

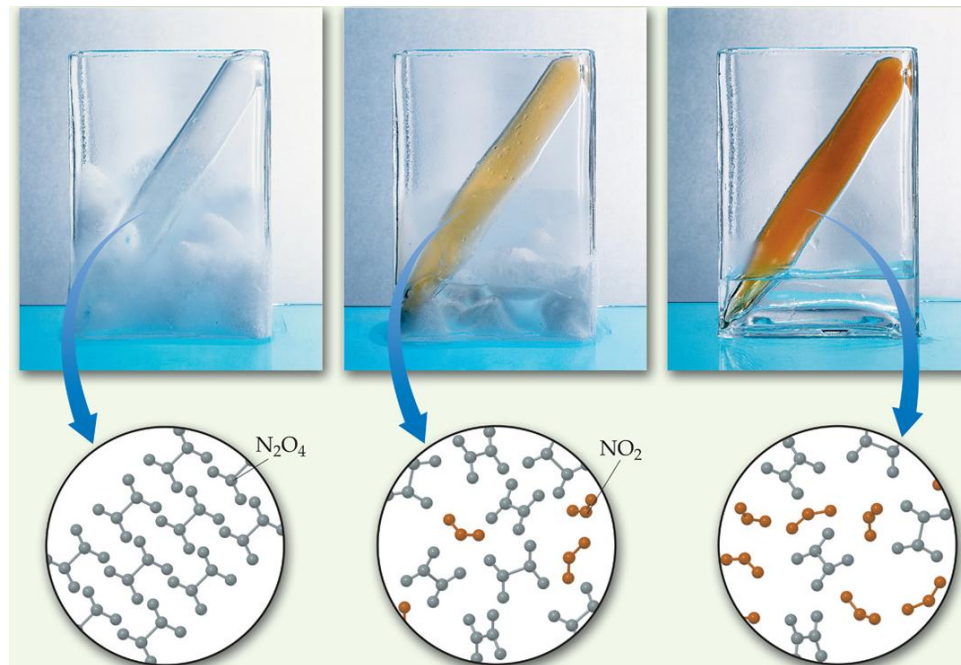
CHEMISTRY

The Central Science
8th Edition

Chapter 15 Chemical Equilibrium

Kozet YAPSAKLI

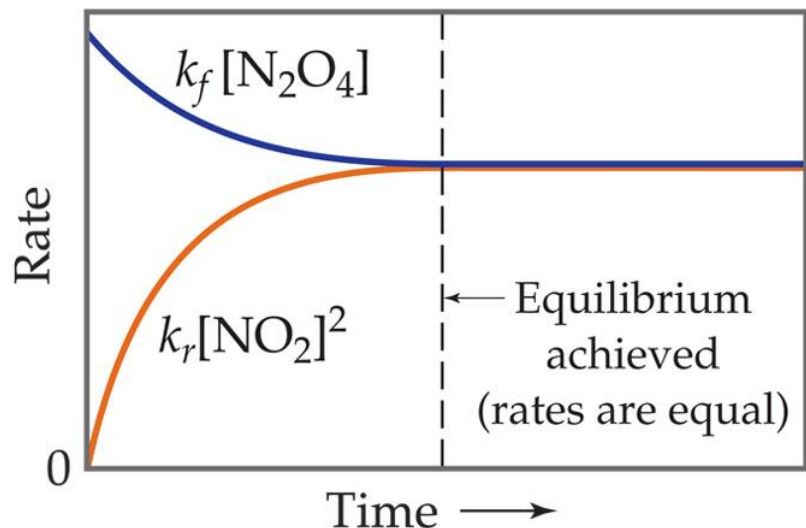
The Concept of Equilibrium



- Chemical equilibrium is the point at which the concentrations of all species are constant.
- Chemical equilibrium occurs when opposing reactions are proceeding at equal rates.



The Concept of Equilibrium

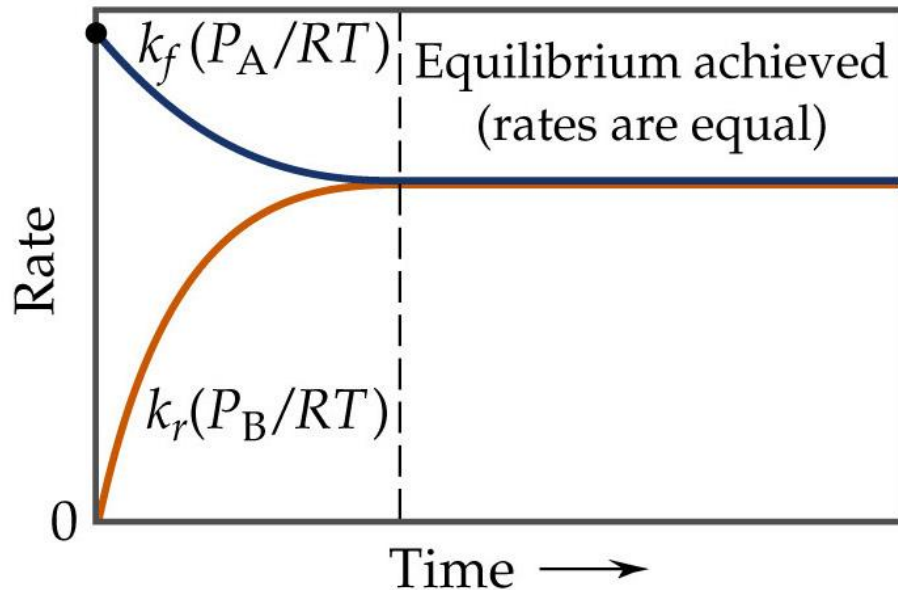
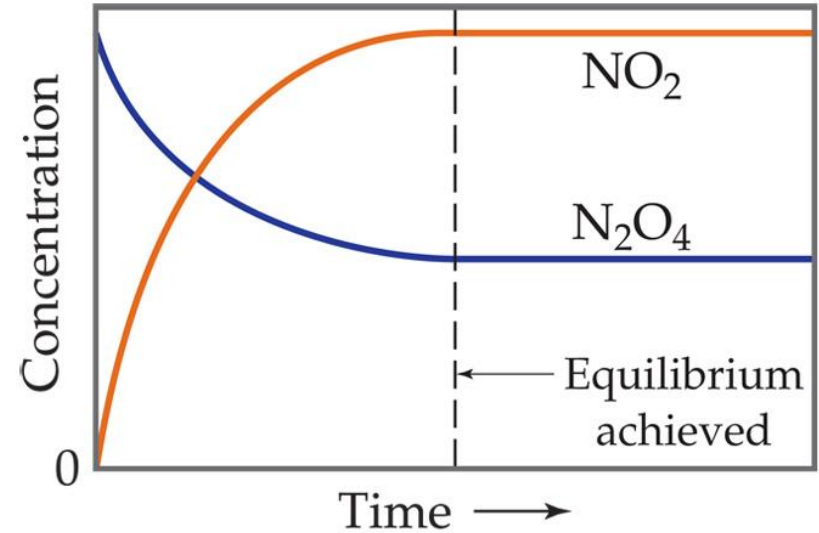


- As a system approaches *equilibrium*, both the *forward* and *reverse* reactions are occurring.
- At equilibrium, the forward and reverse reactions are proceeding *at the same rate*.



A System at Equilibrium

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



$$\text{Rate} = k_f [A]$$

$$\text{Rate} = k_r [B]$$

$$PV = nRT, \quad \text{so} \quad M = (n/V) = (P/RT)$$

$$\text{Rate} = k_f \frac{P_A}{RT}$$

Equilibrium

- In a system at equilibrium, both the forward and reverse reactions are being carried out; as a result, we write its equation with a double arrow



- Consider

Forward reaction: $A \rightarrow B$ Rate = $k_f [A]$

Reverse reaction: $B \rightarrow A$ Rate = $k_r [B]$

- At equilibrium $k_f [A] = k_r [B]$.



The Equilibrium Constant



The Equilibrium Constant

- Forward reaction:



at equilibrium

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

- Rate law:

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

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

Rewriting this, it becomes

- Reverse reaction:



- Rate law:

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

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

Equilibrium



The Equilibrium Constant

- To generalize this expression, consider the reaction



- The equilibrium expression for this reaction would be

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



The Equilibrium Constant

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

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

From the *ideal gas* law we know that

$$P = \frac{n}{V} RT \qquad K_p = K_c (RT)^{\Delta n}$$

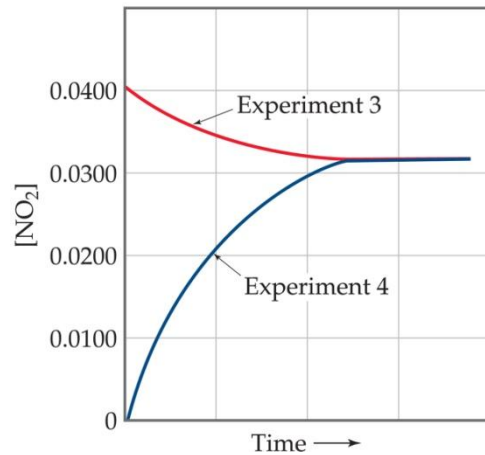
$\Delta n = (\text{moles of gaseous product}) - (\text{moles of gaseous reactant})$

The Equilibrium Constant

- K_{eq} is based on the **molarities of reactants** and products at equilibrium.
- As you can see, the 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 NO_2 and N_2O_4 are.
- The **same equilibrium** is established not matter **how** the reaction is **begun**.

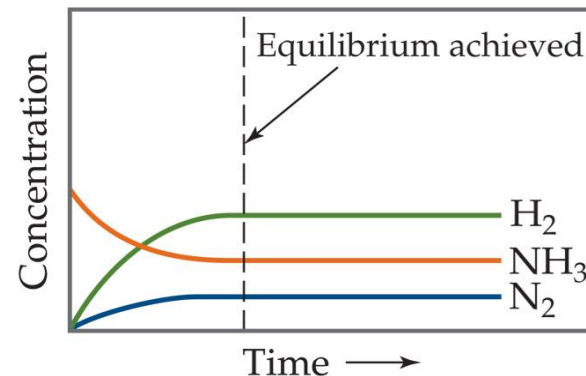
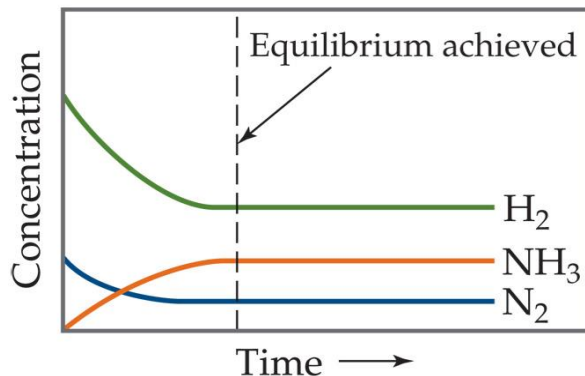
Experiment	Initial N_2O_4 Concentration (M)	Initial NO_2 Concentration (M)	Equilibrium N_2O_4 Concentration (M)	Equilibrium NO_2 Concentration (M)	K_c
1	0.0	0.0200	0.00140	0.0172	0.211
2	0.0	0.0300	0.00280	0.0243	0.211
3	0.0	0.0400	0.00452	0.0310	0.213
4	0.0200	0.0	0.00452	0.0310	0.213

Equilibrium can be reached from either direction

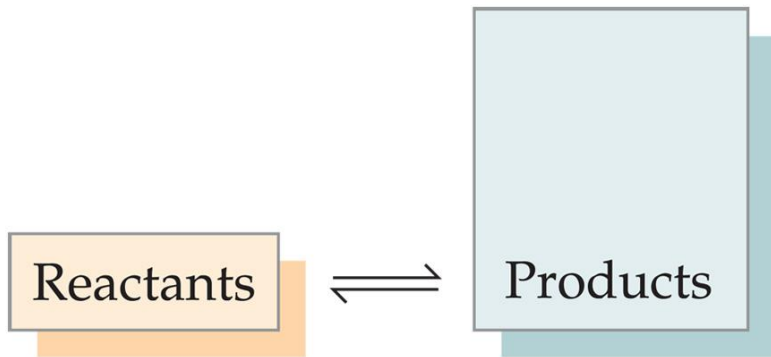


This is the data from the last two trials from the table on the previous slide.

It does not 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.

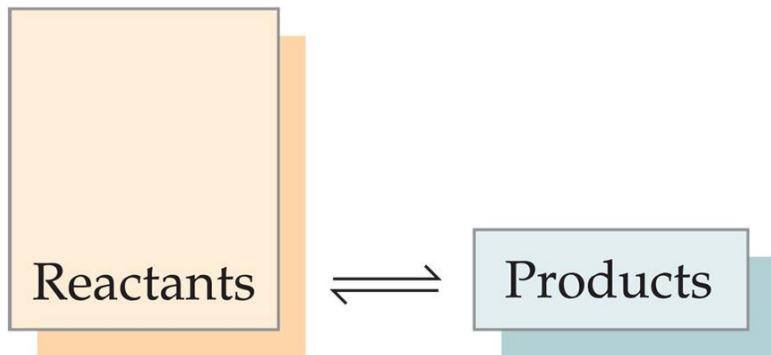


What Does the Value of K Mean?



(a) $K \gg 1$

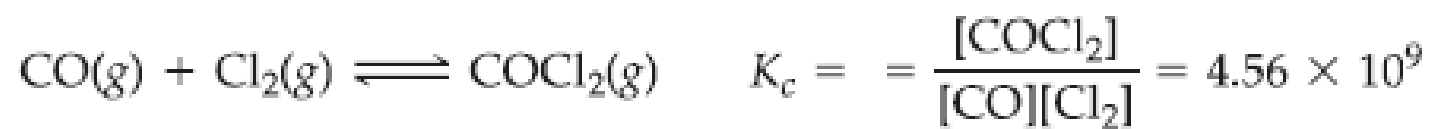
- If $K \gg 1$, the reaction is *product-favored*; product predominates at equilibrium.



(b) $K \ll 1$

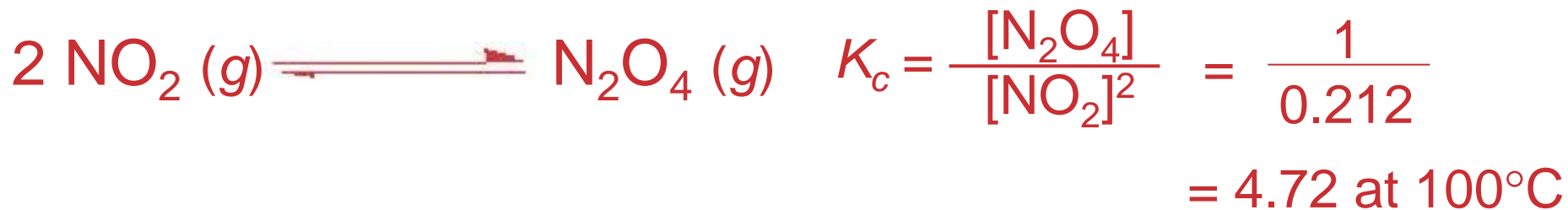
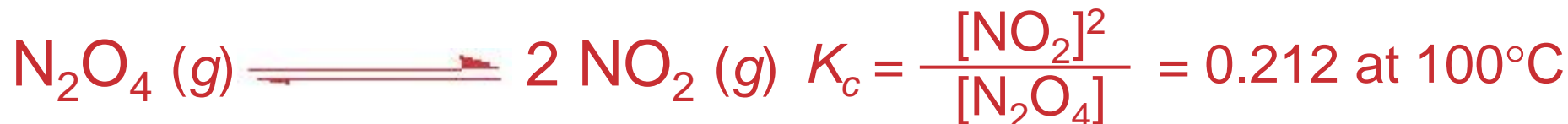
- If $K \ll 1$, the reaction is *reactant-favored*; reactant predominates at equilibrium.





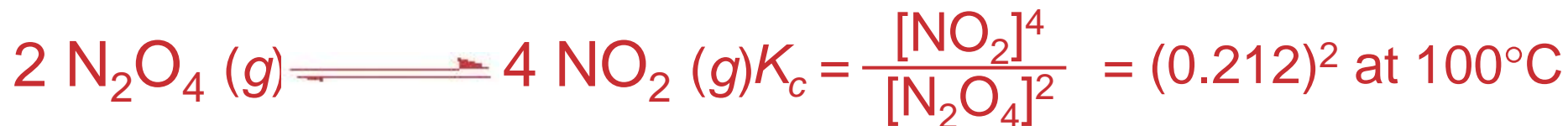
Manipulating Equilibrium Constants

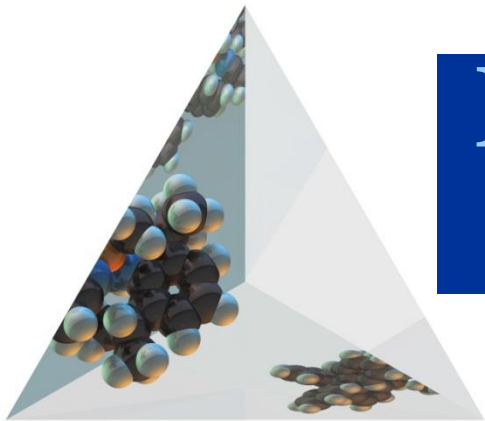
The equilibrium constant of a reaction in the reverse reaction is the reciprocal of the equilibrium constant of the forward reaction.



Manipulating Equilibrium Constants

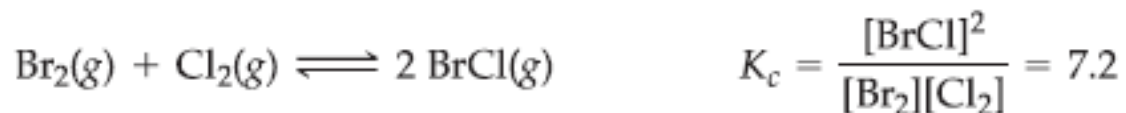
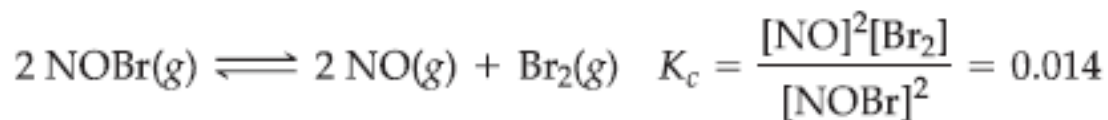
The equilibrium constant of a reaction that has been multiplied by a number is the equilibrium constant raised to a power that is equal to that number.





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.



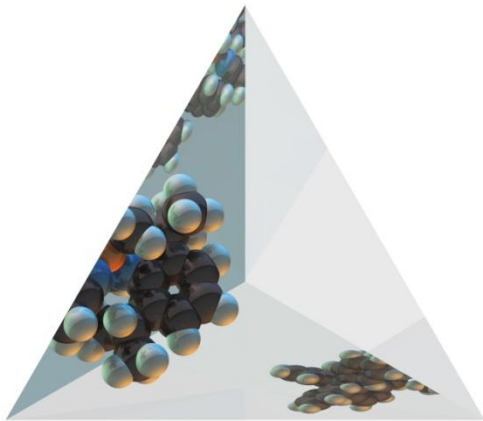
The net sum of these two equations is



and the equilibrium-constant expression for the net equation is the product of the expressions for the individual steps:

$$K_c = \frac{[\text{NO}]^2[\text{BrCl}]^2}{[\text{NOBr}]^2[\text{Cl}_2]} = \frac{[\text{NO}]^2[\text{Br}_2]}{[\text{NOBr}]^2} \times \frac{[\text{BrCl}]^2}{[\text{Br}_2][\text{Cl}_2]}$$





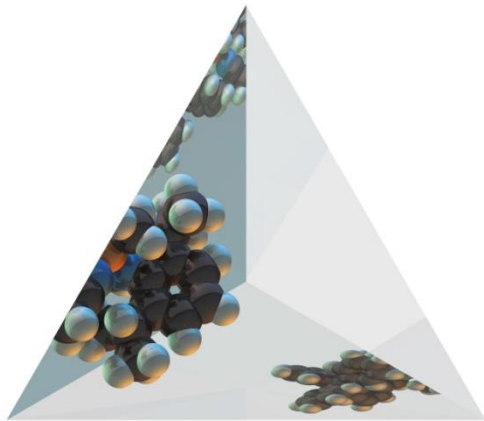
SAMPLE EXERCISE 15.5 | Combining Equilibrium Expressions

Given the following information,

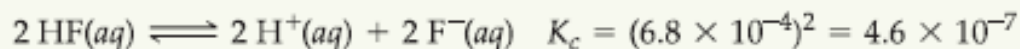


determine the value of K_c for the reaction

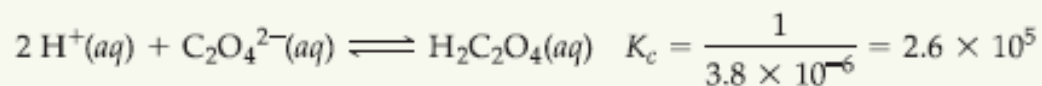




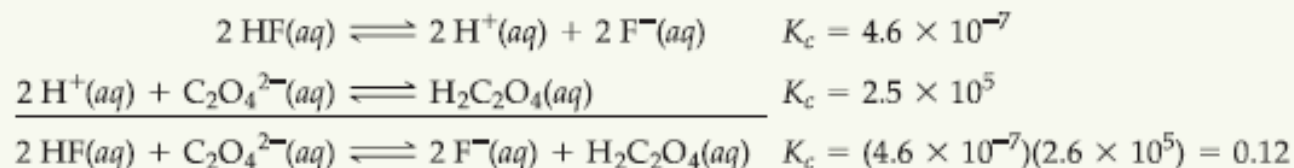
Solve: If we multiply the first equation by 2 and make the corresponding change to its equilibrium constant (raising to the power 2), we get



Reversing the second equation and again making the corresponding change to its equilibrium constant (taking the reciprocal) gives



Now we have two equations that sum to give the net equation, and we can multiply the individual K_c values to get the desired equilibrium constant.



Heterogeneous Equilibrium



Heterogeneous Equilibria

- When all reactants and products are in one phase, the equilibrium is homogeneous.
- If one or more reactants or products are in a different phase, the equilibrium is heterogeneous.
- The Heterogeneous Equilibria of solids and liquids are essentially 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.

Heterogeneous Equilibria

- The concentrations of solids and liquids are essentially constant
- We ignore the concentrations of pure liquids and pure solids in equilibrium constant expressions.



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



Equilibrium Calculations



Equilibrium Calculations

- To solve such a problem, use the following procedure
 - Write initial and equilibrium concentrations (or partial pressures) given.
 - Calculate the change in concentration.
 - Use stoichiometry on the change in concentration line only to calculate the changes in concentration of all species.
 - calculate the equilibrium concentrations.



Predicting the Direction of Reaction

- We define Q , for a general reaction



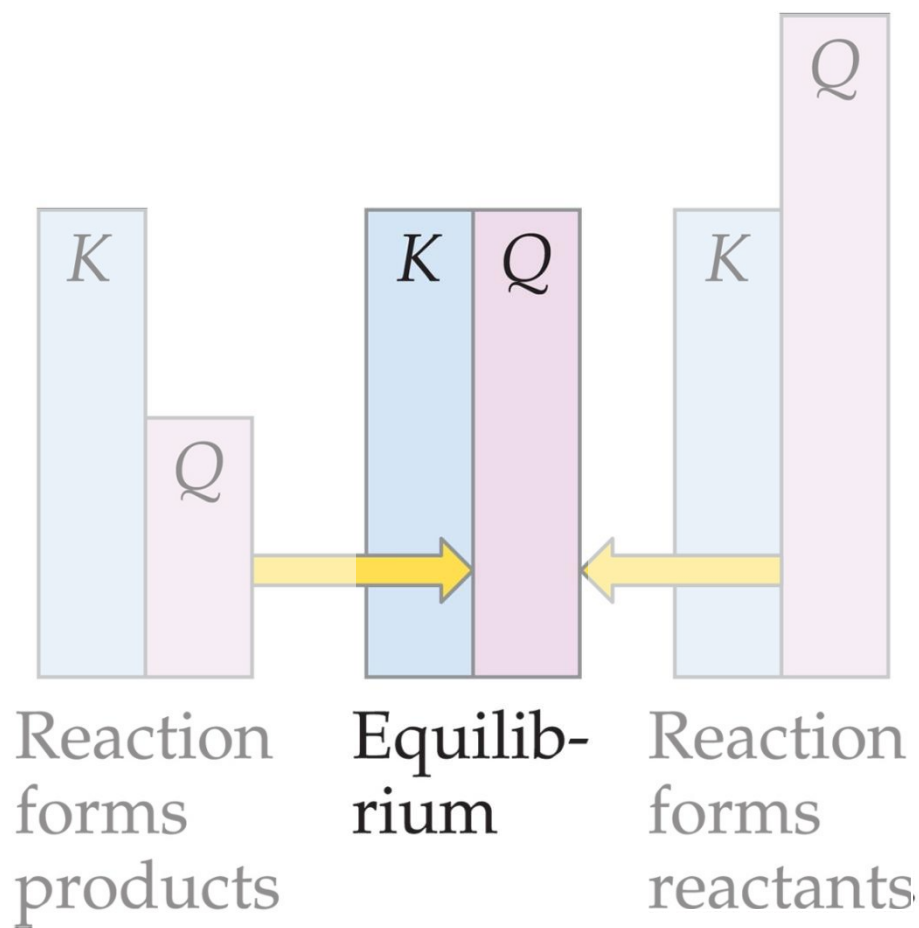
as

$$Q = \frac{[\text{P}]^p [\text{Q}]^q}{[\text{A}]^a [\text{B}]^b}$$

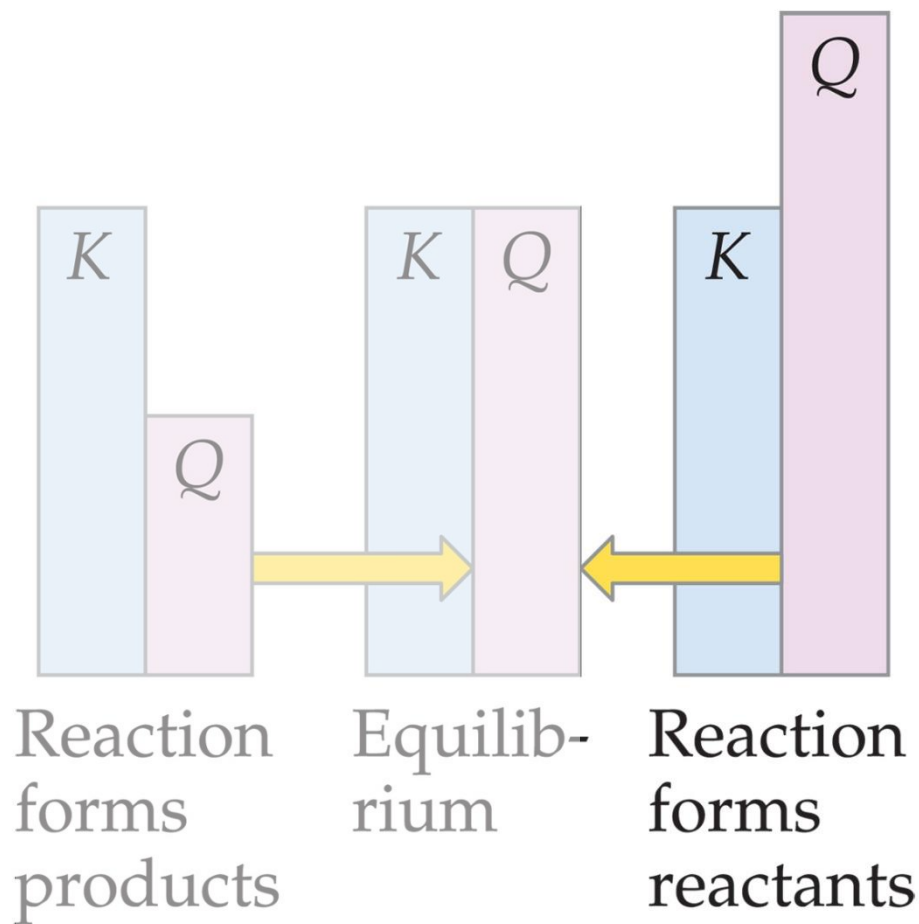
where $[\text{A}]$, $[\text{B}]$, $[\text{P}]$, and $[\text{Q}]$ are molarities at any time.

- $Q = K$ only at equilibrium.

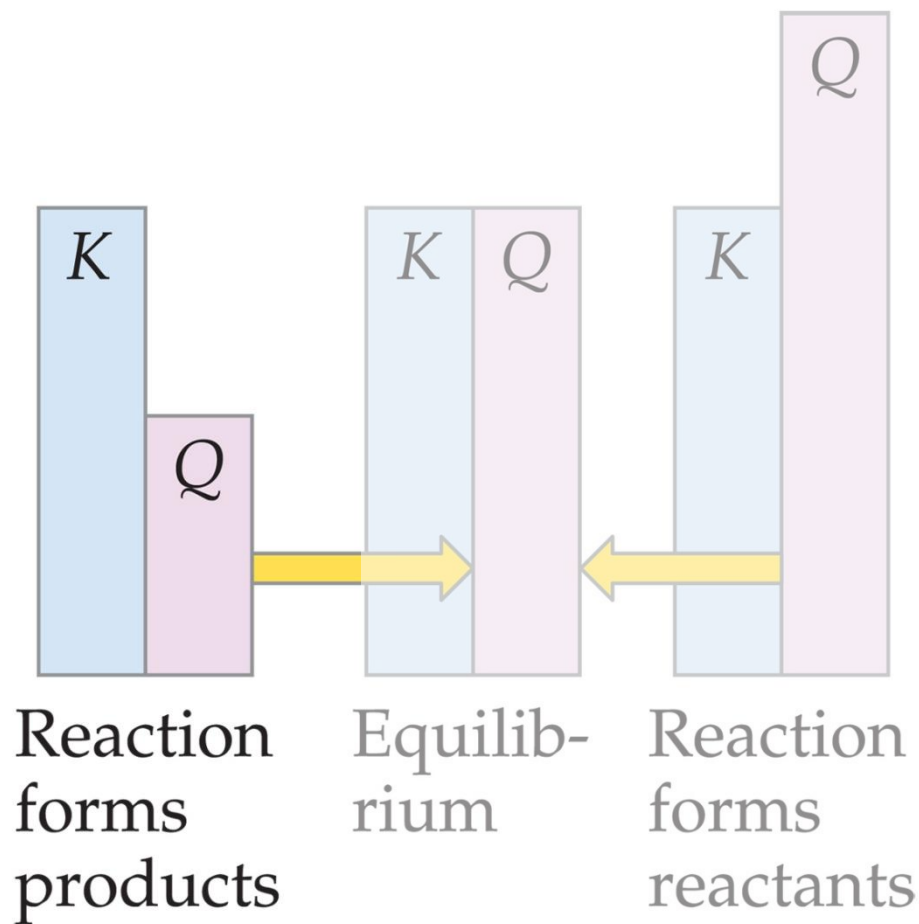
If $Q = K$,
the system is at equilibrium.



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.



Applications of Equilibrium Constants

Problem

The following reaction has an equilibrium constant K_c of 3.07×10^{-4} at 24°C :



For each of the following compositions, decide whether the reaction is at equilibrium. If not, decide which direction the reaction should go.

(a) $[\text{NOBr}] = 0.0610 \text{ M}$, $[\text{NO}] = 0.0151 \text{ M}$, $[\text{Br}_2] = 0.0108 \text{ M}$

(b) $[\text{NOBr}] = 0.115 \text{ M}$, $[\text{NO}] = 0.0169 \text{ M}$, $[\text{Br}_2] = 0.0142 \text{ M}$

(c) $[\text{NOBr}] = 0.181 \text{ M}$, $[\text{NO}] = 0.0123 \text{ M}$, $[\text{Br}_2] = 0.0201 \text{ M}$

Ans.: a.) goes left; b.) equilibrium; c.) goes right

Le Châtelier's Principle



Le Châtelier's Principle

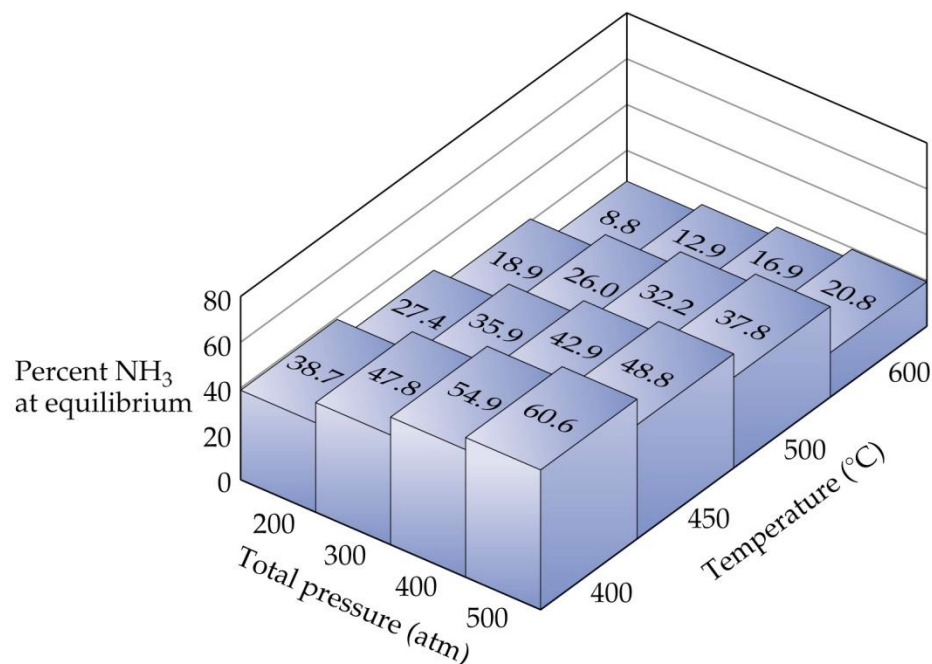
“If a system at *equilibrium* is *disturbed* by a change in *temperature*, *pressure*, or the *concentration* of one of the components, the system will *shift its equilibrium position* so as to counteract the effect of the disturbance.”



- Consider the production of ammonia



- As the pressure increases, the amount of ammonia present at equilibrium increases.
- As the temperature decreases, the amount of ammonia at equilibrium increases.



Change in Reactant or Product Concentrations

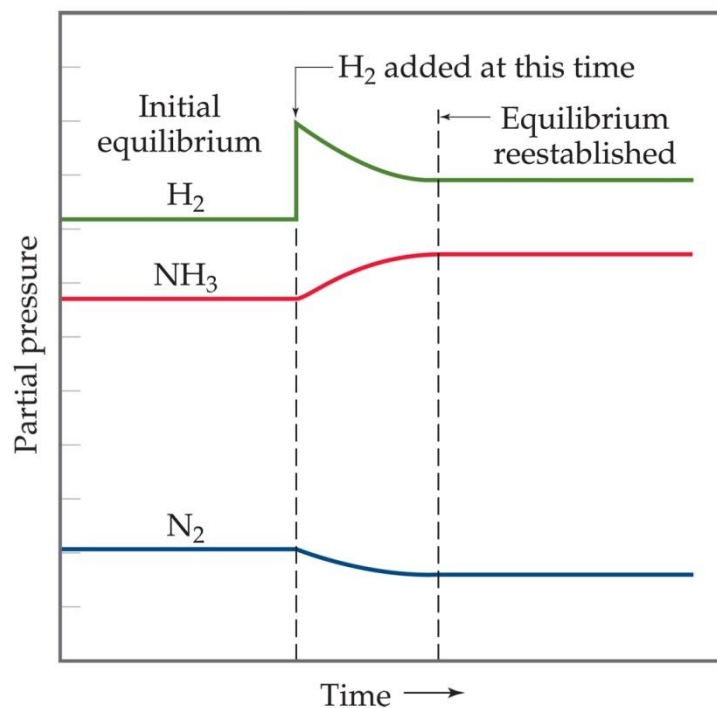
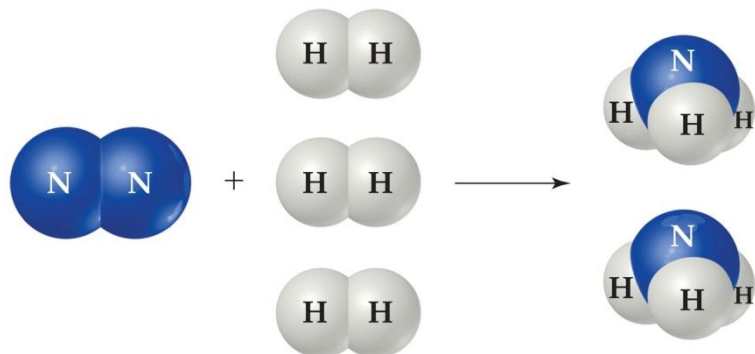
- Consider the Haber process



- If H_2 is added while the system is at equilibrium, the system must respond to counteract the added H_2 (by Le Châtelier).
- The system must consume the H_2 and produce products until a new equilibrium is established.
- So, $[\text{H}_2]$ and $[\text{N}_2]$ will decrease and $[\text{NH}_3]$ increases.



The Haber Process



- Adding a reactant or product shifts the equilibrium away from the increase.
- Removing a reactant or product shifts the equilibrium towards the decrease.



Effects of Volume and Pressure Changes

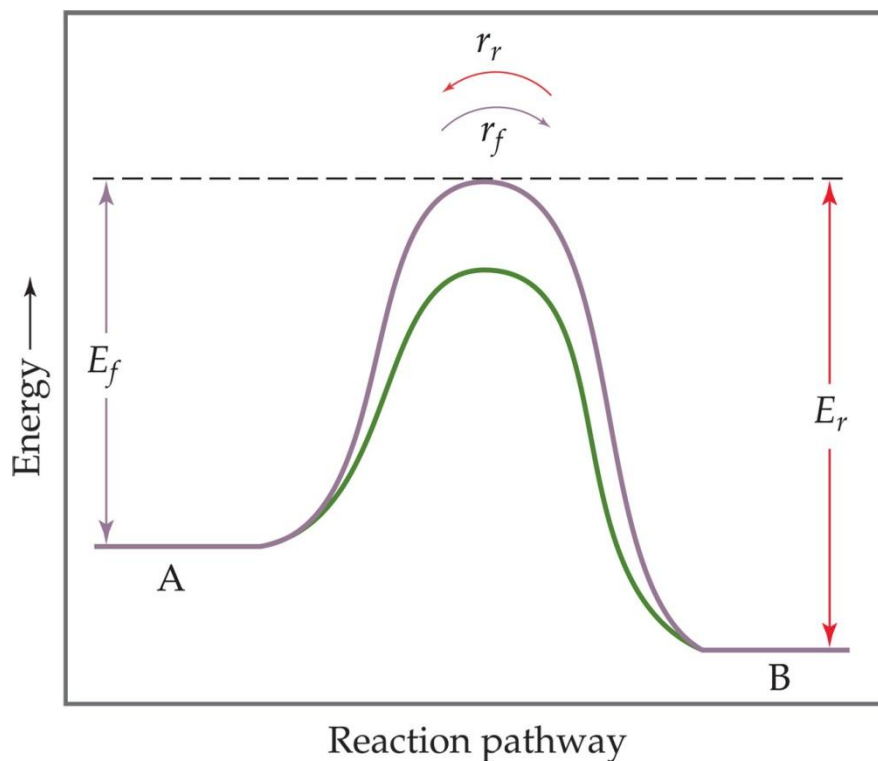
- As volume is decreased pressure increases.
- Le Châtelier's Principle: if pressure is increased the system will shift to counteract the increase.
- That is, the system shifts to remove gases and decrease pressure.
- An increase in pressure favors the direction that has *fewer moles of gas*.
- In a reaction with the same number of product and reactant moles of gas, pressure has no effect.



Effect of Temperature Changes

- The equilibrium constant is temperature dependent.
- For an endothermic reaction, $\Delta H > 0$ and *heat* can be considered as a *reactant*.
- For an exothermic reaction, $\Delta H < 0$ and *heat* can be considered as a *product*.
- Adding heat favors away from the increase:
 - if $\Delta H > 0$, adding heat --- the forward reaction,
 - if $\Delta H < 0$, adding heat --- the reverse reaction.
- Removing heat, favors towards the decrease:
 - if $\Delta H > 0$, cooling --- the reverse reaction,
 - if $\Delta H < 0$, cooling --- the forward reaction

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



lowers the activation energy barrier

decrease the time taken to reach equilibrium.

