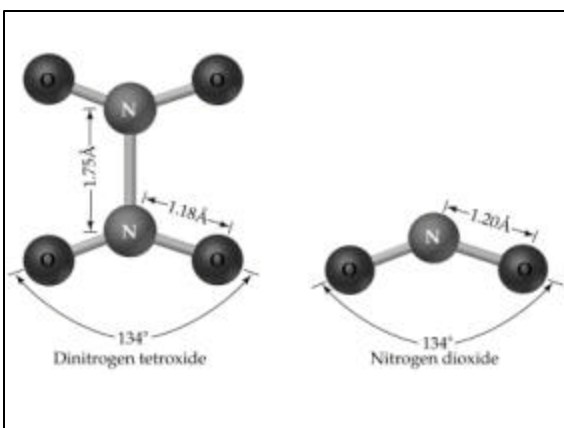


The Concept of Equilibrium

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

$$\text{N}_2\text{O}_4(g) \rightarrow 2\text{NO}_2(g)$$
- At some time, the color stops changing and we have a mixture of N_2O_4 and NO_2 .
- Chemical equilibrium is the point at which the concentrations of all species are constant.

- Using the collision model:
 - as the amount of NO_2 builds up, there is a chance that two NO_2 molecules will collide to form N_2O_4 .
 - At the beginning of the reaction, there is no NO_2 so the reverse reaction ($2\text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g)$) does not occur.

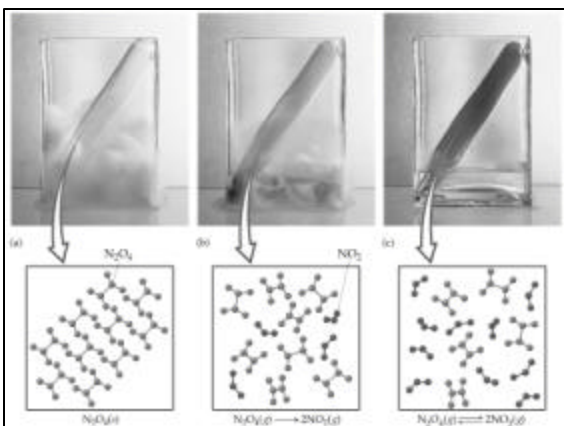


The Concept of Equilibrium

- The point at which the rate of decomposition:

$$\text{N}_2\text{O}_4(g) \rightarrow 2\text{NO}_2(g)$$
 equals the rate of dimerization:

$$2\text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g)$$
 This is dynamic equilibrium.
- The equilibrium is dynamic because the reaction has not stopped: the opposing rates are equal.
- Consider frozen N_2O_4 : only white solid is present. On the microscopic level, only N_2O_4 molecules are present.



The Concept of Equilibrium

- As the substance warms it begins to decompose:

$$\text{N}_2\text{O}_4(g) \rightarrow 2\text{NO}_2(g)$$
- A mixture of N_2O_4 (initially present) and NO_2 (initially formed) appears light brown.
- When enough NO_2 is formed, it can react to form N_2O_4 :

$$2\text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g)$$

The Concept of Equilibrium

- At equilibrium, as much N_2O_4 reacts to form NO_2 as NO_2 reacts to re-form N_2O_4 :



- The double arrow implies the process is dynamic.
- Consider

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

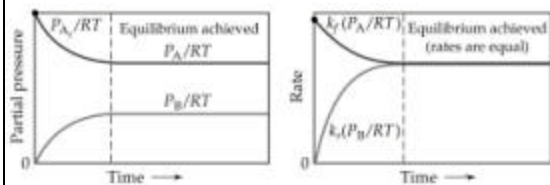
Reverse reaction: $B \rightarrow A$ Rate = $k_r[B]$

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

The Concept of Equilibrium

- For an equilibrium we write $A \rightleftharpoons B$
- As the reaction progresses
 - $[A]$ decreases to a constant,
 - $[B]$ increases from zero to a constant.
 - When $[A]$ and $[B]$ are constant, equilibrium is achieved.
- Alternatively:
 - $k_f[A]$ decreases to a constant,
 - $k_r[B]$ increases from zero to a constant.
 - When $k_f[A] = k_r[B]$ equilibrium is achieved.

The Concept of Equilibrium

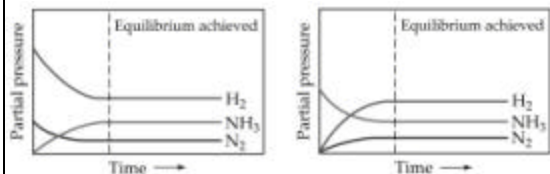


The Equilibrium Constant

- Consider the Haber Process:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
- If we start with a mixture of nitrogen and hydrogen (in any proportions), the reaction will reach equilibrium with a constant concentration of nitrogen, hydrogen and ammonia.
- However, if we start with just ammonia and no nitrogen or hydrogen, the reaction will proceed and N_2 and H_2 will be produced until equilibrium is achieved.

The Equilibrium Constant



- Regardless of the initial composition of reactants or products, the same ratio of concentrations is achieved at equilibrium.

The Equilibrium Constant

- For a general reaction in the gas phase

$$aA + bB \rightleftharpoons cC + dD$$
 the equilibrium constant expression is

$$K_{eq} = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

where K_{eq} is the equilibrium constant.

The Equilibrium Constant

- For a general reaction



the equilibrium constant expression for everything in solution is

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

where K_{eq} is the equilibrium constant.

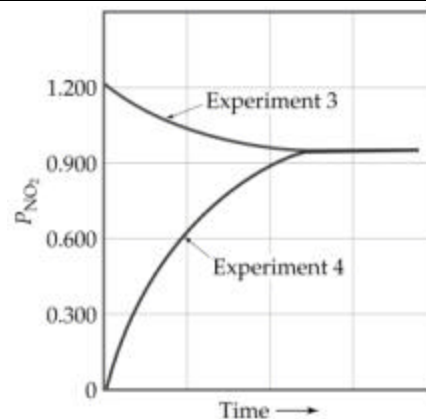
The Equilibrium Constant

- K_{eq} is based on the molarities of reactants and products at equilibrium.
- We generally omit the units of the equilibrium constant.
- Note that the equilibrium constant expression has products over reactants.
- The same equilibrium is established no matter how the reaction is begun.

The Equilibrium Constant

TABLE 15.1 Initial and Equilibrium Partial Pressures (P) of N_2O_4 and NO_2 at 100°C

Experiment	Initial N_2O_4 Partial Pressure (atm)	Initial NO_2 Partial Pressure (atm)	Equilibrium N_2O_4 Partial Pressure (atm)	Equilibrium NO_2 Partial Pressure (atm)	K_{eq}
1	0.0	0.923	0.509	0.726	0.45
2	0.0	0.955	0.607	0.744	0.46
3	0.96	0.22	0.138	0.564	0.46
4	0.922	0.0	0.138	0.564	0.45



The Equilibrium Constant

The Magnitude of Equilibrium Constants

- The equilibrium constant, K , is the ratio of products to reactants.
- Therefore, the larger K the more products are present at equilibrium.
- Conversely, the smaller K the more reactants are present at equilibrium.
- If $K \gg 1$, then products dominate at equilibrium and equilibrium lies to the right.

The Equilibrium Constant

The Magnitude of Equilibrium Constants

- If $K \ll 1$, then reactants dominate at equilibrium and the equilibrium lies to the left.



The Equilibrium Constant

The Direction of the Chemical Equation and K_{eq}

- An equilibrium can be approached from any direction.
- Example:



- has

$$K_{eq} = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = 6.46$$

The Equilibrium Constant

The Direction of the Chemical Equation and K_{eq}

- In the reverse direction:



$$K_{eq} = \frac{P_{\text{N}_2\text{O}_4}}{P_{\text{NO}_2}^2} = 0.155 = \frac{1}{6.46}$$



The Equilibrium Constant

Other Ways to Manipulate Chemical Equations and K_{eq} Values

- The reaction



has

$$K_{eq} = \frac{P_{\text{NO}_2}^4}{P_{\text{N}_2\text{O}_4}^2}$$

which is the square of the equilibrium constant for

$$\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$$

The Equilibrium Constant

Other Ways to Manipulate Chemical Equations and K_{eq} Values

- Equilibrium constant for the reverse direction is the inverse of that for the forward direction.
- When a reaction is multiplied by a number, the equilibrium constant is raised to that power.
- The equilibrium constant for a reaction which is the sum of other reactions is the product of the equilibrium constants for the individual reactions.

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.
- Consider:



– experimentally, the amount of CO_2 does not seem to depend on the amounts of CaO and CaCO_3 . Why?

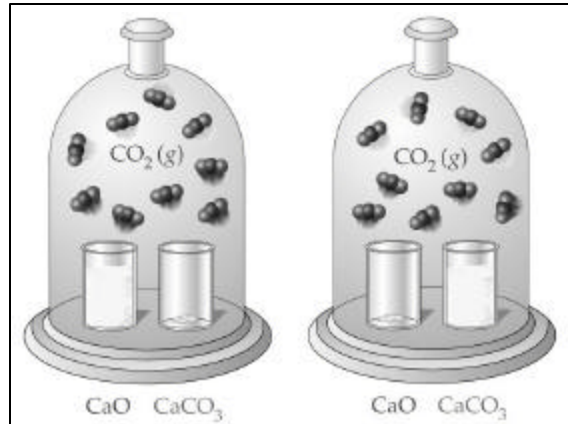
Heterogeneous Equilibria

- The concentration of a solid or pure liquid is its density divided by molar mass.
- Neither density nor molar mass is a variable, the concentrations of solids and pure liquids are constant.
- For the decomposition of CaCO_3 :

$$K_{eq} = \frac{[\text{CaO}]}{[\text{CaCO}_3]} \times [\text{CO}_2] = \text{constant} \times [\text{CO}_2]$$

Heterogeneous Equilibria

- We ignore the concentrations of pure liquids and pure solids in equilibrium constant expressions.
- The amount of CO_2 formed will not depend greatly on the amounts of CaO and CaCO_3 present.



Calculating Equilibrium Constants

- Proceed as follows:
 - Tabulate initial and equilibrium concentrations (or partial pressures) given.
 - If an initial and equilibrium concentration is given for a species, calculate the change in concentration.
 - Use stoichiometry on the change in concentration line only to calculate the changes in concentration of all species.
 - Deduce the equilibrium concentrations of all species.
- Usually, the initial concentration of products is zero. (This is not always the case.)

Applications of Equilibrium Constants

Predicting the Direction of Reaction

- We define Q , the reaction quotient, for a general reaction

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

as

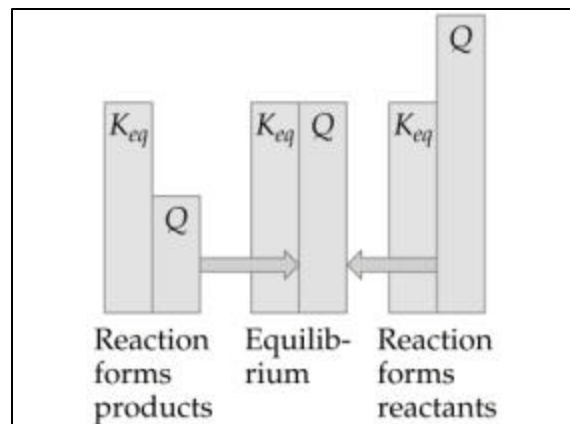
$$Q = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

- $Q = K$ only at equilibrium.

Applications of Equilibrium Constants

Predicting the Direction of Reaction

- If $Q > K$ then the reverse reaction must occur to reach equilibrium (i.e., products are consumed, reactants are formed, the numerator in the equilibrium constant expression decreases and Q decreases until it equals K).
- If $Q < K$ then the forward reaction must occur to reach equilibrium.



Applications of Equilibrium Constants

Calculating Equilibrium Constants

- The same steps used to calculate equilibrium constants are used.
- Generally, we do not have a number for the change in concentration line.
- Therefore, we need to assume that x mol/L of a species is produced (or used).
- The equilibrium concentrations are given as algebraic expressions.

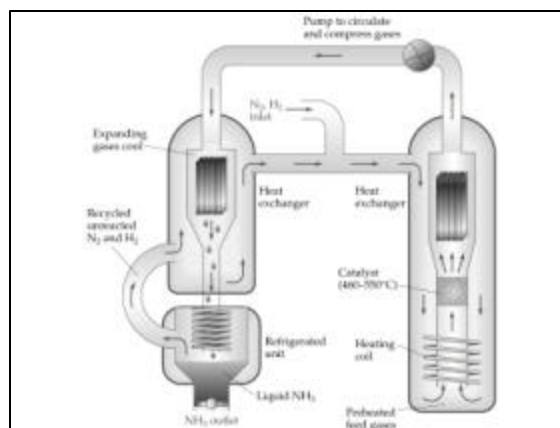
Le Châtelier's Principle

- Le Châtelier's Principle: if a system at equilibrium is disturbed, the system will move in such a way as to counteract the disturbance.

Le Châtelier's Principle

Change in Reactant or Product Concentrations

- Adding a reactant or product shifts the equilibrium away from the increase.
- Removing a reactant or product shifts the equilibrium towards the decrease.
- To optimize the amount of product at equilibrium, we need to flood the reaction vessel with reactant and continuously remove product (Le Châtelier).
- We illustrate the concept with the industrial preparation of ammonia.



Le Châtelier's Principle

Change in Reactant or Product Concentrations

- N₂ and H₂ are pumped into a chamber.
- The pre-heated gases are passed through a heating coil to the catalyst bed.
- The catalyst bed is kept at 460 - 550 °C under high pressure.
- The product gas stream (containing N₂, H₂ and NH₃) is passed over a cooler to a refrigeration unit.
- In the refrigeration unit, ammonia liquefies not N₂ or H₂.

Le Châtelier's Principle

Change in Reactant or Product Concentrations

- The unreacted nitrogen and hydrogen are recycled with the new N₂ and H₂ feed gas.
- The equilibrium amount of ammonia is optimized because the product (NH₃) is continually removed and the reactants (N₂ and H₂) are continually being added.

Effects of Volume and Pressure Changes

- As volume is decreased pressure increases.

Le Châtelier's Principle

Effects of Volume and Pressure Changes

- 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.

Le Châtelier's Principle

Effects of Volume and Pressure Changes



- An increase in pressure (by decreasing the volume) favors the formation of colorless N_2O_4 .
- The instant the pressure increases, the system is not at equilibrium and the concentration of both gases has increased.
- The system moves to reduce the number moles of gas (i.e. the forward reaction is favored).



Le Châtelier's Principle

Effects of Volume and Pressure Changes

- A new equilibrium is established in which the mixture is lighter because colorless N_2O_4 is favored.

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.



Le Châtelier's Principle

Effect of Temperature Changes

- Adding heat (i.e. heating the vessel) favors away from the increase:
 - if $\Delta H > 0$, adding heat favors the forward reaction,
 - if $\Delta H < 0$, adding heat favors the reverse reaction.
- Removing heat (i.e. cooling the vessel), favors towards the decrease:
 - if $\Delta H > 0$, cooling favors the reverse reaction,
 - if $\Delta H < 0$, cooling favors the forward reaction.

Le Châtelier's Principle

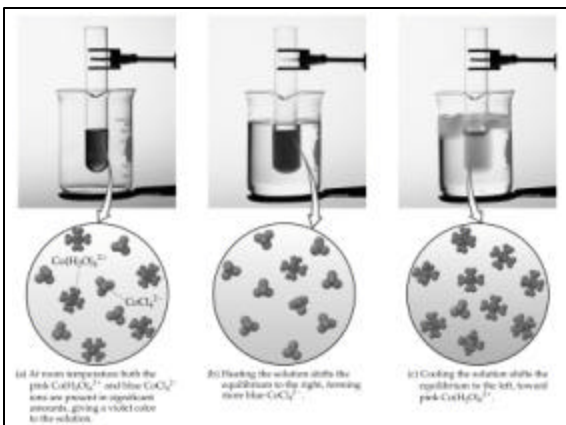
Effect of Temperature Changes

- Consider
 $\text{Cr}(\text{H}_2\text{O})_6^{2+}(aq) + 4\text{Cl}^-(aq) \rightleftharpoons \text{CoCl}_4^{2-}(aq) + 6\text{H}_2\text{O}(l)$
for which $\Delta H > 0$.
 - $\text{Co}(\text{H}_2\text{O})_6^{2+}$ is pale pink and CoCl_4^{2-} is blue.
 - If a light purple room temperature equilibrium mixture is placed in a beaker of warm water, the mixture turns deep blue.
 - Since $\Delta H > 0$ (endothermic), adding heat favors the forward reaction, i.e. the formation of blue CoCl_4^{2-} .

Le Châtelier's Principle

Effect of Temperature Changes

- Consider
 $\text{Cr}(\text{H}_2\text{O})_6^{2+}(aq) + 4\text{Cl}^-(aq) \rightleftharpoons \text{CoCl}_4^{2-}(aq) + 6\text{H}_2\text{O}(l)$
 - If the room temperature equilibrium mixture is placed in a beaker of ice water, the mixture turns bright pink.
 - Since $\Delta H > 0$, removing heat favors the reverse reaction which is the formation of pink $\text{Co}(\text{H}_2\text{O})_6^{2+}$.



Le Châtelier's Principle

The Effect of Catalysis

- A catalyst lowers the activation energy barrier for the reaction.
- Therefore, a catalyst will decrease the time taken to reach equilibrium.
- A catalyst does not effect the composition of the equilibrium mixture.

