

Chemical Kinetics and Equilibrium

Part 2: Chemical Equilibrium

David A. Katz

Department of Chemistry
Pima Community College
Tucson, AZ USA

The Concept of Equilibrium

Kinetics applies to the *speed* of a reaction, the concentration of product appearing (or of reactant disappearing) per unit time

Equilibrium applies to the *extent* of a reaction, the concentration of product that has appeared given unlimited time, or when no further macroscopic change occurs.

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

The Cobalt(II) Chloride Equilibrium



Solution of cobalt(II) chloride in dilute hydrochloric acid.



Solution in an ice bath.



Solution in a boiling water bath.

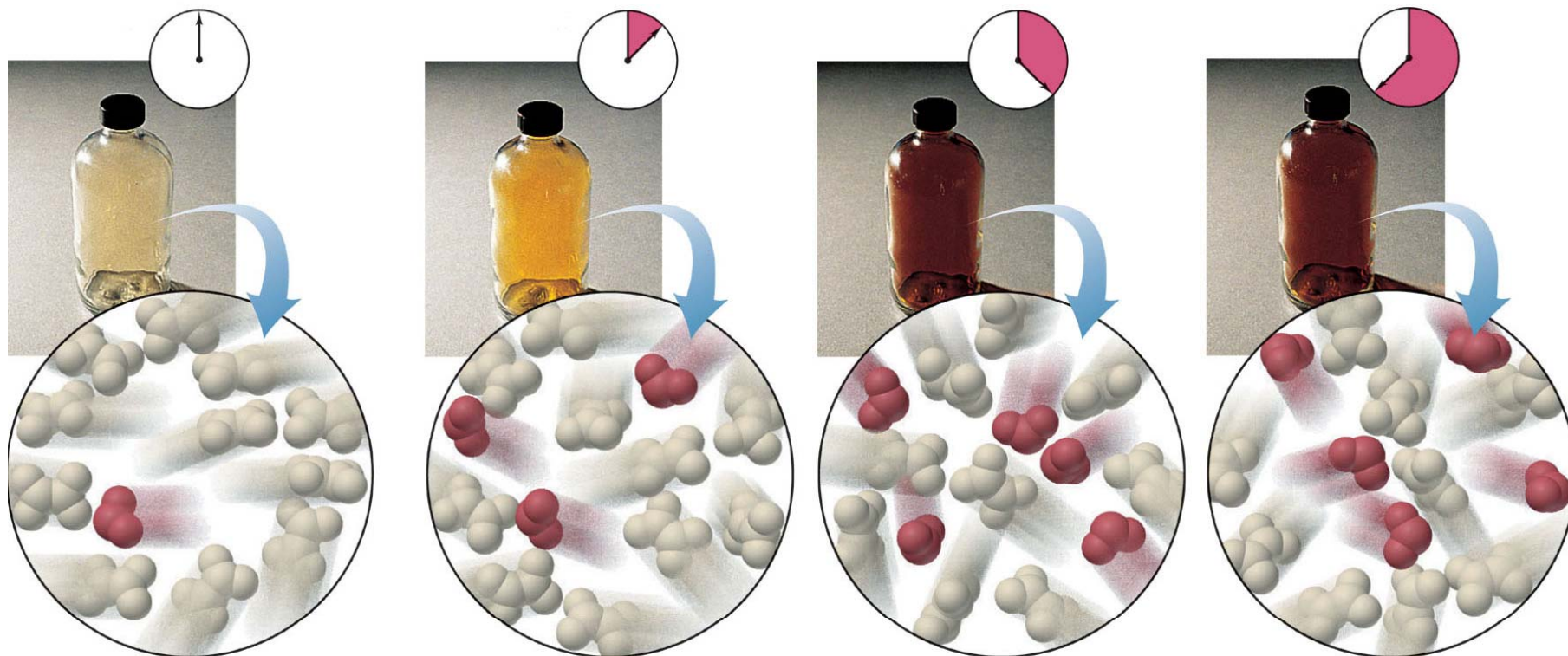


Solution after adding excess hydrochloric acid.



Solution after adding excess water.

The equilibrium system

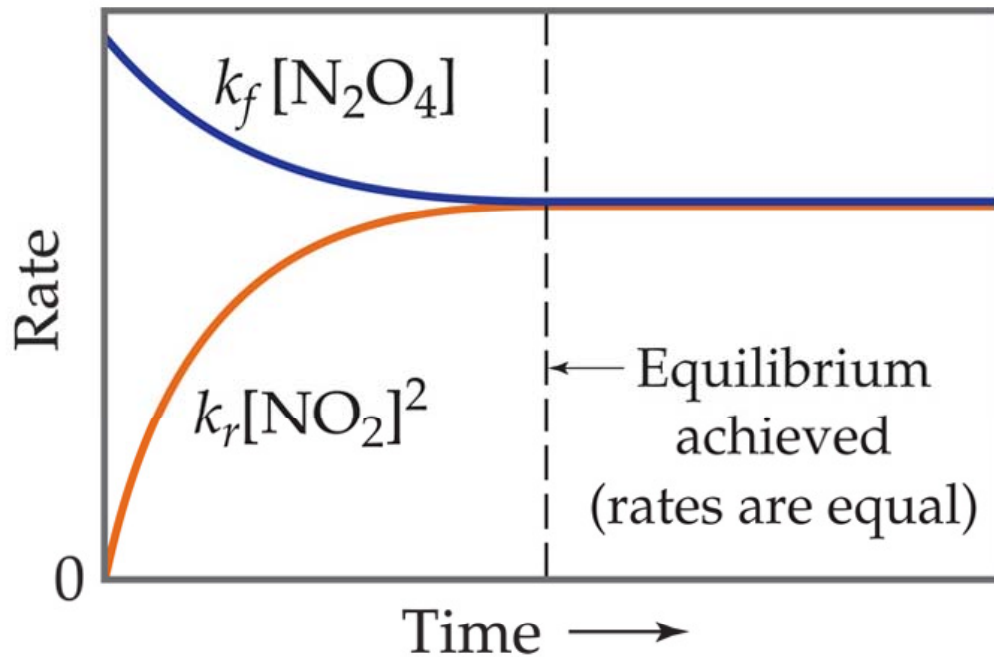


Initially, N_2O_4 (colorless) is added to the reaction container

As the system moves toward an equilibrium condition, the color changes as more NO_2 (red-brown) is formed

When equilibrium is reached, the numbers of N_2O_4 and NO_2 molecules is constant and the color remains unchanged

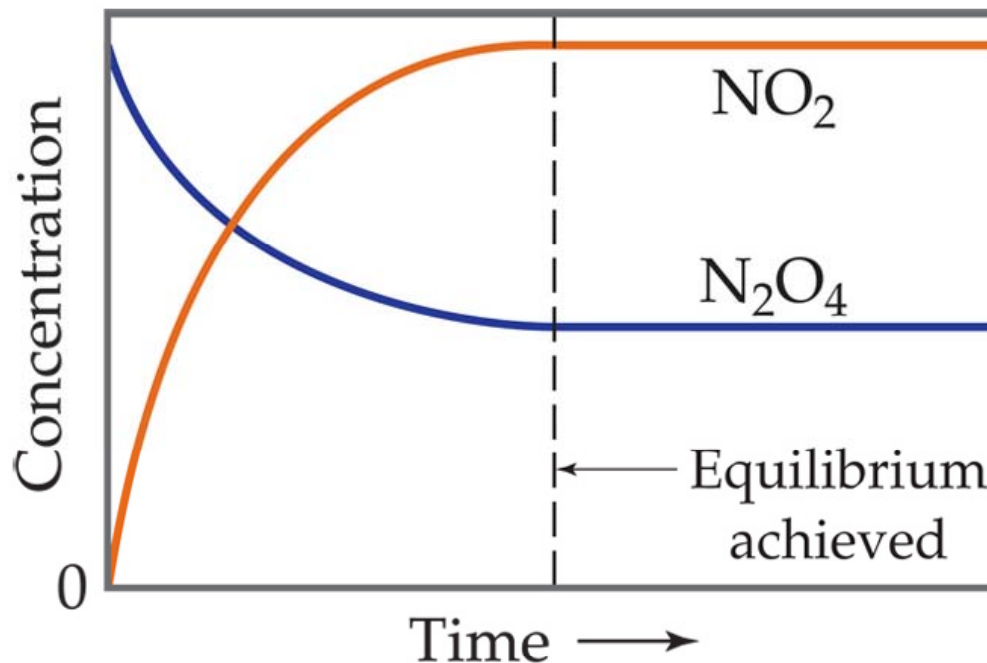
The Concept of Equilibrium



- 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

A system at equilibrium is *dynamic* on the molecular level, that is, both the forward and the reverse reactions are still taking place at the same rate.

$$\text{rate}_{\text{forward}} = \text{rate}_{\text{backward}}$$

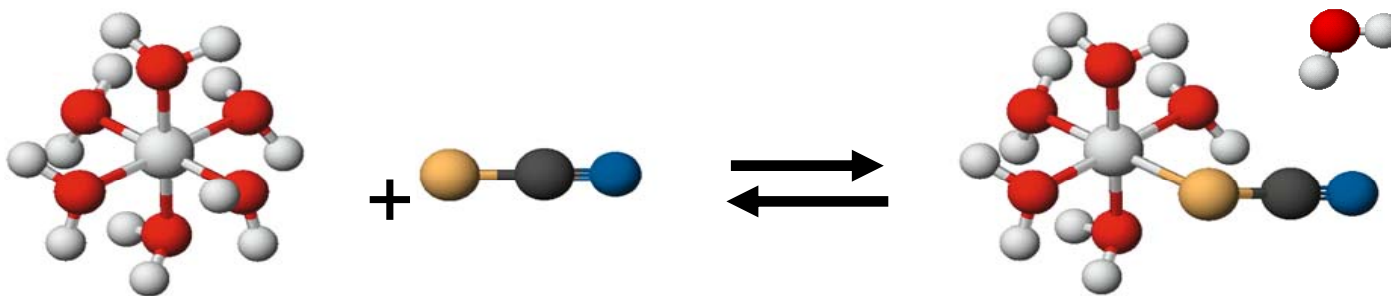
No net change is observed because changes in one direction are balanced by changes in the other.

To show an equilibrium system, we write its equation with a double arrow



Chemical Equilibrium

Iron(III) and thiocyanate



The Equilibrium Constant

The Equilibrium Constant

- Forward reaction:



- Rate law:

$$\text{Rate} = k_f [\text{N}_2\text{O}_4]$$

- Reverse reaction:



- Rate law:

$$\text{Rate} = k_r [\text{NO}_2]^2$$

The Equilibrium Constant

- At equilibrium

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

- Substitute the rate equations

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

- Rewriting this, it becomes

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

The Equilibrium Constant

The ratio of the rate constants is a constant at that temperature, so the constants are combined into a single constant, and the expression becomes

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

The Equilibrium Constant

- To generalize this expression, consider the reaction



- The equilibrium expression for this reaction would be

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

- This equation is known as the **Law of Mass Action**

The Equilibrium Constant

- For any reaction of the form:



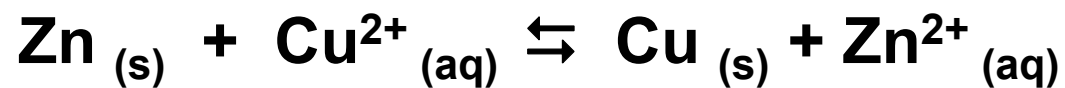
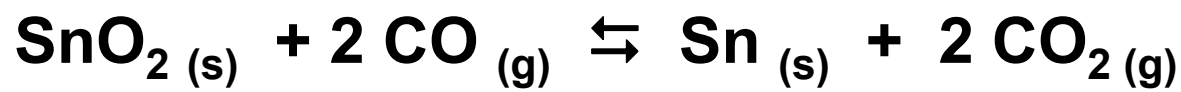
- The equilibrium expression is $K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

The values of a, b, c, and d are those of the coefficients in the balanced chemical equation.

Note that this is *equilibrium*, not *kinetics*.

Equilibrium is a State Function, that is, the value of K_c depends on the concentrations of the reactants and the products.

What Are the Equilibrium Expressions for These Equilibria?



The Equilibrium Constant

Because 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 to solve for P, we get

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

Note that n/V is moles/liter or Molarity, so

$$P = MRT$$

Relationship between K_c and K_p

Substituting for P into the expression for K_p for each substance, the relationship between K_c and K_p becomes

$$K_p = \frac{(M_C RT)^c (M_D RT)^d}{(M_A RT)^a (M_B RT)^b}$$

Factor out the RT terms to get

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

Where:

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

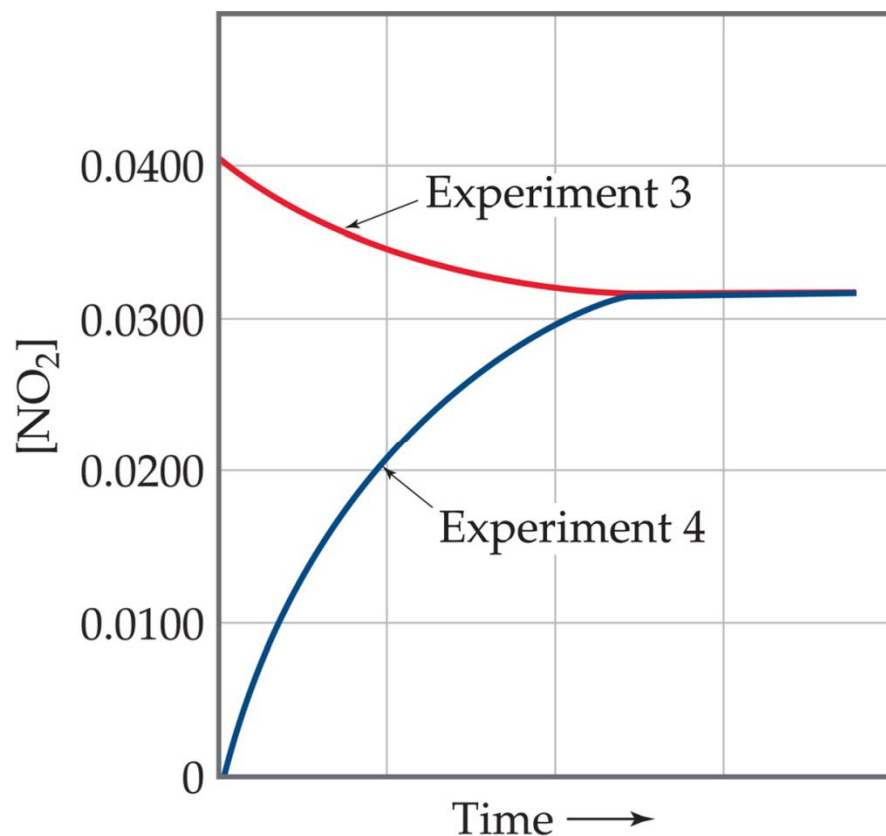
Equilibrium Can Be Reached from Either Direction

Experiment	Initial N ₂ O ₄ Concentration (M)	Initial NO ₂ Concentration (M)	Equilibrium N ₂ O ₄ Concentration (M)	Equilibrium NO ₂ Concentration (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

Examining the data in the table, above, the equilibrium ratio of $[\text{NO}_2]^2$ to $[\text{N}_2\text{O}_4]$ remains constant at this temperature no matter what the initial concentrations of NO₂ and N₂O₄ are.

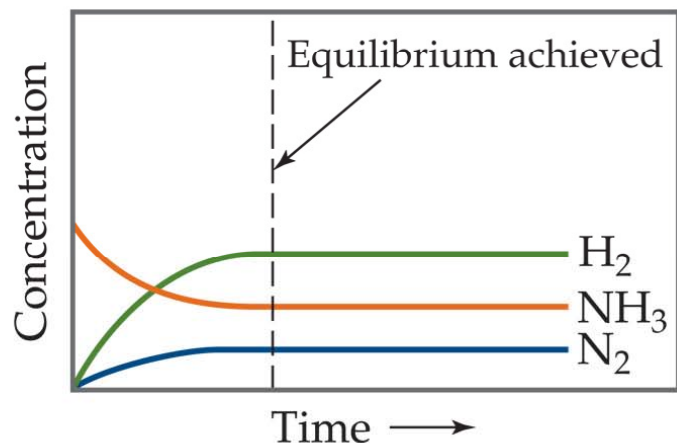
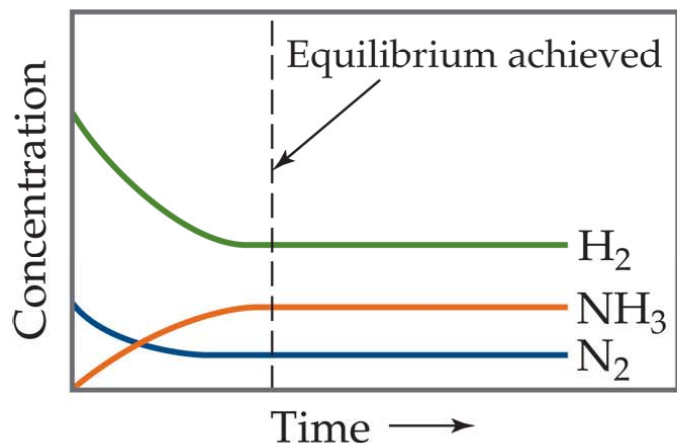
Note: There must be sufficient quantities of compounds to reach an equilibrium condition

Equilibrium Can Be Reached from Either Direction



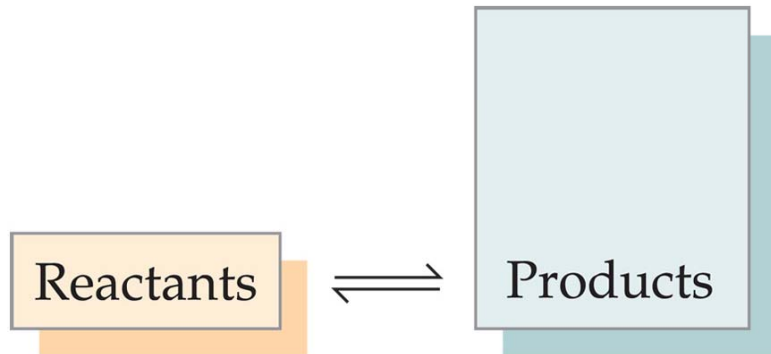
This is the data from the last two trials from the table on the previous slide.

Equilibrium Can Be Reached from Either Direction



It does not matter whether we start with N₂ and H₂ or whether we start with NH₃. We will have the same proportions of all three substances at equilibrium at the specified temperature.

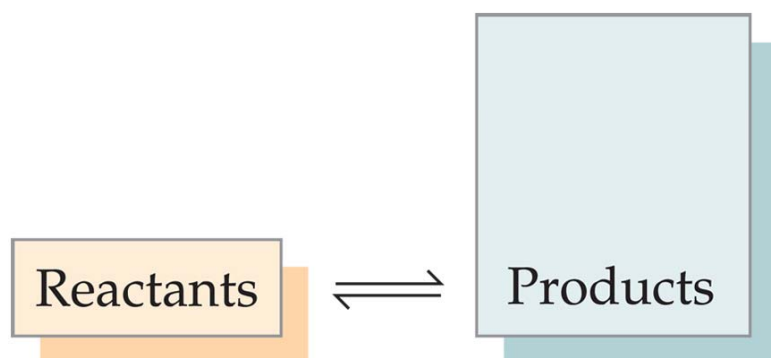
What Does the Value of K Mean?



(a) $K \gg 1$

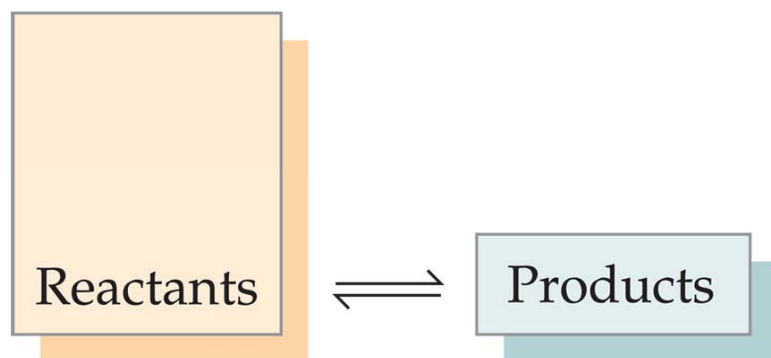
- If $K \gg 1$, the reaction is *product-favored*; product predominates at equilibrium.

What Does the Value of K Mean?



(a) $K \gg 1$

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



(b) $K \ll 1$

- If $K \ll 1$, 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.



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

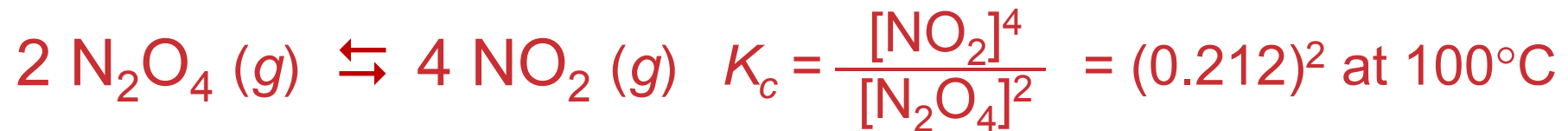
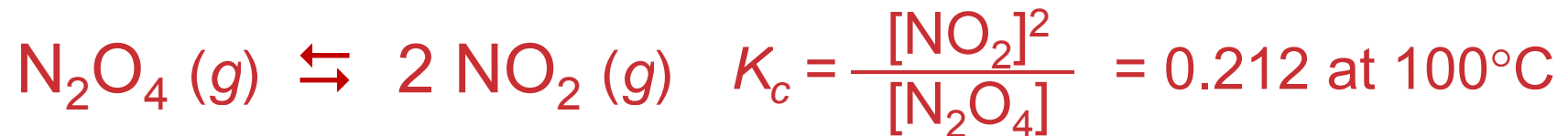


$$K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = \frac{1}{0.212}$$

$$= 4.72 \text{ at } 100^\circ\text{C}$$

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.



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.

Heterogeneous Equilibria

The Concentrations of Solids and Liquids Are Considered to be Constant

Both can be obtained by dividing 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 Considered to be Constant

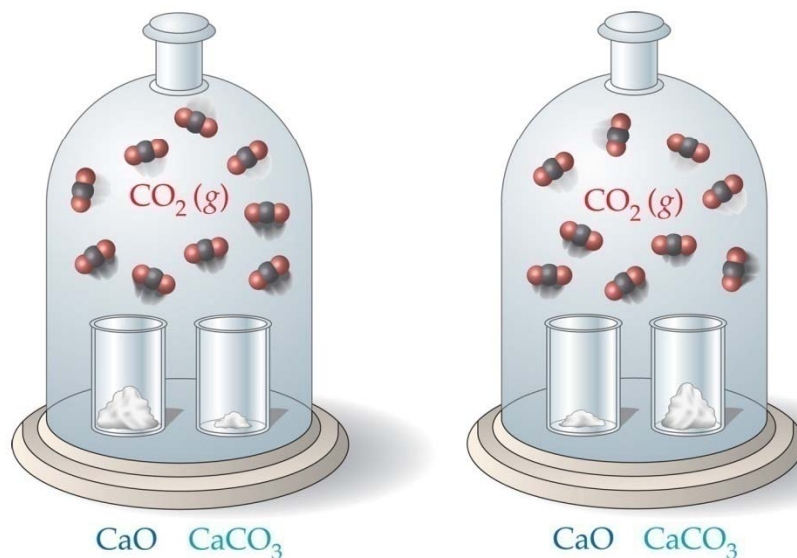
Therefore, the concentrations of solids and liquids do not appear in the equilibrium expression



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



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

Equilibrium Calculations

A closed system initially containing

$1.000 \times 10^{-3} \text{ M H}_2$ and $2.000 \times 10^{-3} \text{ M I}_2$

At 448°C is allowed to reach equilibrium. Analysis of the equilibrium mixture shows that the concentration of HI is $1.87 \times 10^{-3} \text{ M}$. Calculate K_c at 448°C for the reaction taking place, which is



What Do We Know?

(This is our initial data)

	$[\text{H}_2], M$	$[\text{I}_2], M$	$[\text{HI}], M$
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change			
At equilibrium			1.87×10^{-3}

Determine changes:
[HI] Increases by $1.87 \times 10^{-3} M$

	$[H_2], M$	$[I_2], M$	$[HI], M$
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...

	$[\text{H}_2], M$	$[\text{I}_2], M$	$[\text{HI}], M$
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 substitute the concentrations into the equilibrium constant expression

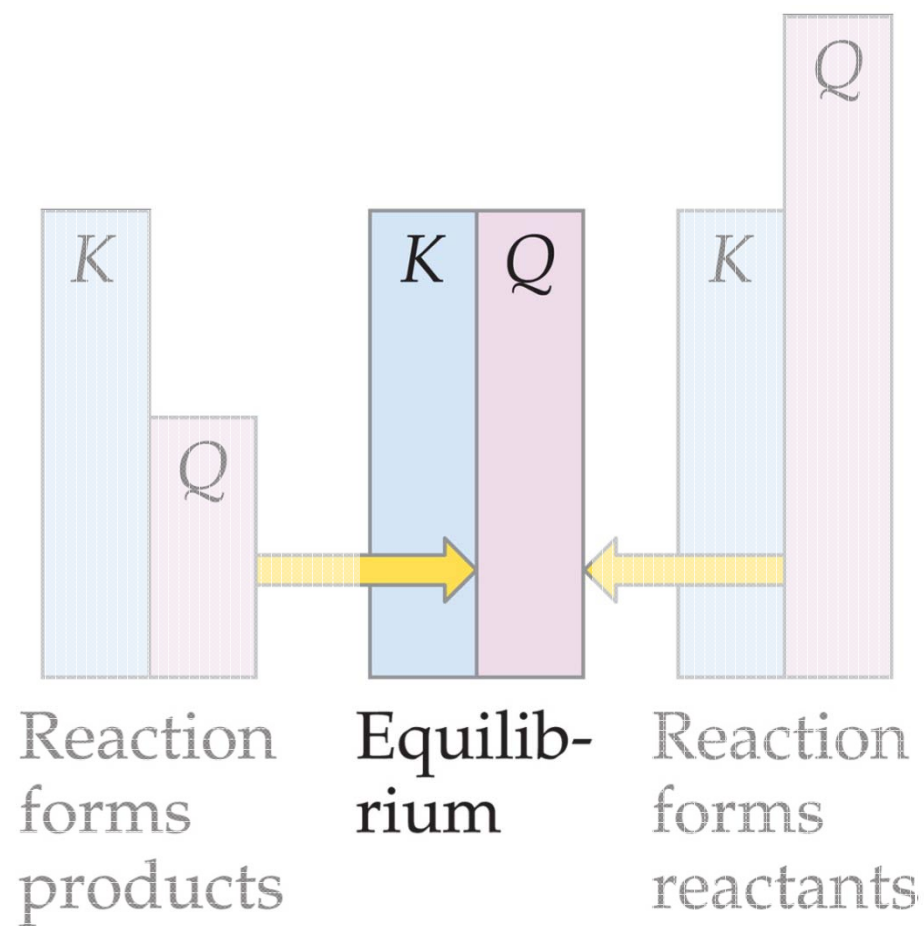
$$\begin{aligned}K_c &= \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} \\&= \frac{(1.87 \times 10^{-3})^2}{(6.5 \times 10^{-5})(1.065 \times 10^{-3})} \\&= 51\end{aligned}$$

Note that the equilibrium value has no units

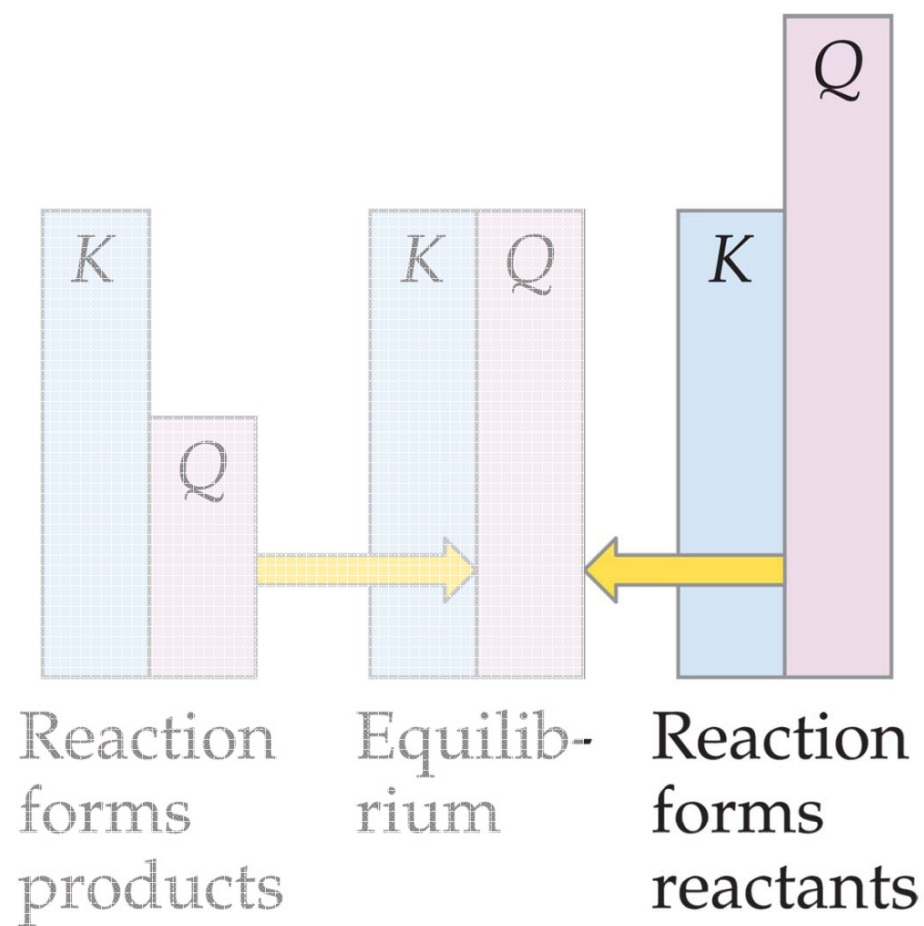
The Reaction Quotient (Q)

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

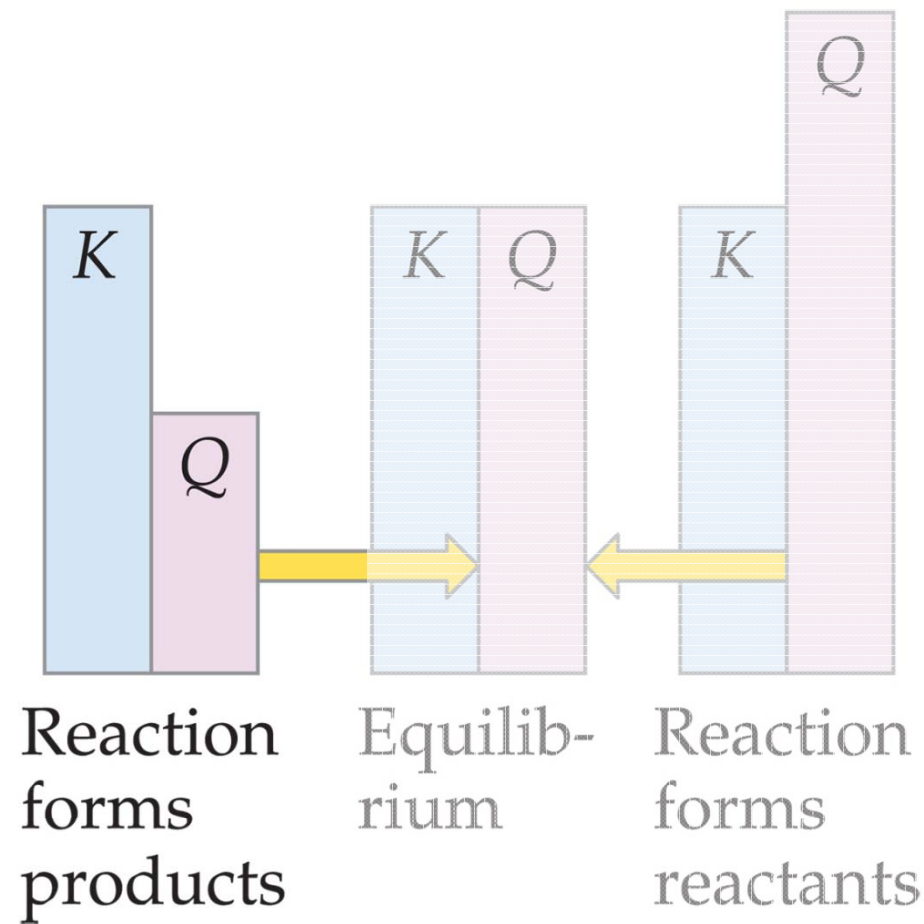
If $Q = K$,
the system is at equilibrium.



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.



Le Châtelier's Principle

Le Châtelier's Principle

Henri Louis Le Châtelier (1850-1936)

In 1884, Le Chatelier stated:

Any system in stable chemical equilibrium, subjected to the influence of an external cause which tends to change either its temperature or its condensation (pressure, concentration, number of molecules in unit volume), either as a whole or in some of its parts, can only undergo such internal modifications as would, if produced alone, bring about a change of temperature or of condensation of opposite sign to that resulting from the external cause.

In 1888, he restated this as:

Every change of one of the factors of an equilibrium occasions a rearrangement of the system in such a direction that the factor in question experiences a change in a sense opposite to the original change.



Le Châtelier's Principle

Our modern statement is:

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.

Le Châtelier's Principle

Effect of a change in T:

change in K

therefore change in P or concentrations at equilibrium

Change in concentration (Add or take away reactant or product):

K does not change

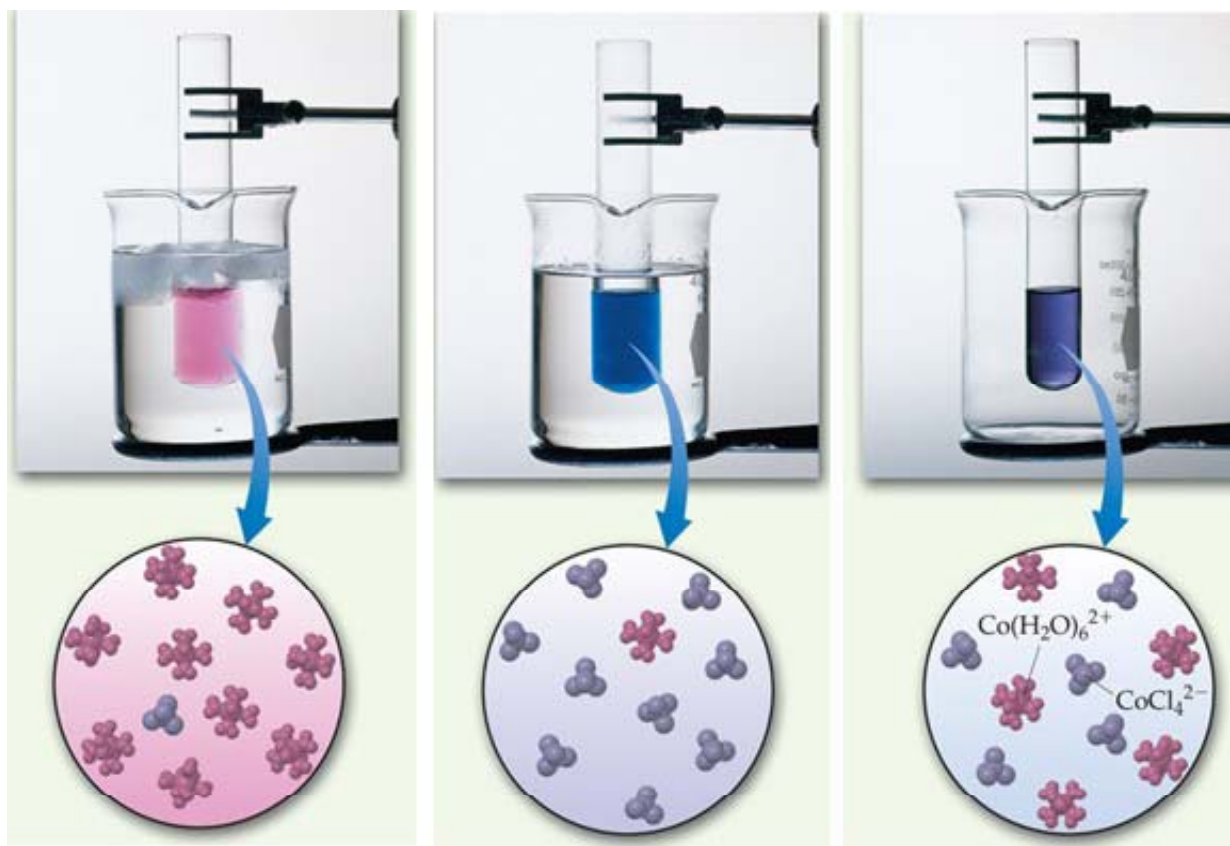
Reaction adjusts to new equilibrium “position”

Use a catalyst:

reaction comes more quickly to equilibrium.

K not changed.

The Effect of Changes in Temperature



Predicting the Effect of a Change in Concentration on the Equilibrium Position

PROBLEM: To improve air quality and obtain a useful product, sulfur is often removed from coal and natural gas by treating the fuel contaminant hydrogen sulfide with O_2 ;



What happens to

- (a) $[H_2O]$ if O_2 is added? (b) $[H_2S]$ if O_2 is added?
(c) $[O_2]$ if H_2S is removed? (d) $[H_2S]$ if sulfur is added?

SOLUTION: Write an expression for Q and compare it to K when the system is disturbed to see in which direction the reaction will progress.

$$Q = \frac{[H_2O]^2}{[H_2S]^2[O_2]}$$

(a) When O_2 is added, the denominator increases, so Q decreases. The reaction must progress to the right to come back to K . Therefore **$[H_2O]$ increases.**

Predicting the Effect of a Change in Concentration on the Equilibrium Position

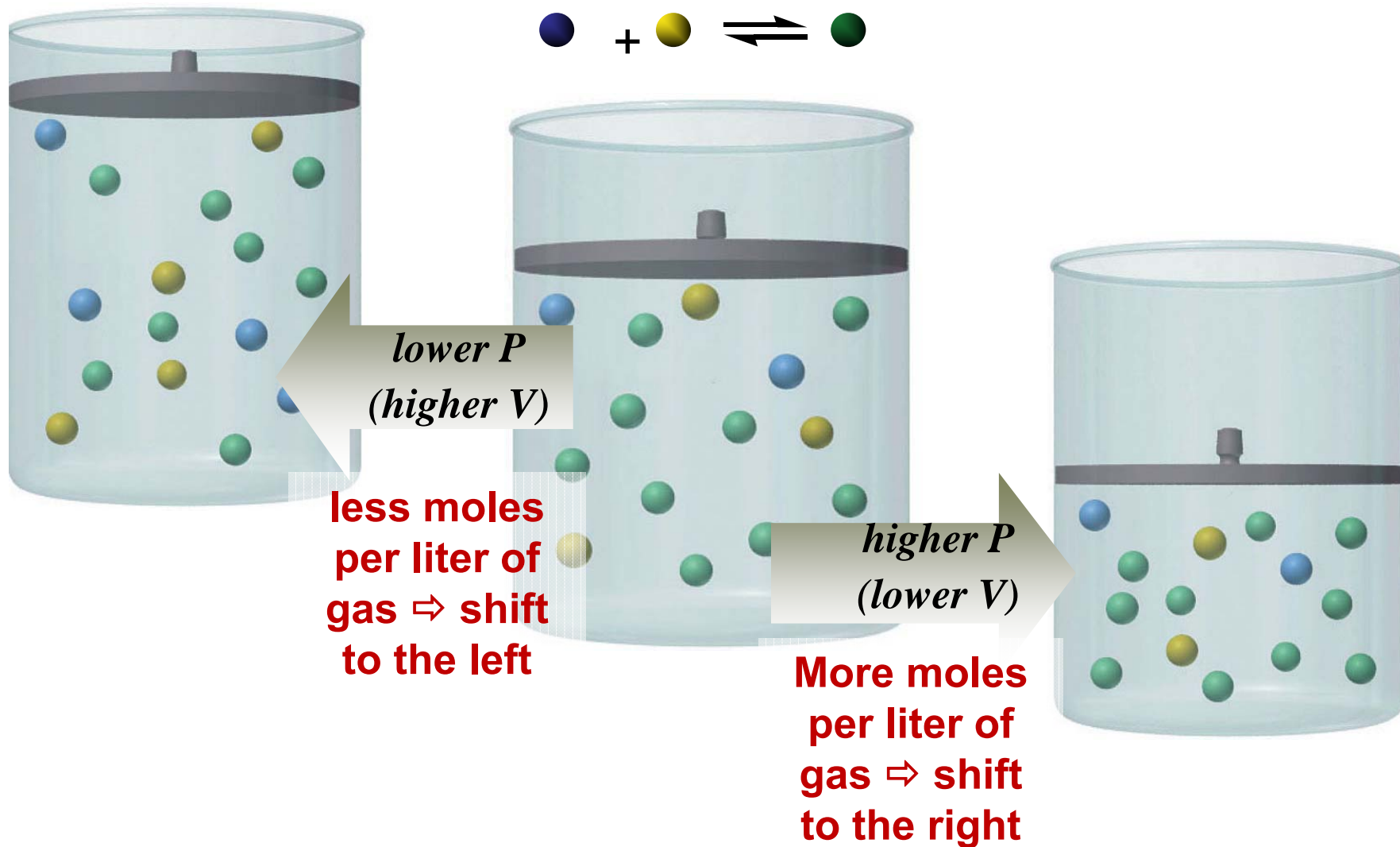
$$Q = \frac{[\text{H}_2\text{O}]^2}{[\text{H}_2\text{S}]^2[\text{O}_2]}$$

(b) When O_2 is added, the denominator increases and Q decreases. The reaction must progress to the right to come back to K . Therefore **$[\text{H}_2\text{S}]$ decreases.**

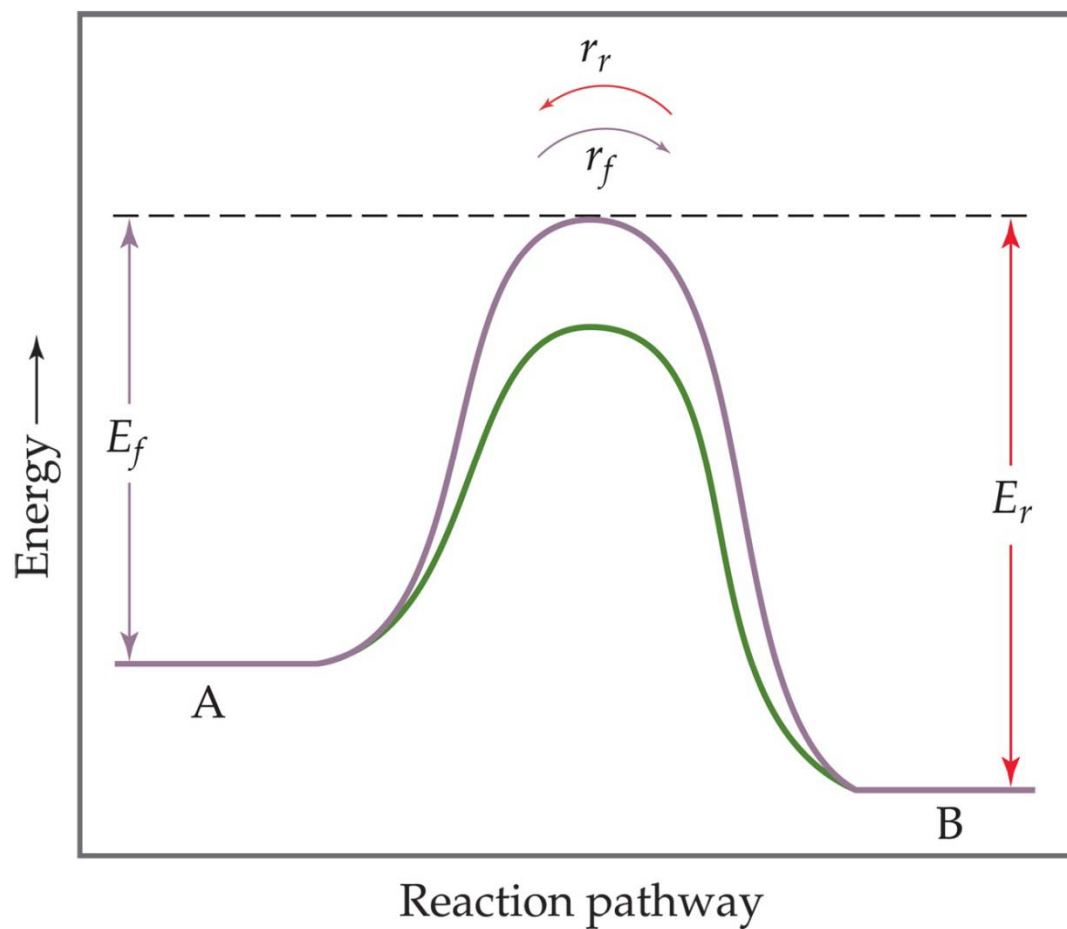
(c) When H_2S is removed, the denominator decreases and Q increases. The reaction must progress to the left to come back to K . Therefore **$[\text{O}_2]$ increases.**

(d) Sulfur is not part of the Q (K) expression because it is a solid. Therefore, as long as some sulfur is present the reaction is unaffected. **$[\text{H}_2\text{S}]$ is unchanged.**

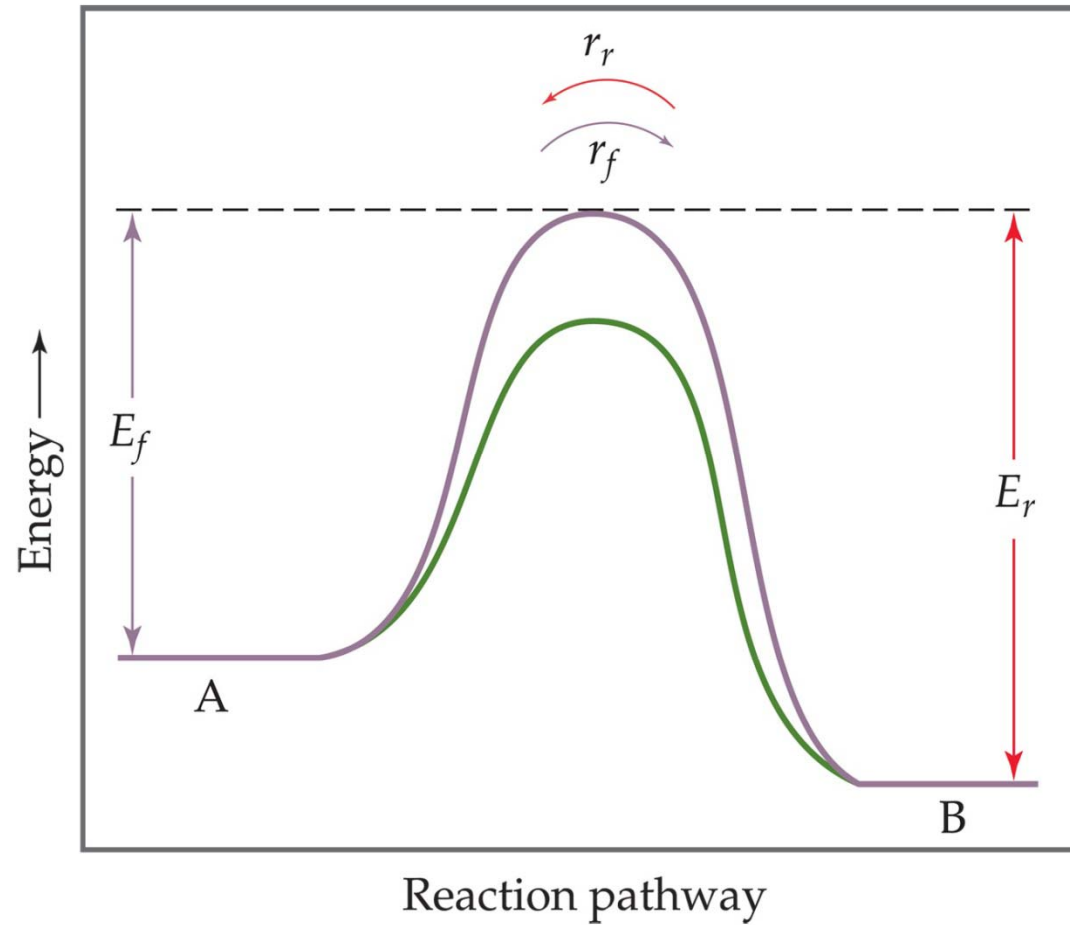
The effect of pressure (volume) on an equilibrium system



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



Equilibrium is achieved faster, but the equilibrium composition remains unaltered.



The Effect of Various Changes on an Equilibrium System

Disturbance	Net Direction of Reaction	Effect on Value of K
Concentration		
Increase [reactant]	Toward formation of product	None
Decrease [reactant]	Toward formation of reactant	None
Increase [product]	Toward formation of reactant	None
Decrease [product]	Toward formation of product	None
Pressure		
Increase P (decrease V)	Toward formation of fewer moles of gas	None
Decrease P (increase V)	Toward formation of more moles of gas	None
Increase P (add inert gas, no change in V)	None; concentrations unchanged	None
Temperature		
Increase T	Toward absorption of heat	Increases if $\Delta H_{\text{rxn}}^0 > 0$ Decreases if $\Delta H_{\text{rxn}}^0 < 0$
Decrease T	Toward release of heat	Increases if $\Delta H_{\text{rxn}}^0 < 0$ Decreases if $\Delta H_{\text{rxn}}^0 > 0$
Catalyst added	None; forward and reverse equilibrium attained sooner; rates increase equally	None

The Haber-Bosch Process

The Haber-Bosch process is the transformation of atmospheric nitrogen and hydrogen into ammonia (NH₃) for the production of ammonia-based fertilizers.

Initially developed by Fritz Haber (1868-1934) in 1905 by passing a mixture of N₂ and H₂ over an iron catalyst at 1000°C. Later, Haber modified the process by increasing the pressure to 150-200 atm. over a catalyst at 500°C.

In 1908, BASF acquired the process and assigned Carl Bosch (1874-1940) the task of scaling the process up to industrial quantities. Bosch's modifications of the Haber process provided ammonium sulphate for use as a fertilizer for the soil.



In 1914, Germany's supplies of sodium and potassium nitrates for making explosives were blocked off by the Allied forces. Using the Haber-Bosch process, they were able to produce explosives, prolonging World War I.

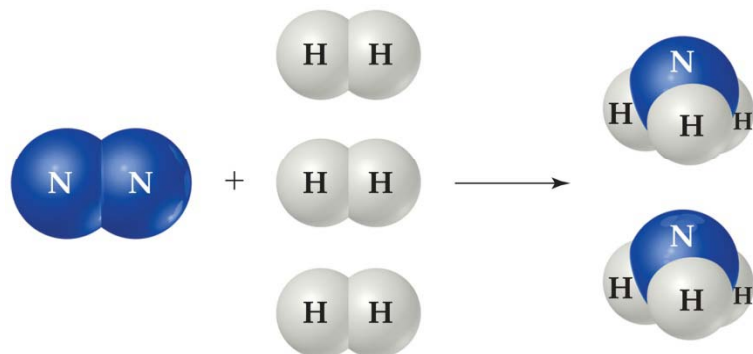


Fritz Haber

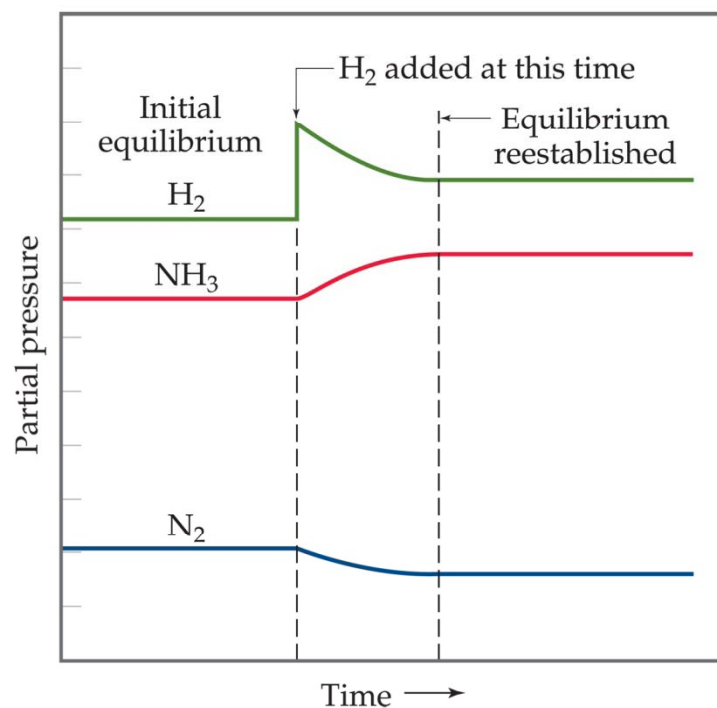


Carl Bosch

The Haber-Bosch Process

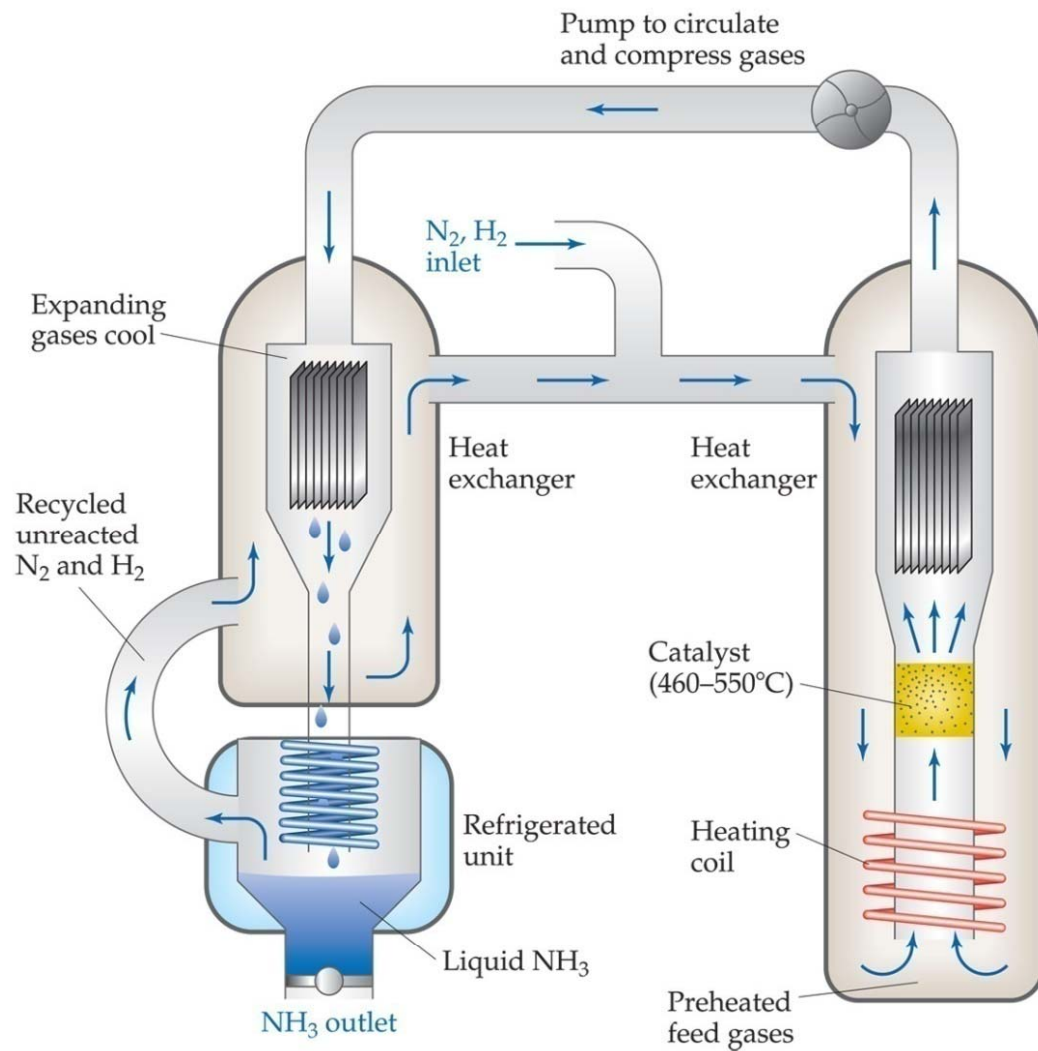


$$K = 3.5 \times 10^8 \text{ at } 298 \text{ K}$$



If H₂ is added to the system, N₂ will be consumed and the two reagents will form more NH₃.

The Haber-Bosch Process



This apparatus helps push the equilibrium to the right by removing the ammonia (NH₃) from the system as a liquid.

Effect of Temperature on K_c for Ammonia Synthesis

T (K)	K_c
200.	7.17×10^{15}
300.	2.69×10^8
400.	3.94×10^4
500.	1.72×10^2
600.	4.53×10^0
700.	2.96×10^{-1}
800.	3.96×10^{-2}

Percent yield of ammonia vs. temperature (°C) at five different operating pressures

