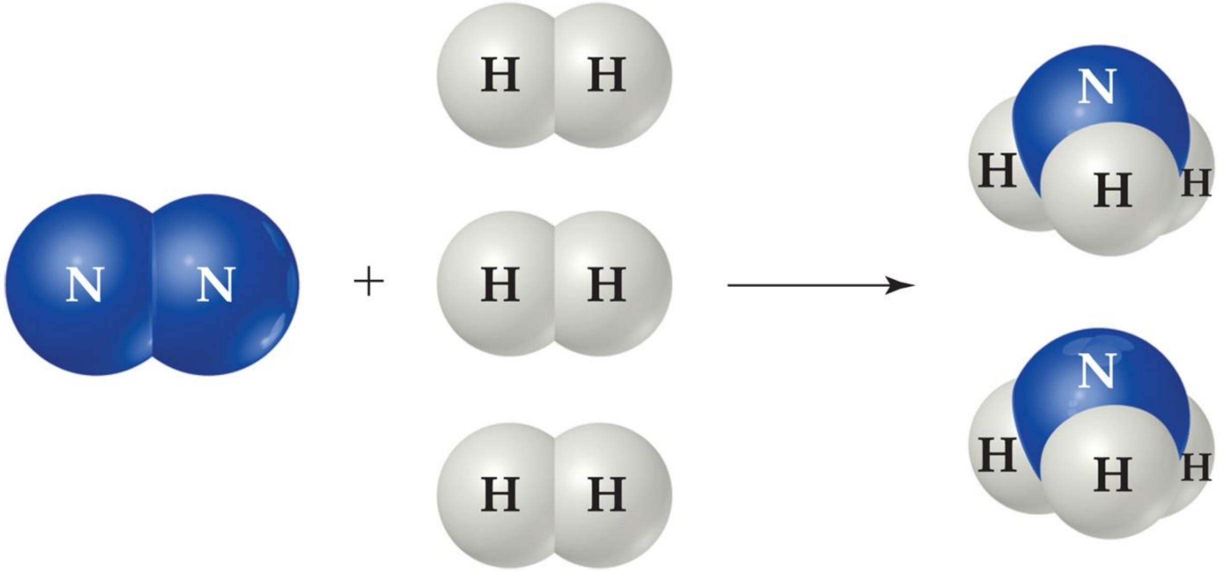
Le Châtelier's Principle

Le Châtelier's Principle

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

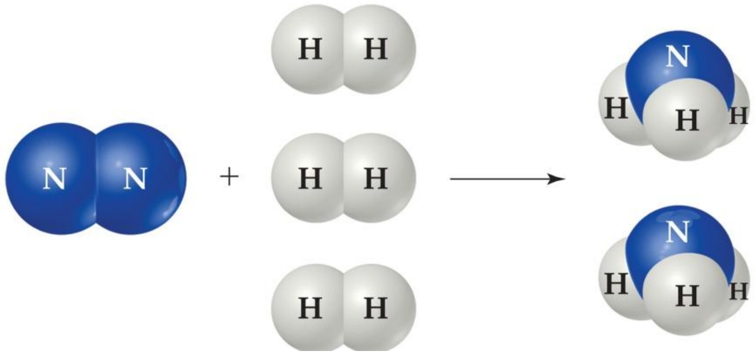
The Haber Process

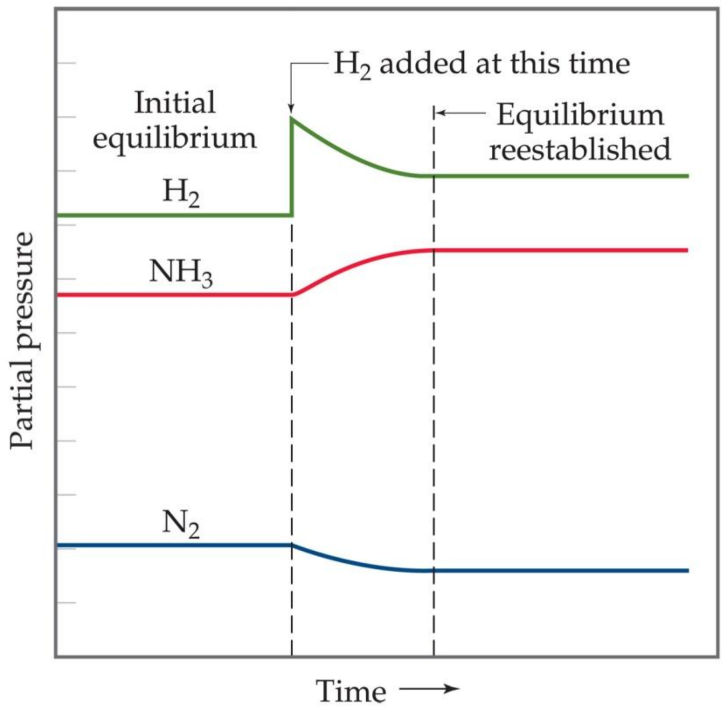
The transformation of nitrogen and hydrogen into ammonia (NH_3) is of tremendous significance in agriculture, where ammonia-based fertilizers are of utmost importance.



Equilibrium

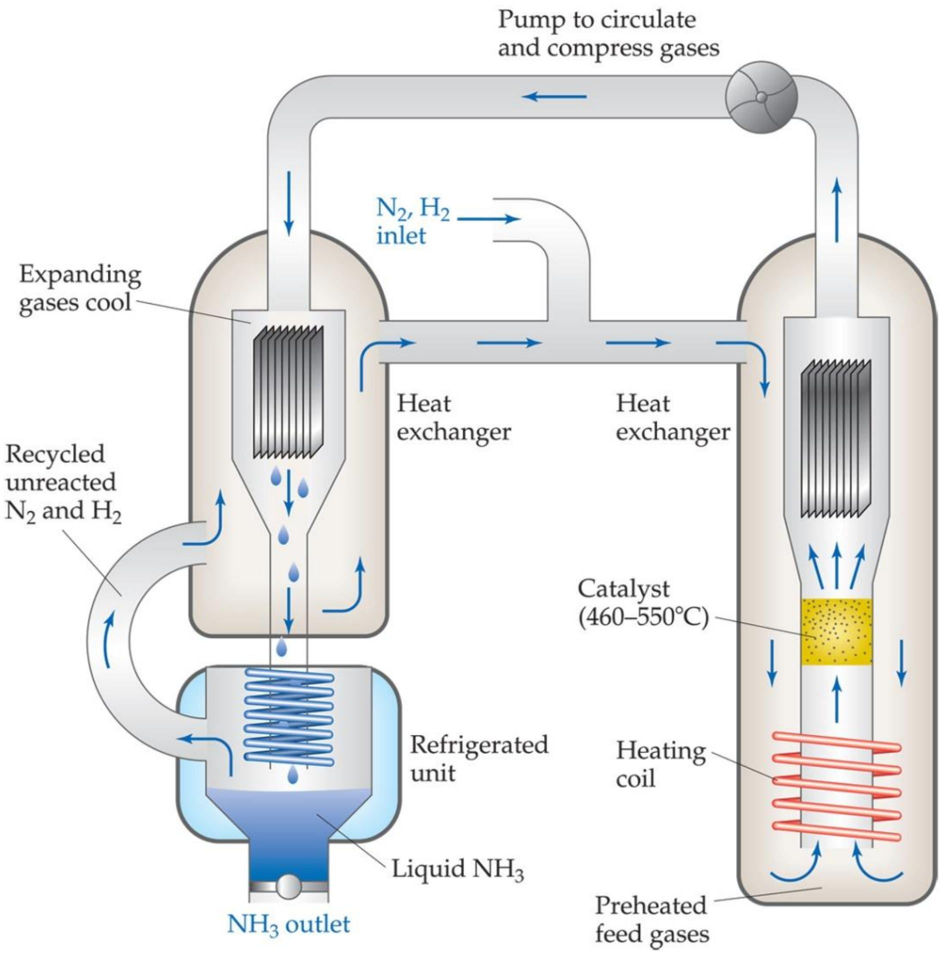
The Haber Process





If H_2 is added to the system, N_2 will be consumed and the two reagents will form more NH_3.

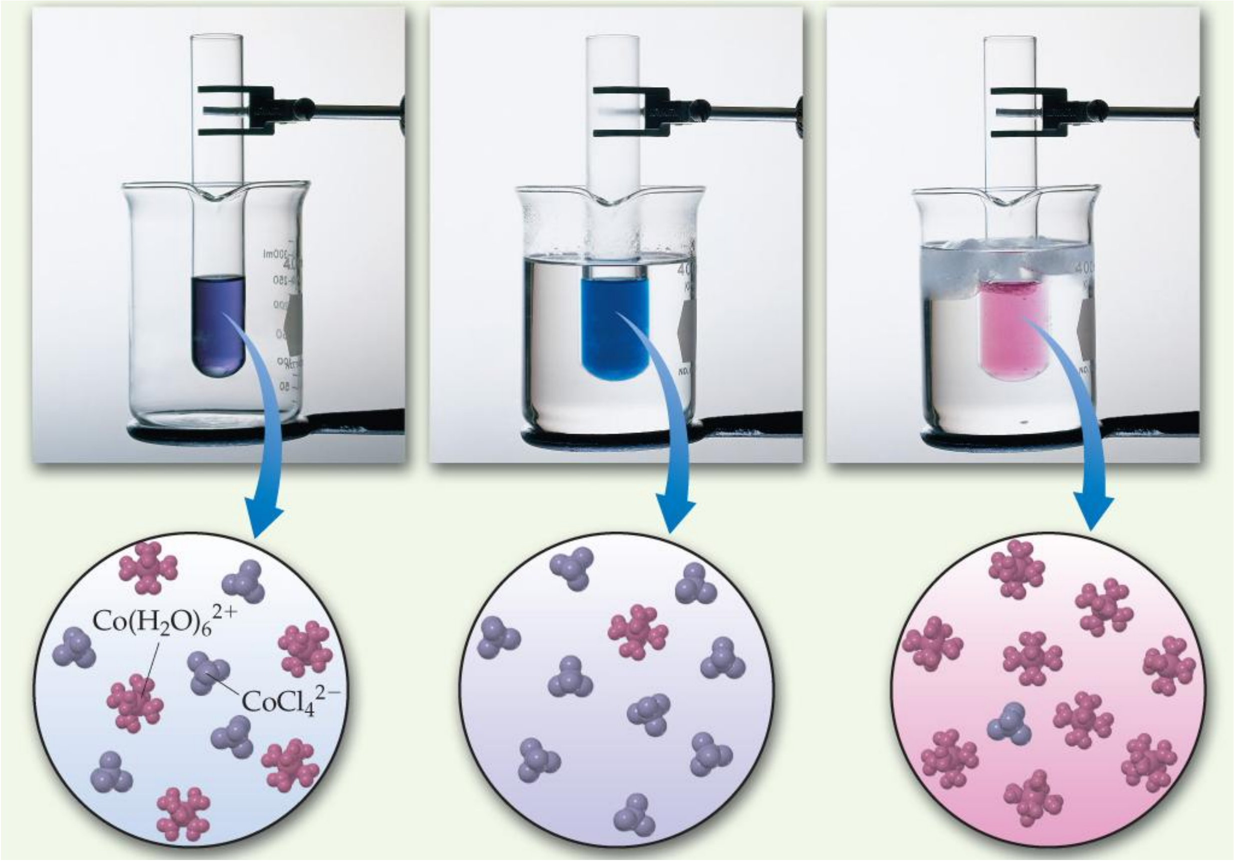
The Haber Process



This apparatus helps push the equilibrium to the right by removing the ammonia (NH_3) from the system as a liquid.

The Effect of Changes in Temperature

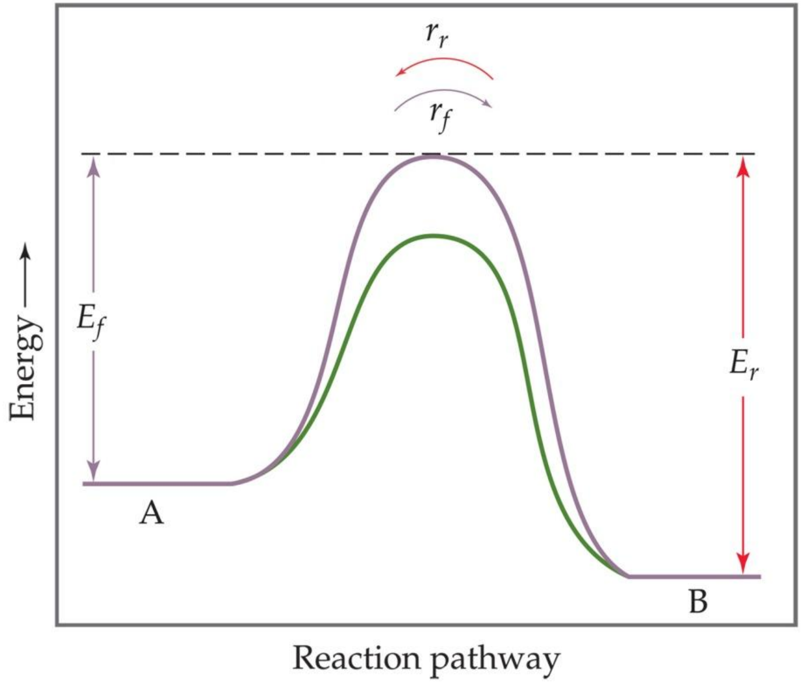
$Co(H_2O)_6^{2+}{}_{(aq)} + 4\ Cl_{(aq)}$ Photo - JPEG decompressor are needed to see this picture. $CoCl_{4\ (aq)} + 6\ H_2O_{\ (l)}$



Equilibrium

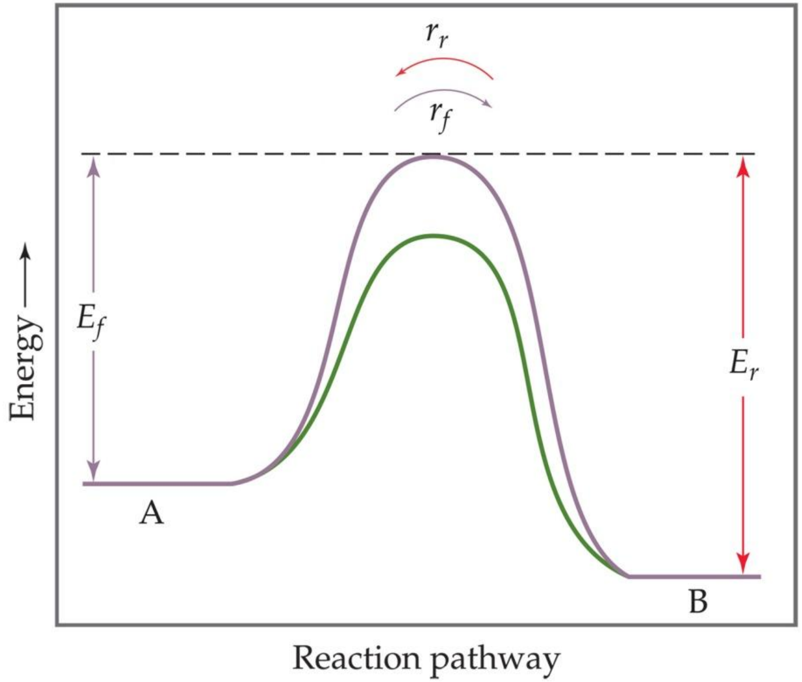
Catalysts

Catalysts



Catalysts increase the rate of both the forward *and* reverse reactions.

Catalysts



When one uses a catalyst, equilibrium is achieved faster, but the equilibrium composition remains unaltered.