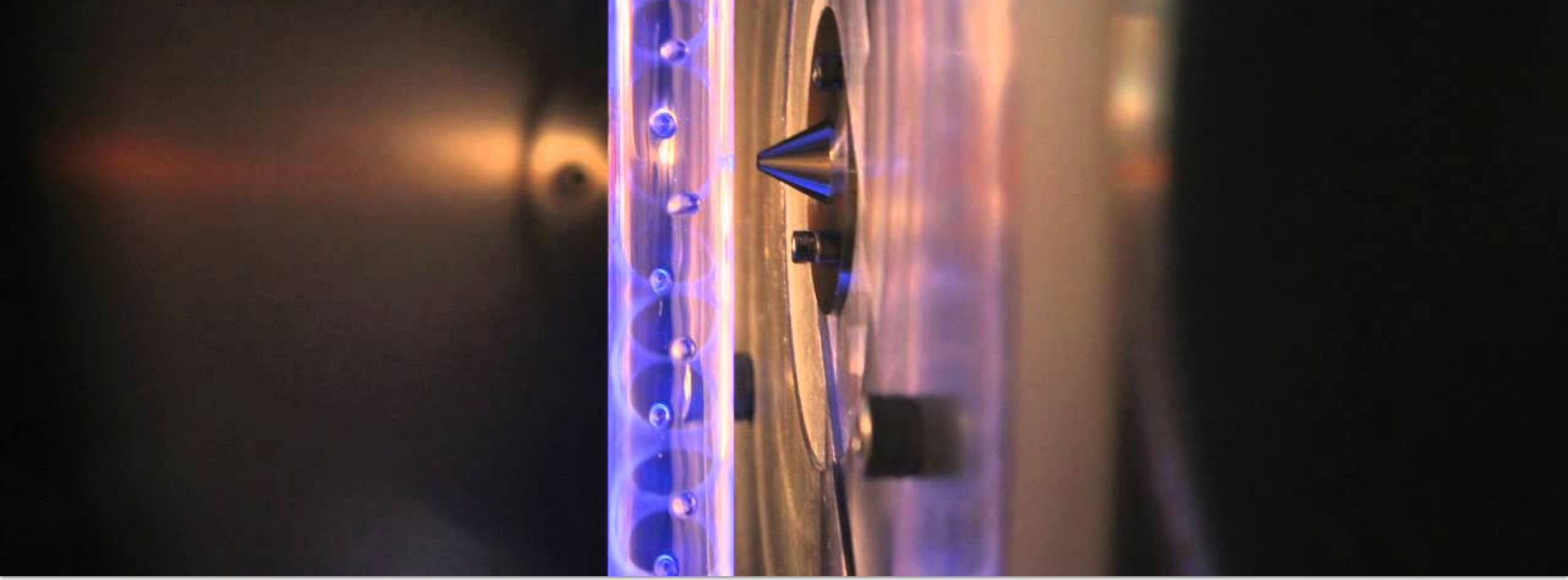


Unit 7
Equilibrium

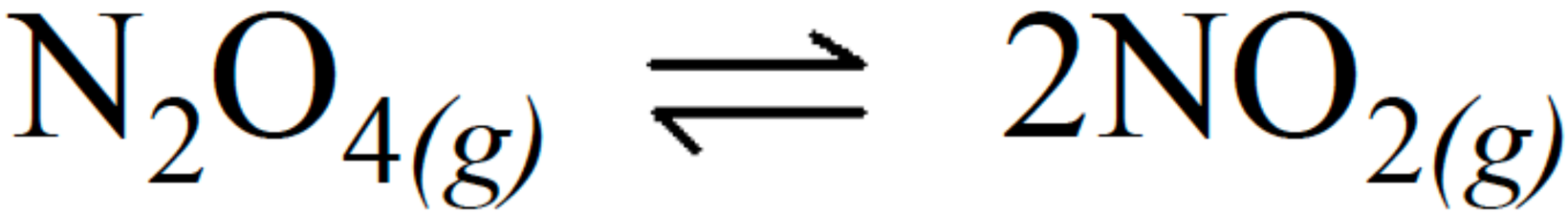
7.1 Introduction to Equilibrium
7.2 Direction of Reversible Reactions
7.3 Reaction Quotient & Equilibrium Constant

- Establishing Equilibrium
- Equilibrium Constants (K_c and K_p)
- Reaction Quotients (Q_c and Q_p)

Dynamic Equilibrium

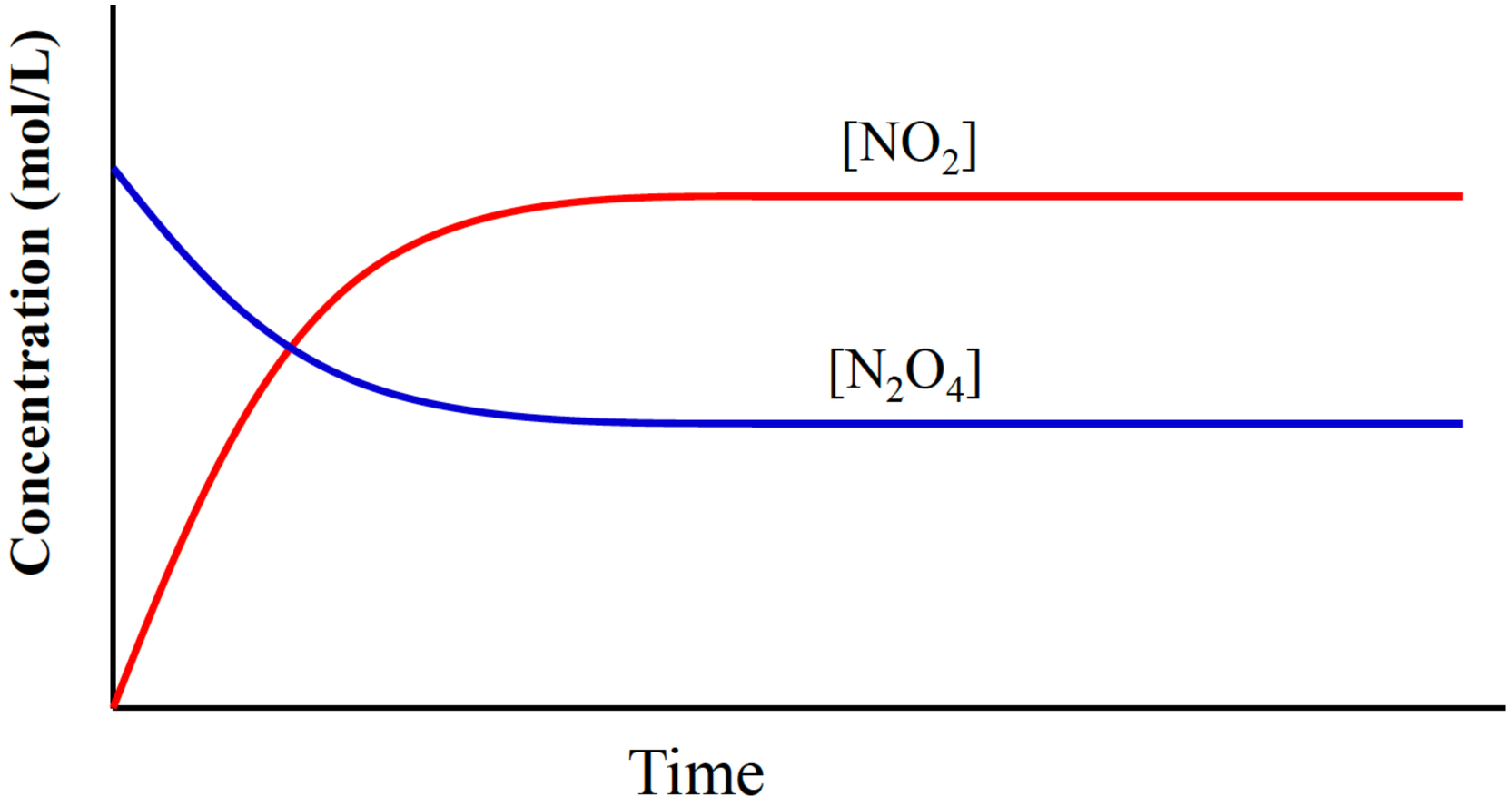
Most reactions do not go to completion.

- Here, all of the reactants **do not** get used up.
- The system reaches a dynamic state where reactants are continually turning into products, and products are continually turning back into reactants.



Dynamic Equilibrium

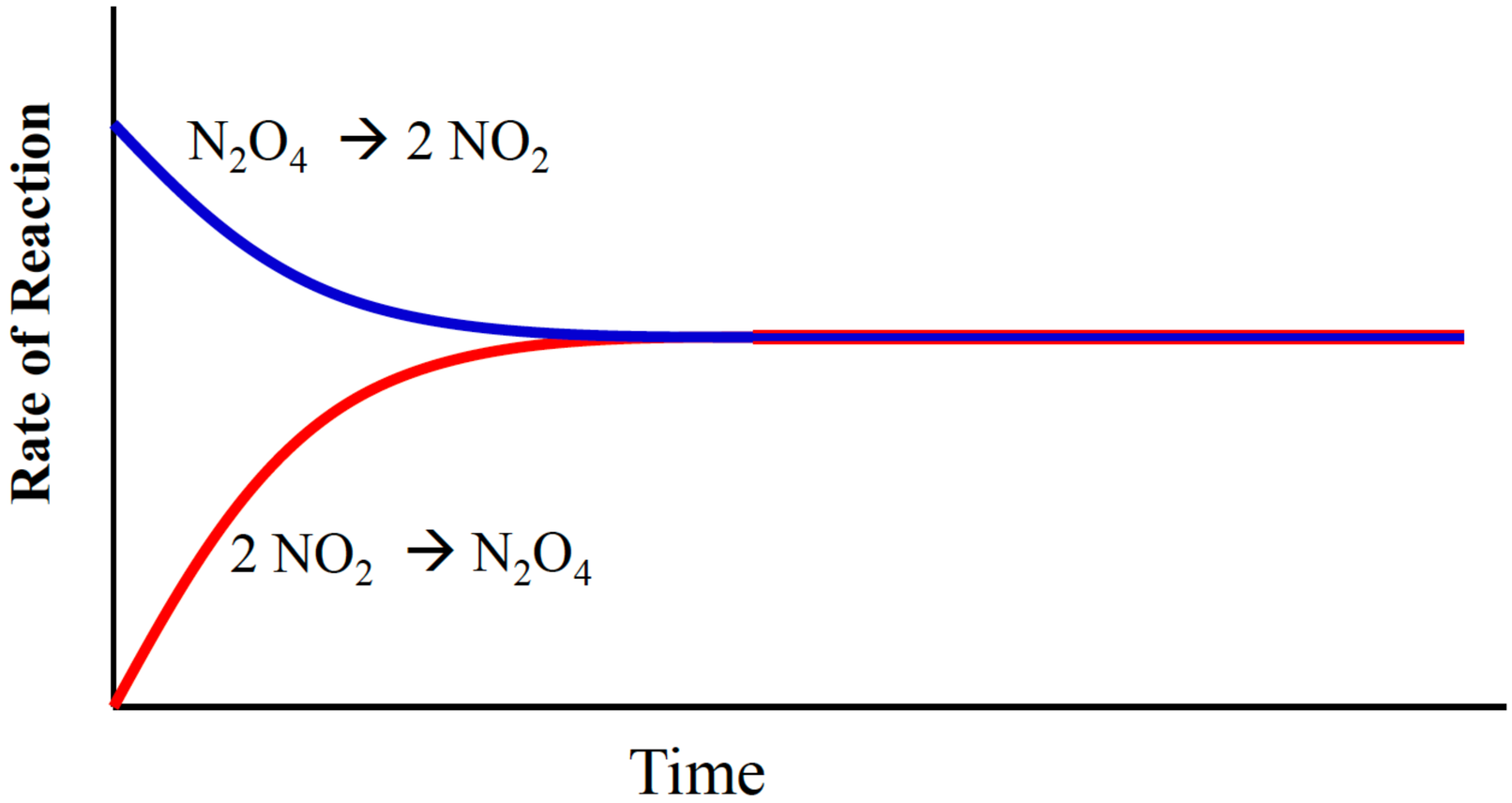
$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$



In this example, the system *initially contains only reactants*, N_2O_4, and eventually establishes equilibrium.

Dynamic Equilibrium

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



In this example, the system *initially contains only reactants*, N_2O_4, and eventually establishes equilibrium.

Establishing Chemical Equilibrium

- When the rate of the forward reaction is greater than the rate of the reverse reaction, there is a net conversion of reactants into products.
- The reversible reaction is proceeding to the right.
- When the rate of the reverse reaction is greater than the the rate of the forward reaction, there is a net conversion of products into reactants.
- The reversible reaction is proceeding to the left.

Once Equilibrium is Established

- **No observable changes occur even though…**
  - Forward and reverse reactions continue to take place.
  - The rate of the forward reaction EQUALS the rate of the reverse reaction.
- **Concentrations and/or partial pressures of all species remain constant, yet they will rarely be equal to one another.**

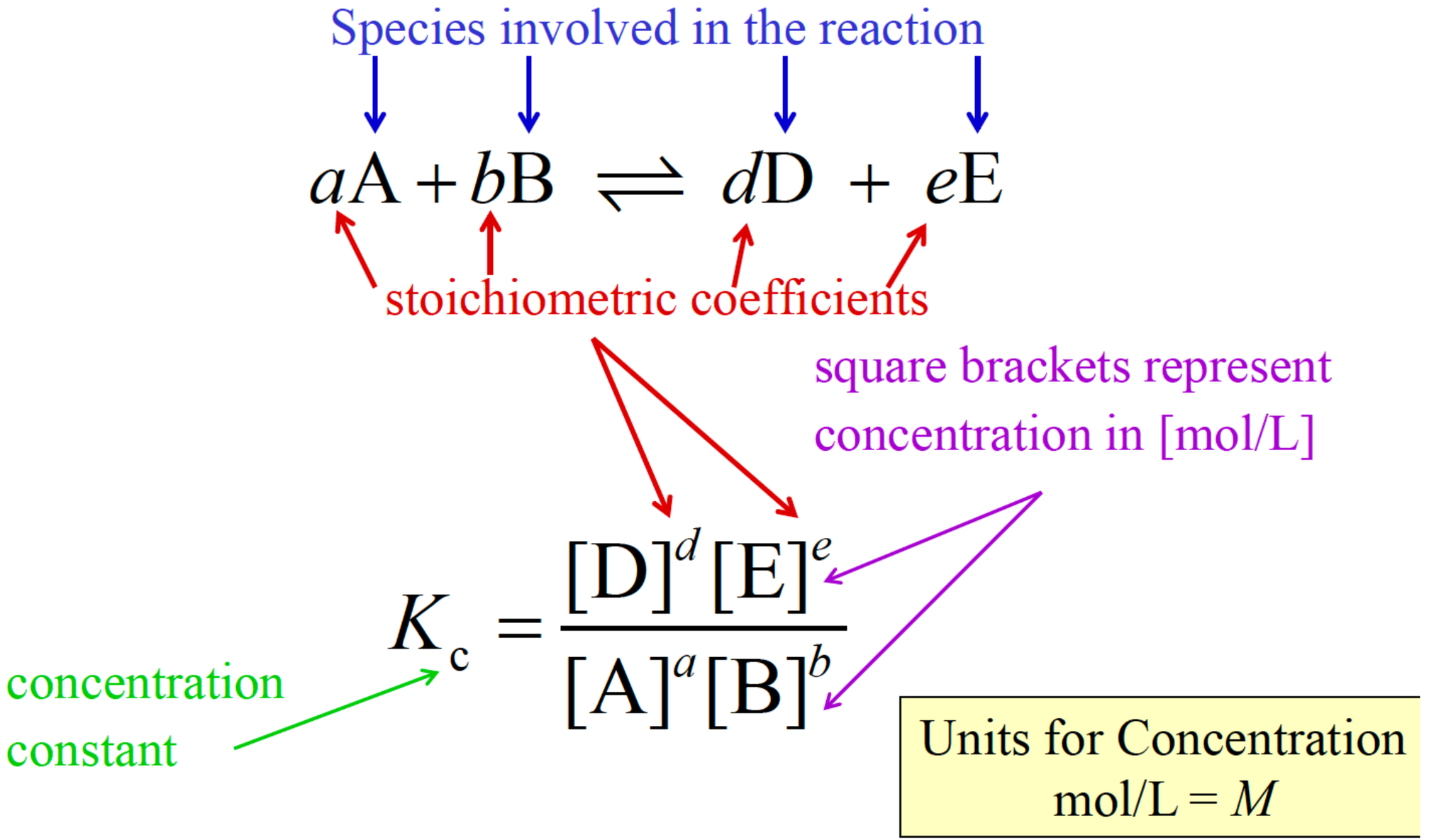
Maintaining Equilibrium

Closed System

Volume Remains Constant

Temperature Remains Constant

The Equilibrium Constant (K_{eq})



Example: Equilibrium Expression (K_c)

Write the equilibrium expression, K_c, for:

$$N_2(g) + O_2(g) \rightleftarrows 2NO(g)$$

$$K_c = \frac{[NO]^2}{[N_2][O_2]}$$

Example: Equilibrium Expression (K_c)

Write the equilibrium expression, K_c, for:

$$NiO(s) + CO(g) \rightleftarrows Ni(s) + CO_2(g)$$

$$K_c = \frac{[CO_2]}{[CO]}$$

- [NiO] has not changed.
- Concentration is measured in mol/L.
- Both pieces have the same density, so both contain the same number of particles per unit volume.

Example: Equilibrium Expression (K_c)

Write the equilibrium expression, K_c, for:

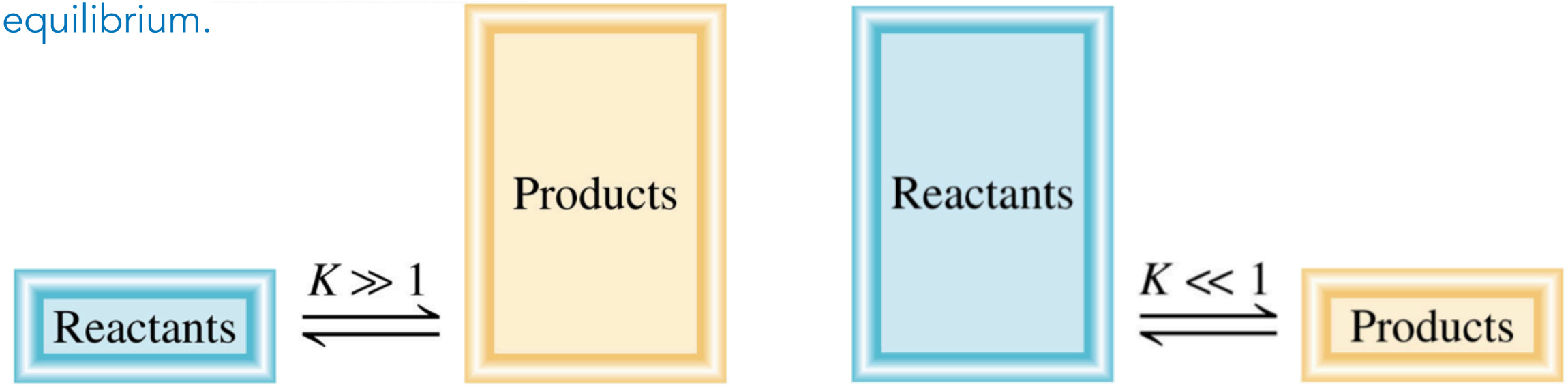
$$4HCl(aq) + O_2(g) \rightleftarrows 2Cl_2(g) + 2H_2O(l)$$

$$K_c = \frac{[Cl_2]^2}{[HCl]^4[O_2]}$$

- Adding or taking away small amounts of water in a reaction that takes place in an aqueous solution does not affect the overall concentration of H_2O

Details About the Equilibrium Constant, K

- K indicates how far a reaction will proceed towards the products at a given temperature.
- Small K means little to no reaction
- Large K means the reaction goes to or near completion
- Intermediate K means significant amounts of reactants and products are present at equilibrium.



The Reaction Quotient (Q)

- **The reaction quotient, Q_c, describes relative concentrations of products and reactants at any point in time.**

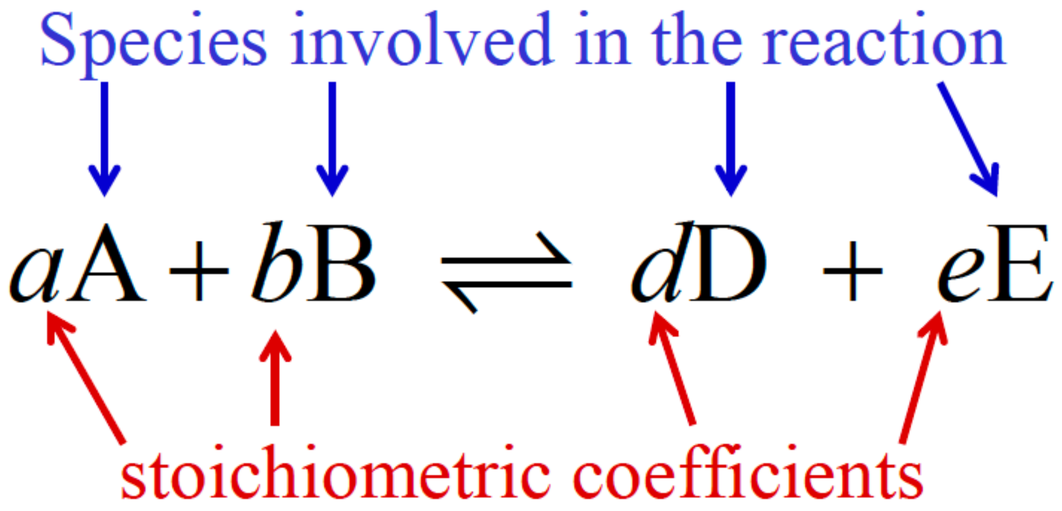
- **The expression for Q_c is the same as that for K_c.**

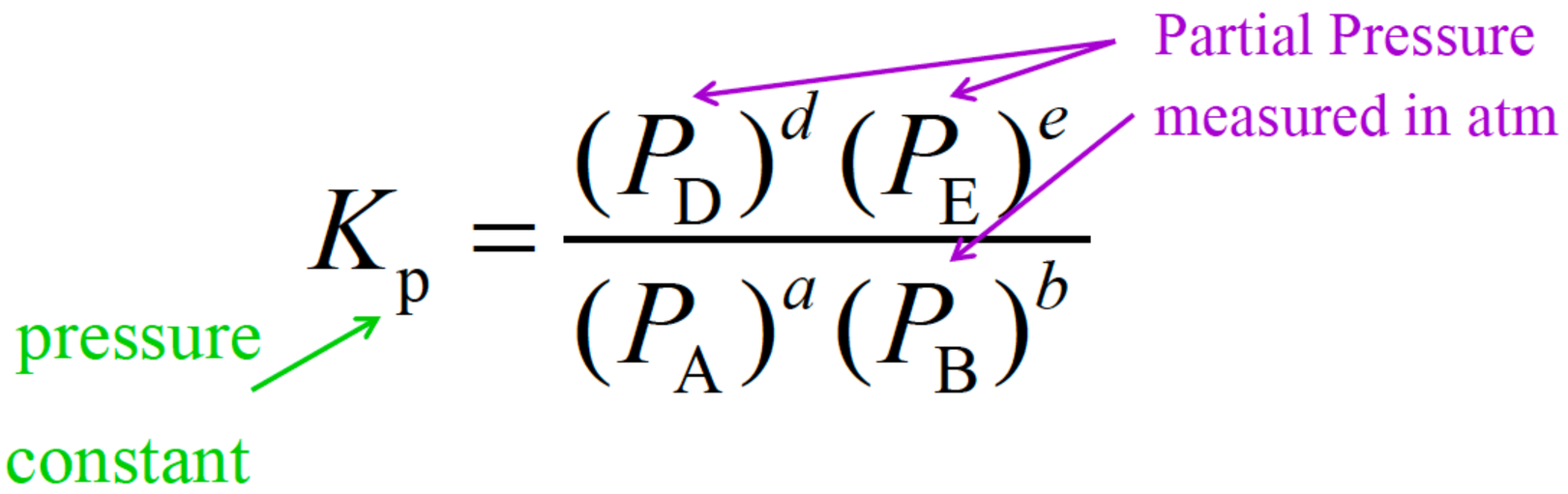
- When the system is at equilibrium, $Q_c = K_c$
- When $Q_c < K_c$: The reaction will tend toward the products
- When $Q_c > K_c$: The reaction will tend toward the reactants

$$aA + bB \rightleftharpoons dD + eE$$

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

For gases, K_p is often used





For gases, K_p is often used

- The partial pressure of a gas in a system is the pressure exerted by that specific gas.
- The partial pressures of all the gases in a system sum up to the total pressure in that system.
- 1 mole of one type of gas will exert the same pressure as 1 mole of a different type of gas, under the same conditions of volume and temperature.
- 2 moles of a gas will exert twice as much pressure.

Example: Equilibrium Constant (K_p)

Write the equilibrium expression, K_p, for:

$$2NO_2(g) + Cl_2(g) \rightleftarrows 2NOCl(g)$$

$$K_p = \frac{(P_{NOCl})^2}{(P_{NO_2})^2(P_{Cl_2})}$$

You must use round brackets in the K_p expression.

Example: Equilibrium Constant (K_p)

$$CH_4(g) + 2H_2S(g) \rightleftarrows CS_2(g) + 4H_2(g)$$

- At 1000 K, the equilibrium partial pressures for the reaction above are CH_4 = 0.20 atm, H_2S = 0.25 atm, CS_2 = 0.52 atm and H_2 = 0.10 atm. What is K_p?

Practice

For the reaction $N_2O_4(g) \rightleftarrows 2NO_2(g)$, $K_c = 0.21$ at 100°C. At a point during the reaction, $[N_2O_4] = 0.12$ M and $[NO_2] = 0.55$ M. Is the reaction at equilibrium at that time? If not, in which direction is it proceeding?

Answer:

$Q_c = [NO_2]^2/[N_2O_4] = (0.55)^2/(0.12) = 2.52$

$2.52 \neq 0.21$ so it is not at equilibrium, and since

$2.52 > 0.21$, the rxn must proceed to the LEFT, making more reactants to reach equilibrium.

7.4 Calculating the Equilibrium Constant
7.5 Magnitude of the Equilibrium Constant
7.6 Properties of the Equilibrium Constant

Example: Calculating K_c

A system establishes equilibrium at 500.0°C in accordance with the chemical equation below and the following concentrations were measured. Calculate the value of the equilibrium constant, K_c.

$$[N_2] = 1.50 \times 10^{-5}\, M$$

$$[H_2] = 3.45 \times 10^{-1}\, M$$

$$[NH_3] = 2.00 \times 10^{-4}\, M$$

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

Example: Calculating K_p

A system establishes equilibrium at 485°C in accordance with the chemical equation below and the following partial pressures were measured. Calculate the value of the equilibrium constant, K_p.

$$[H_2] = 0.035 \text{ atm}$$

$$[I_2] = 0.045 \text{ atm}$$

$$[HI] = 0.280 \text{ atm}$$

$$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$$

What K_{eq} Tells Us

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

$$K_P = \frac{(P_{H_2})(P_{I_2})}{(P_{HI})^2} = 0.0184 \quad \text{at 698 K}$$

$$(P_{HI})^2 > (P_{H_2})\,(P_{I_2})$$

Mostly Reactants

What K_{eq} Tells Us

$$2\,NO_{(g)} \rightleftharpoons N_{2(g)} + O_{2(g)}$$

$$K_c = \frac{[N_2][O_2]}{[NO]^2} = 2.4 \times 10^3 \quad \text{at 2273 K}$$

$[NO]^2 \ll [N_2]\,[O_2]$

Mostly Products

What K_{eq} Tells Us

$K_{eq} >> 1$ (mostly products)
(equilibrium lies far to the right)

$K_{eq} << 1$ (mostly reactants)
(equilibrium lies far to the left)

$K_{eq} \approx 1$ (~ equal amounts of each)
(equilibrium lies in the middle)

Manipulating K & Q

There are three ways in which K and Q can be manipulated.

1. Coefficient Rule
2. Reciprocal Rule
3. Multiple Equilibria Rule

Coefficient Rule

When coefficients are changed by a factor of *n*, K_{eq} is raised to the power of *n*.

(i) $$2\,A_{(g)} + B_{(aq)} \rightleftharpoons 6\,D_{(aq)}$$

$$K_c^{\,i} = \frac{[D]^6}{[A]^2[B]}$$

½(i) = (ii) $$A_{(g)} + \tfrac{1}{2}B_{(aq)} \rightleftharpoons 3\,D_{(aq)}$$

$$K_c^{\,ii} = \frac{[D]^3}{[A][B]^{\frac{1}{2}}} = \left[\frac{[D]^6}{[A]^2[B]}\right]^{\frac{1}{2}}$$

$$\boxed{K_c^{\,ii} = (K_c^{\,i})^{1/2}}$$

Reciprocal Rule

When a reaction is reversed, the new K_{eq} value is the inverse of the old K_{eq} value.

(i)

$$2\,A_{(g)} + B_{(aq)} \rightleftharpoons 6\,D_{(aq)}$$

$$K_c^{\,i} = \frac{[D]^6}{[A]^2[B]}$$

$(i)^{-1} = (iii)$

$$6\,D_{(aq)} \rightleftharpoons 2\,A_{(g)} + B_{(aq)}$$

$$K_c^{\,iii} = \frac{[A]^2[B]}{[D]^6}$$

$$K_c^{\,iii} = 1 \,/\, K_c^{\,i}$$

Multiple Equilibria Rule

When two or more reactions are combined, the new K_{eq} is the product of the K_{eq} values from the individual reactions.

(i) $2\,A_{(g)} + B_{(aq)} \rightleftharpoons 6\,D_{(aq)}$

(iv) $3\,E_{(aq)} + B_{(aq)} \rightleftharpoons 2\,A_{(g)} + F_{(aq)}$

(v) $3\,E_{(aq)} + 2\,B_{(aq)} \rightleftharpoons 6D_{(aq)} + F_{(aq)}$

$$\frac{[D]^6}{[A]^2\,[B]} \times \frac{[A]^2\,[F]}{[E]^3\,[B]} = \frac{[D]^6\,[F]}{[E]^3\,[B]^2}$$

$$K_c^{\,i} \times K_c^{\,iv} = K_c^{\,v}$$

7.7 Calculating Equilibrium Concentrations

- Calculating Equilibrium Partial Pressures & Concentration
- ICE Charts

Warm-up: Calculating Equilibrium Partial Pressures

Suppose you start out with only $H_2O(g)$ in a rigid container at 25°C, and its initial partial pressure is recorded to be 0.784 atm. What are the partial pressures of each species when the system reaches equilibrium?

($K_p = 2.0 \times 10^{-42}$)

$$2\,H_2O_{(g)} \rightleftharpoons 2\,H_{2(g)} + O_{2(g)}$$

Warm-up: Calculating Equilibrium Partial Pressures

($K_p = 2.0 \times 10^{-42}$)

$$2\,H_2O_{(g)} \rightleftharpoons 2\,H_{2(g)} + O_{2(g)}$$

Initial	0.784	0	0
Change	-2x	+2x	+x
Equilibrium	0.784 - 2x	2x	x

Warm-up: Calculating Equilibrium Partial Pressures

($K_p = 2.0 \times 10^{-42}$)

$$2\,H_2O_{(g)} \rightleftharpoons 2\,H_{2(g)} + O_{2(g)}$$

Initial	0.784	0	0
Change	-2x	+2x	+x
Equilibrium	0.784 - 2x	2x	x

$$K_p = \frac{(P_{H_2})^2\,(P_{O_2})}{(P_{H_2O})^2} = \frac{(2x)^2\,(x)}{(0.784 - 2x)^2}$$

$$2.0 \times 10^{-42} = \frac{4x^3}{(0.784)^2}$$

When $K_{eq} < 1 \times 10^{-4}$ you can usually ignore this (x) to avoid the difficult math.

Example: Calculating Equilibrium Concentrations

Find the equilibrium concentrations of all species if 0.194 mol of $COCl_2$ is allowed to come to equilibrium in a 5.8 L container at 25°C. ($K_c = 7.28 \times 10^{-38}$)

$$COCl_{2(g)} \rightleftharpoons CO_{(g)} + Cl_{2(g)}$$

Initial	3.3×10^{-2}	0	0
Change	-x	+x	+x
Equilibrium	3.3×10^{-2} - x	x	x

$$COCl_{2(g)} + H_2O_{(l)} \rightarrow CO_{2(g)} + 2\ HCl_{(aq)}$$

7.8 Representations of Equilibrium
7.9 Introduction to Le Chatelier's Principle
7.10 Reaction Quotient & Le Chatelier's Principle

Le Chatelier's Principle

When a system at equilibrium is subjected to a stress, the equilibrium will shift in order to reduce that stress.

The only three stresses are changes in:

1. Pressure
2. Concentration
3. Temperature

Stress from Increasing Pressure

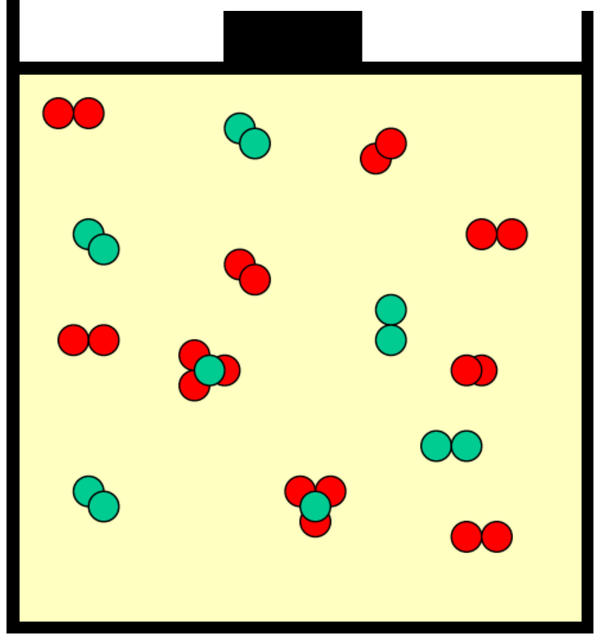
If the **pressure** on a system at equilibrium is **increased**, Q changes and the reaction will proceed toward the side with **fewer moles of gas** to reduce the stress.

This changes the equilibrium concentrations, but it **does not** change the Equilibrium Constant (K_{eq}).

Stress from Increasing Pressure

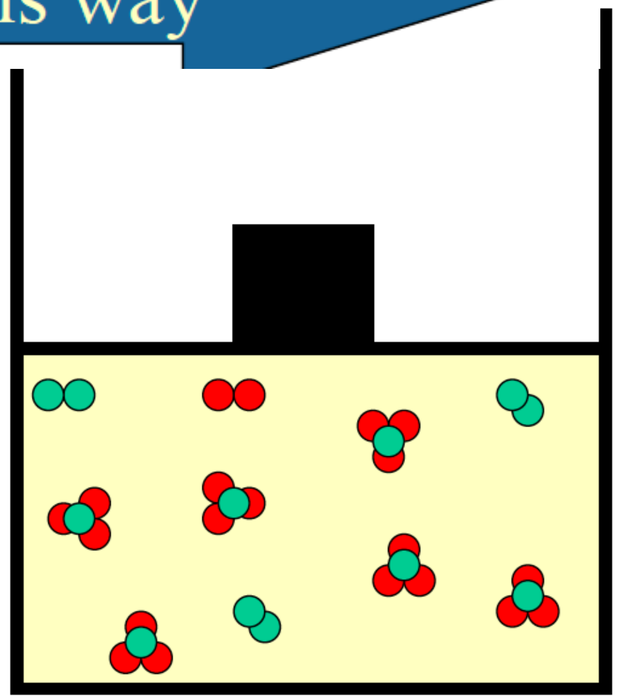
$$N_{2(g)} + 3\ H_{2(g)} \rightleftharpoons 2\ NH_{3(g)}$$

Reaction proceeds this way



14 gaseous molecules

2 NH_3, 5 N_2, 7 H_2



10 gaseous molecules

6 NH_3, 3 N_2, 1 H_2

Stress from Decreasing Pressure

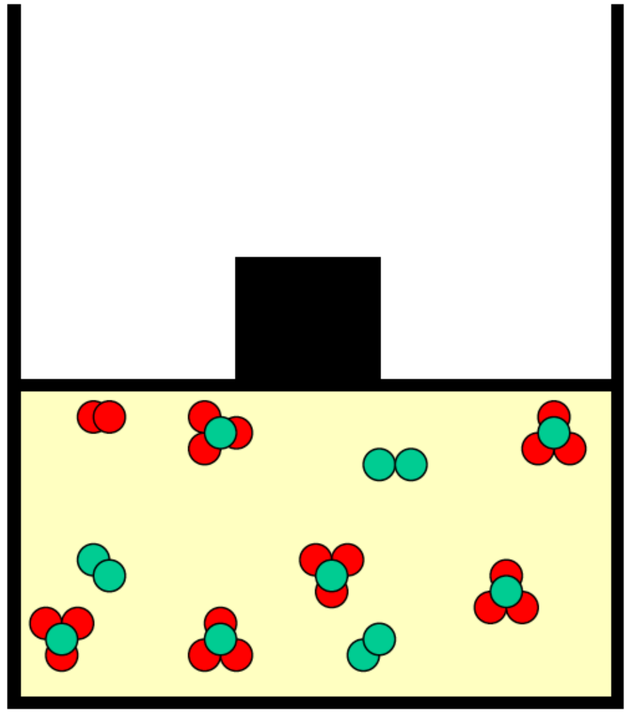
If the **pressure** on a system at equilibrium is **decreased**, Q changes and the reaction will proceed toward the side with **more moles of gas** to reduce the stress.

This changes the equilibrium concentrations, but it **does not** change the Equilibrium Constant (K_{eq}).

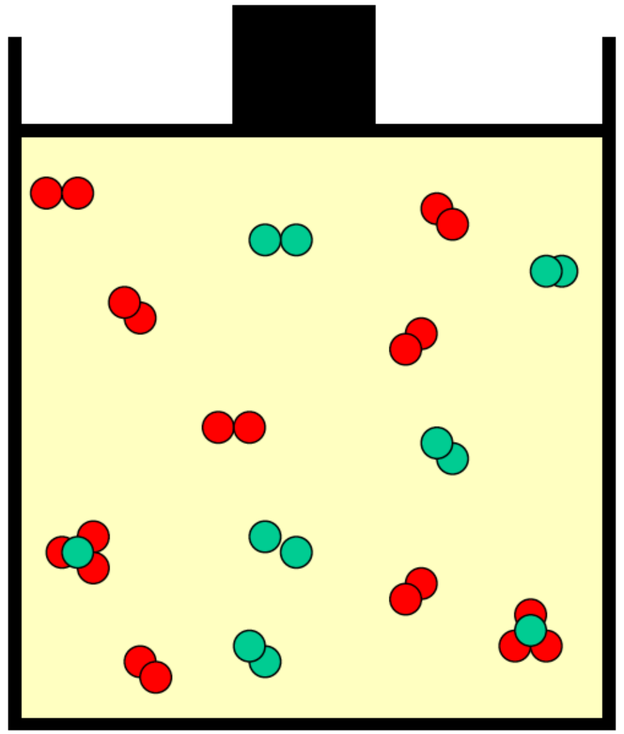
Stress from Decreasing Pressure

$$N_{2(g)} + 3\ H_{2(g)} \rightleftharpoons 2\ NH_{3(g)}$$

Reaction proceeds this way



10 gaseous molecules



14 gaseous molecules

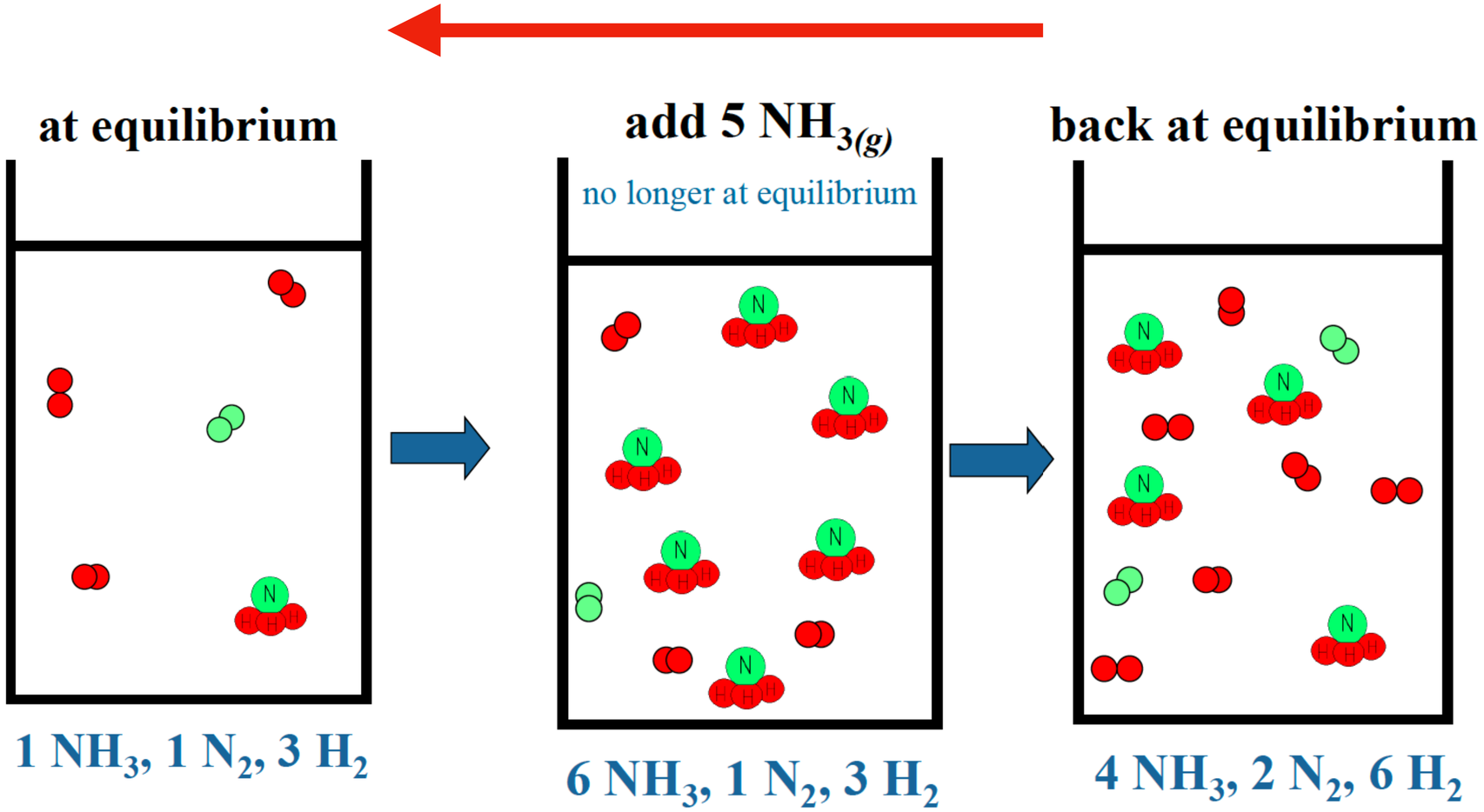
Stress from Increasing Concentration

If the **concentration** on a system at equilibrium is **increased**, Q changes and the reaction will proceed in the direction that will **reduce the concentration** of that species.

This increases the equilibrium concentrations, but it does not change the Equilibrium Constant (K_{eq}).

Adding more NH_3 to the system

$$N_{2(g)} + 3\,H_{2(g)} \rightleftharpoons 2\,NH_{3(g)}$$



Stress from Decreasing Concentration

If the **concentration** on a system at equilibrium is **decreased**, Q changes and the reaction will proceed in the direction that will **increase the concentration** of that species.

This increases the equilibrium concentrations, but it does not change the Equilibrium Constant (K_{eq}).

Stress from Dilution

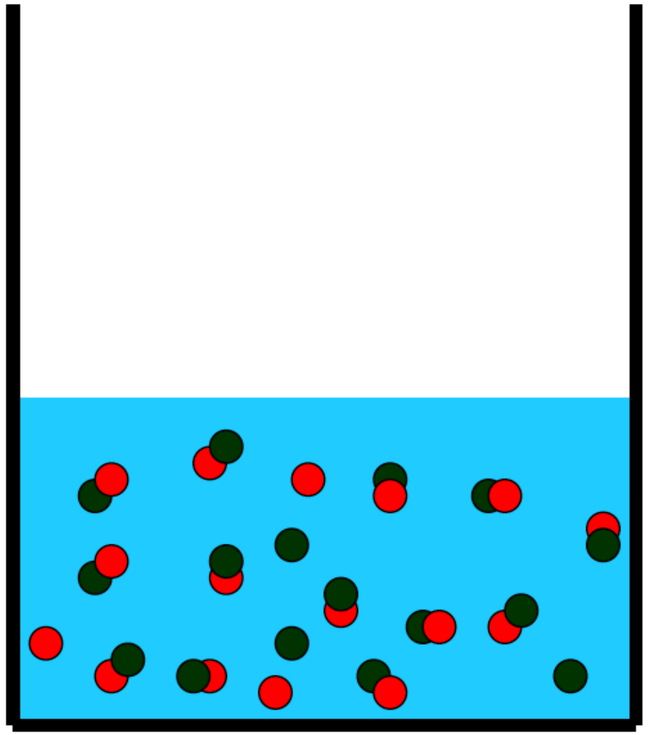
If **solvent is added** to a system at equilibrium, Q changes and the reaction will proceed toward the side with **more particles** to reduce that stress.

This increases the equilibrium concentrations, but it **does not** change the Equilibrium Constant (K_{eq}).

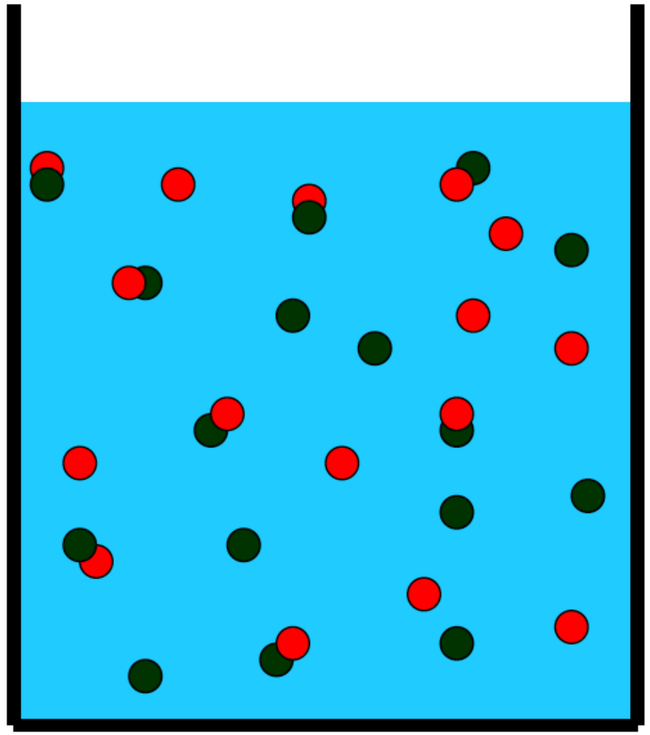
Stress from Dilution

$$HF_{(aq)} \rightleftharpoons H^{+}_{(aq)} + F^{-}_{(aq)}$$

Reaction will proceed this way



13 aqueous HF



8 aqueous HF

Stress from Changing Temperature

This is the **only stress** that **changes the equilibrium constant** (K_{eq})

$$N_{2(g)} + 3\ H_{2(g)} \rightleftharpoons 2\ NH_{3(g)} + \text{heat}$$

Cooling (taking heat away) shifts the equilibrium in the direction that produces heat.

$$N_{2(g)} + 3\ H_{2(g)} \rightleftharpoons 2\ NH_{3(g)} + \text{heat}$$

Adding heat (increasing the temperature) shifts the equilibrium in the direction that absorbs heat.

Example: Stress from Temperature Changes

A system represented by the chemical equation below is in a state of equilibrium at 25°C. Describe the color change that would occur if the temperature of the system increases to 75°C.

$$\underset{\text{Colorless}}{N_2O_4(g)} \rightleftharpoons \underset{\text{Brown}}{2\ NO_2(g)} \qquad \Delta H = +57.2\text{kJ}$$

- When heat is added, the reaction will proceed to the right.
- The system would become a darker shade of brown, because [NO_2] would increase.

Example: Stress from Temperature Changes

A system represented by the chemical equation below is in a state of equilibrium at 5°C. If the temperature of the system increases to 99.0°C, will the pH increase, decrease or remain the same?

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-{}_{(aq)} + H_3O^+{}_{(aq)} \qquad \Delta H = +1.2\text{kJ}$$

- When heat is added, the reaction will proceed to the right.
- The pH would decrease, because $[H_3O^+]$ would increase.

Example: Stress from Temperature Changes

A system represented by the chemical equation below is in a state of equilibrium in a cylinder at 25.00°C. If the volume of the cylinder was increased, would the temperature increase, decrease or remain the same while the system attempts to re-establish equilibrium? Justify your answer.

$$N_{2(g)} + 3\ H_{2(g)} \rightleftharpoons 2\ NH_{3(g)} \quad \Delta H = -92\ kJ$$

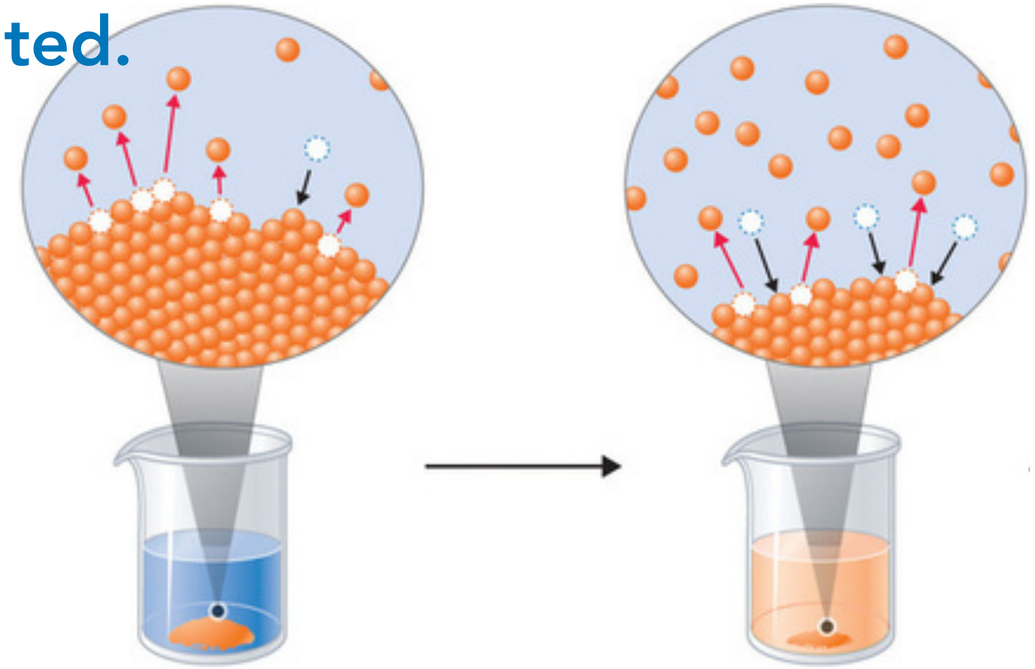
- The temperature will decrease.
- The rate of the reverse reaction would be greater than the rate of the forward reaction.
- The reverse reaction is endothermic.

7.11 Introduction to Solubility Equilibria
7.12 Common-Ion Effect

- The Solubility Product Constant (K_{sp})
- Predicting Precipitates

Saturation & Equilibrium

- **Saturated Solution**
  - The solvent has dissolved the maximum amount of solute that can at a certain temperature, and some solid solute remains on the bottom.
- A solution is at equilibrium when it is saturated.



(a) Unsaturated solution (b) Saturated solution

The Solubility Product Constant (K_{sp})

- **This is K_{sp} for ionic compounds in water.**

$$CaCO_{3(s)} \rightleftharpoons Ca^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}$$

$$K_{sp} = [Ca^{2+}]\,[CO_3^{2-}]$$

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

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

K_{sp} values generally range from about 1×10^{-3} to 1×10^{-54} or compounds that are considered to be insoluble. ONLY DEPENDENT ON TEMPERATURE

Solubility Rules

All salts containing **Na^+, K^+, NH_4^+ or NO_3^-** are soluble in water.

$K_{sp} > 1$ for all salts containing these ions, which is why they are considered soluble. The equilibrium lies to the right.

$$NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq)$$

K_{sp} determines the amount of dissociation that occurs as a reaction proceeds at equilibrium.

Example #1

Which compound is the least soluble in water at 298K?

$$CaCO_{3(s)} \rightleftharpoons Ca^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}$$

$$K_{sp} = [Ca^{2+}]\,[CO_3^{2-}] = 8.7 \times 10^{-9} \text{ at } 25\ ^{o}C$$

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

$$K_{sp} = [Pb^{2+}]\,[Cl^{-}]^2 = 1.6 \times 10^{-5} \text{ at } 25\ ^{o}C$$

Solubility

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

- The solubility is the maximum molar concentration of formula units that will dissolve at a given temperature.
  - For every 1 mole of $PbCl_2(s)$ that dissolves, 1 mole of Pb^{2+} ions and 2 moles of Cl^- ions enter the solution.
  - Solubility of $PbCl_2$ = $[Pb^{2+}]$ = 1/2$[Cl^-]$
    - When the **solution is saturated**.

Example: K_{sp} Calculation

- The solubility product constant for lead (II) fluoride is 3.6×10^{-8} at 25°C.

  (a) Write the balanced chemical equation.

  (b) Write the equilibrium expression

  (c) Find the maximum molar concentration of the ions in solution and the molar solubility (*s*) of the solution.

Practice: The solubility of $CaSO_4$ is found to be 0.67 g/L. Calculate the value of K_{sp} for calcium sulfate.

$$CaSO_4\,(s) \leftrightarrow Ca^{+2}\ (aq) + SO_4^{2-}\ (aq)$$

Initial		0	0
Change	-s	+s	+s
Equilibrium		s	s

Step 1: Calculate the number of moles of $CaSO_4$ dissolved in 1 L of solution.

Step 2: Substitute into the K_{sp} expression.

K_{sp} & Q_{sp}

If $Q_{sp} = K_{sp}$

- The system is at equilibrium
- It is a saturated solution with solid and aqueous species.

If $Q_{sp} > K_{sp}$, a precipitate will form

- The reaction will proceed to the left until the system reaches equilibrium

If $Q_{sp} < K_{sp}$, no precipitate forms.

- The solution is unsaturated.
- All of the ions will remain in solution.

Example: Predicting Possible Precipitates

(a) Find K_{sp} for a saturated solution of $PbCl_2$ if the concentration of Cl^- is found to be 0.0325 M.

(b) Will a precipitate of $PbCl_2$ form when 200.0 mL of 3.78×10^{-2} *M* NaCl is mixed with 100.0 mL of 2.45×10^{-2} *M* $Pb(NO_3)_2$. Assume that the temperature of the resulting solution is the same as that from part a.

Solubility & the Common Ion Effect

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

$$NaCl_{(s)} \rightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)}$$

- Cl^- is the common ion that causes the equilibrium in the first reaction to shift
- The presence of a common ion **decreases** the solubility of the salt.
- At a given temperature, K_{sp} depends on the product of the ion concentration. If the concentration of either ion goes up, the other will go down to maintain K_{sp}.

Example: Common Ion Effect

(a) Find [Ba^{2+}] and [SO_4^{2-}] after 0.0200 g of $Ba(NO_3)_2$ is added to a 400.0 mL saturated solution of $BaSO_4$ and equilibrium is established. Assume that the volume remains the same and the final temperature is 25˚C. (K_{sp} = 1.1 x 10^{-10} for $BaSO_4$ at 25˚C)

Example: Predicting Precipitates & the Common Ion Effect

If 0.15 M NaOH is slowly poured into a beaker containing 0.14 M $Ca(NO_3)_2$ and 0.25 M $Fe(NO_3)_2$, which precipitate will form first?

K_{sp} for $Ca(OH)_2 = 8.0 \times 10^{-6}$

K_{sp} for $Fe(OH)_2 = 1.6 \times 10^{-14}$

Step 1: Find $[OH^-]_{max}$ for $Ca(OH)_2$

Step 2: Find $[OH^-]_{max}$ for $Fe(OH)_2$

7.13 pH & Solubility

- pH & Soluble Salts
- Solubility in Weak & Strong Acid Solutions

Autoionization of Water

$$2\ H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

In pure water at 25°C,

$[H_3O^+] = 1.0 \times 10^{-7}$ and $[OH^-] = 1.0 \times 10^{-7}$.

As $[H_3O^+] = [OH^-]$ the solution is neutral.

$$K_w = [H_3O^+]\,[OH^-]$$

$$K_w = (1.0 \times 10^{-7})\,(1.0 \times 10^{-7})$$

$$K_w = 1.0 \times 10^{-14} \quad \text{(at 25 °C)}$$

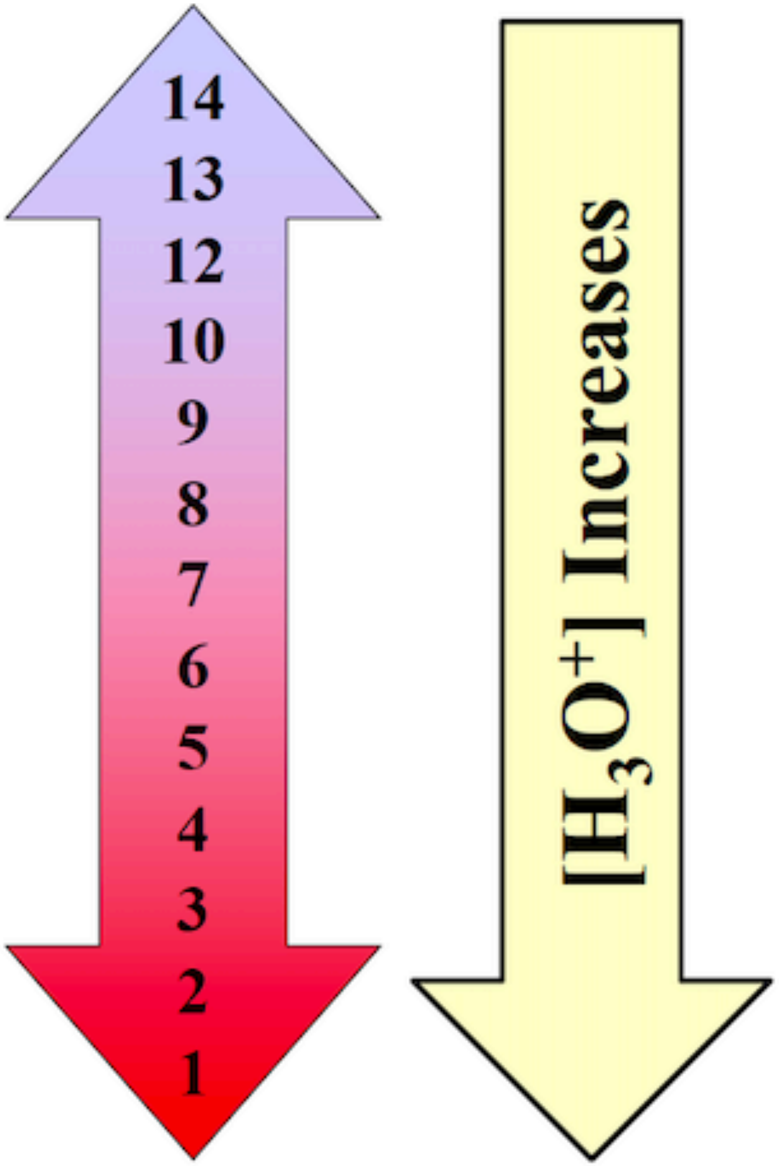
Autoionization of Water

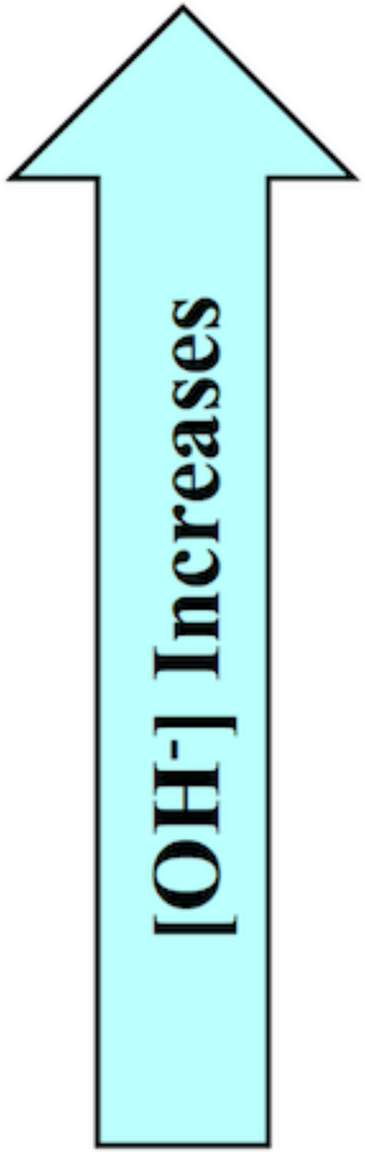
$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

$$K_w = [H_3O^+]\,[OH^-] = 1.0 \times 10^{-14} \quad \text{(at 25 °C)}$$

- This is a constant.
- If you know the concentration of $[H_3O^+]$ you can calculate the concentration of $[OH^-]$ or vise versa.
- Memorize this constant! It's very useful.

The pH Scale





The pH of a solution increases as $[H_3O^+]$ decreases and $[OH^-]$ increases.

The pH of a solution decreases as $[H_3O^+]$ increases and $[OH^-]$ decreases.

Some Cations Acidify Solutions

- Ionic compounds containing NH_4^+ can acidify solutions.
  - NH_4^+ is the conjugate acid of NH_3
  - Therefore, if NH_4NO_3 is added to water:

$$NH_4^+{}_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_{3(aq)} + H_3O^+{}_{(aq)}$$

The pH drops below 7 because $[H_3O^+]$ increases.

Some Cations Acidify Solutions

- The ability to release protons from water increases as:
  - Ionic radius decreases
  - Charge increases (Fe^{3+} decreases the pH more than Fe^{2+})
    - Fe^{3+} is smaller with more net positive charge
- Conjugate acids of strong bases **will not** affect pH
  - Group 1A cations, Ca^{2+}, Sr^{2+}, and Ba^{2+}
    - Large radii and/or small net (+) charge

Some Anions Make Solutions Basic

- Anions that are conjugate bases of weak acids accept protons from water to produce OH-.
  - The conjugate bases of strong acids **will not** raise the pH of a solution.
    - (Cl-, ClO_4-, I-, NO_3-, Br^-, HSO_4- do not accept protons from water)
- Example: $NaCH_3CO_2$ is added to water

$$CH_3COO^-_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH^-_{(aq)}$$

Metal Oxides are Basic

- Metal oxides can form solid hydroxides.

$$MgO_{(s)} \rightarrow Mg^{2+}_{(aq)} + O^{2-}_{(aq)}$$

$$O^{2-}_{(aq)} + H_2O_{(l)} \rightarrow 2\ OH^-_{(aq)}$$

$$MgO_{(s)} + H_2O_{(l)} \rightarrow Mg^{2+}_{(aq)} + 2\ OH^-_{(aq)}$$

$$MgO_{(s)} + H_2O_{(l)} \rightarrow Mg(OH)_{2(s)}$$

- The slight solubility of solid hydroxides increases [OH-] in the solution.

Example: Metal Oxides are Basic

- Write the net ionic equation for the reaction that takes place when solid potassium oxide is dropped into water.

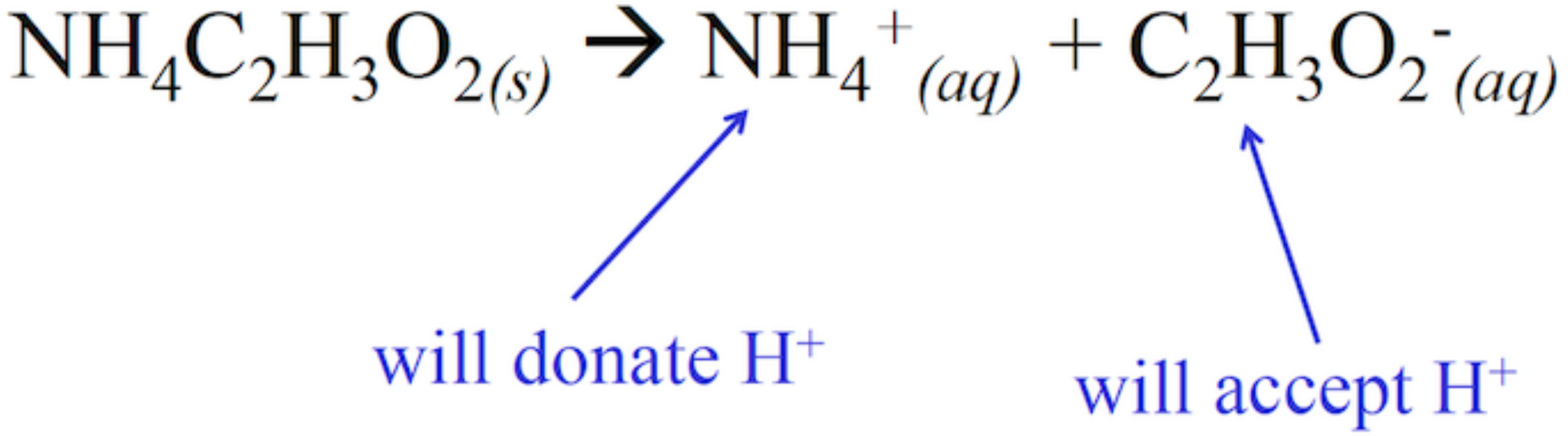
$$K_2O_{(s)} \rightarrow O^{2-}_{(aq)} + 2\,K^{+}_{(aq)}$$

$$O^{2-}_{(aq)} + H_2O_{(l)} \rightarrow 2\,OH^{-}_{(aq)}$$

$$K_2O_{(s)} + H_2O_{(l)} \rightarrow 2\,K^{+}_{(aq)} + 2\,OH^{-}_{(aq)}$$

Salts with Weak Acids & Weak Bases

- Some salts have an acidic cation and a basic anion.
  - Solutions containing these salts tend to have **little or no overall affect on pH**.



Example: Slightly Soluble Ionic Compounds in Strong Acidic Solutions

- Solid magnesium oxide is added to a solution of nitric acid. Write the net ionic equation for the overall reaction.

$$MgO_{(s)} \rightleftharpoons Mg^{2+}_{(aq)} + \cancel{O^{2-}_{(aq)}}$$

$$2\,H^{+}_{(aq)} + \cancel{O^{2-}_{(aq)}} \rightarrow H_2O_{(l)}$$

Net Ionic Equation

$$MgO_{(s)} + 2\,H^{+}_{(aq)} \rightleftharpoons Mg^{2+}_{(aq)} + H_2O_{(l)}$$

7.14 Spontaneity and Solubility

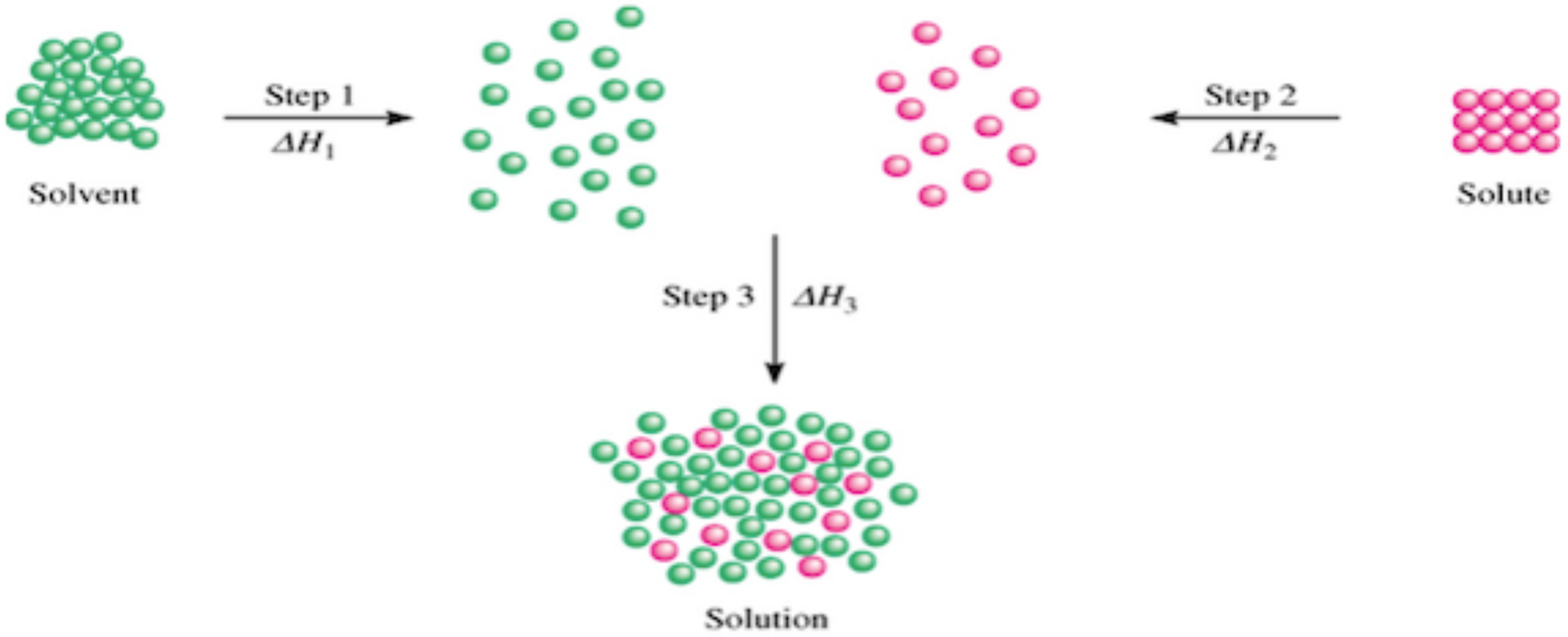
- Energy of Dissolution
- Temperature Implications

Spontaneous Processes

- When a reaction happens under a given set of circumstances, without any outside forces, it is said to be spontaneous.

- Doesn't have to be a FAST reaction, but it will just happen without any 'help'.

  - Iron exposed to water and oxygen forms rust (FeO_2 and Fe_2O_3), but rust does not spontaneously change back to iron.

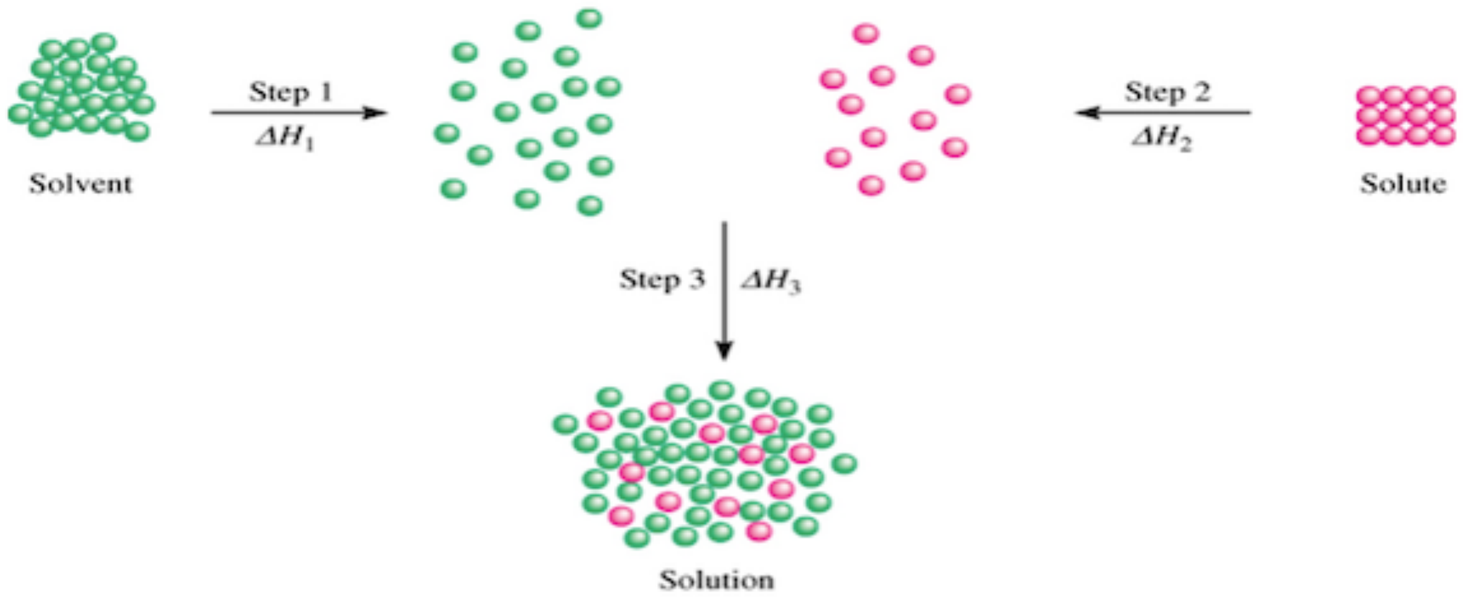


Free Energy of Dissolution

- Microstates - all of the tiny, individual places within a container that the particles can occupy.

- Dissolving a solid into a solution increases the amount of entropy (+ΔS).

$$\Delta G = \Delta H - T\Delta S$$



Step	ΔH	ΔS
1 - Solvent separates (overcomes IMFs)	+	+
2 - Solute separates (overcomes IMFs)	+	+
3 - The solution forms (forming IMFs)	–	–