

Equilibrium

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December 16, 2024

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EQUILIBRIUM INTRODUCTION

- **Dynamic equilibrium:** a balance between forward and reverse processes occurring at the same rate. Requirements for dynamic equilibrium:
 1. The system is a closed system
 2. All components of the chemical system need to be present
 3. The initial concentration of the chemicals stays the same throughout
- **Solubility equilibrium:** a dynamic equilibrium between a solute and a solvent in a saturated solution in a closed system
- **Phase equilibrium:** a dynamic equilibrium between different physical states of a pure substance in a closed system
- **Chemical reaction equilibrium:** a dynamic equilibrium between reactants and products of a chemical reaction in a closed system

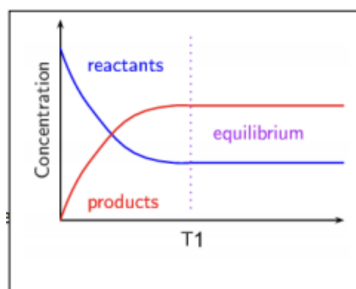


Figure 1: The position of the equilibrium shows that the products are more favoured. This means the percent reaction for reactants is less than 50% and the percent reaction for products is greater than 50%.

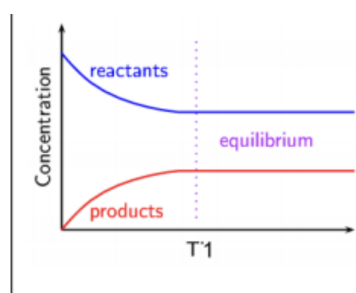


Figure 2: The position of the equilibrium shows that the products are less favoured. This means the percent reaction for reactants is greater than 50% and the percent reaction for products is less than 50%.

Solubility Equilibrium

- For instance, when NaCl is dissolved in water, the ions from the crystal collide with water molecules to dissolve. However, those ions can also collide with the crystal itself, forming ionic bonds, and crystalizing

- Early in the dissolving process, far more ions are entering the dissolved state compared to ions entering the crystal state. At equilibrium, water molecules and ions collide with the crystal at equal rates, hence the rate of dissolution equals the rate of crystalization and no change is observed
- This state is called the **state of dynamic equilibrium**

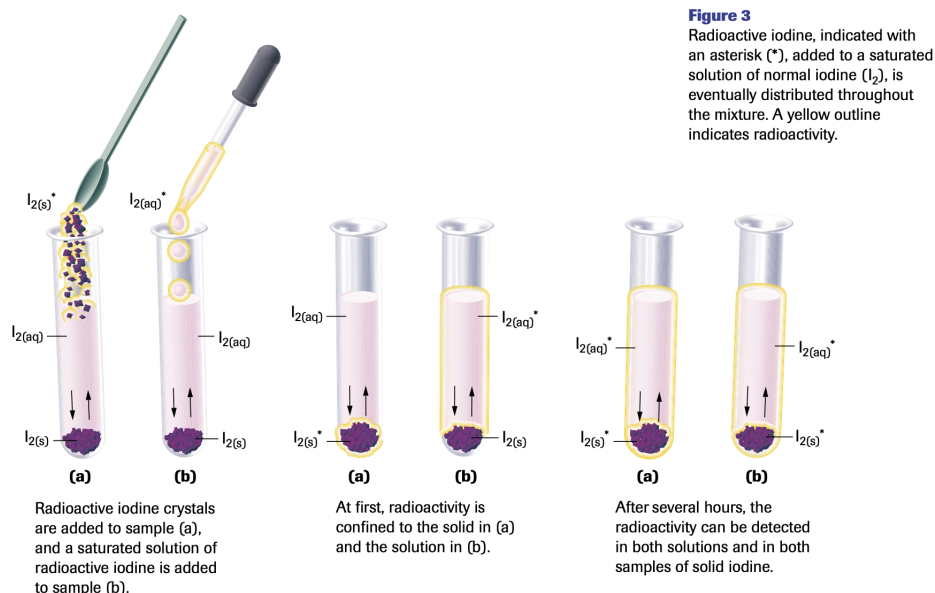


Figure 3: (a) contains solid unsaturated radioactive iodine and (b) contains saturated radioactive iodine. Both are mixed in normal iodine solution. Initially, only the iodine solids in (a) and the solution in (b) are radioactive. However, over time, in both cases (a) and (b), both the solid and solution components are radioactive.

Important. At equilibrium, the forward rates and reverse reaction rates are equal. How we achieved equilibrium is not relevant. For instance, once equilibrium is achieved, it is impossible to tell if we started with separate solutions of $Ca_{(aq)}^{2+}$ and $SO_{4(aq)}^{2-}$, or with excess $CaSO_{4(aq)}$ added to pure water. Initially, the difference is evident, but once the equilibrium is achieved, assuming that the equilibrium positions are identical, there is no difference.

Phase Equilibrium

- An example of **liquid-gas equilibrium** is having a water bottle with the cap closed. A small percentage of liquid water molecules have enough kinetic energy to change into gaseous state. However, simultaneously, there are also gaseous water molecules that are colliding with the liquid water molecules, causing them to turn also into liquid water molecules. In this case, the rate at which both processes are occurring are identical, thus no change is observed
- If the lid was uncapped however, the system becomes an open system and the liquid water will eventually all become gaseous liquid water molecules

- **Note:** the tendency of any liquid to evaporate increases at higher temperatures, so the concentration and pressure of the vapour is greater if the equilibrium is established at a higher temperature
- An example of **solid-liquid equilibrium** is ice/water slush at 0°C and 101.325 kPa. As the temperature of the water drops, the rate of melting decreases while the rate of freezing increases simultaneously, until a temperature of 0°C, where the rates become equal and the mixture will remain constant

Chemical Reaction Equilibrium

- **Quantitative reaction:** a chemical reaction in which virtually all of the limiting reagent is consumed. Often occurs in an **open system**
- A synthesis/decomposition reaction are common types of reversible reactions
- **Reversible reaction:** a reaction that can achieve equilibrium in the forward or reverse direction. Occurs in a **closed system**

Percent Reaction at Chemical Equilibrium

Percent reaction: the yield of product measured at equilibrium compared to the maximum possible yield of product.

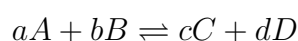
All chemical reactions are considered reversible; the only thing to consider is the extent to which they are reversible. Reactions fall loosely into three categories

- Reactions that favour reactants strongly; the percent reaction is less than 1%. In these reactions, mixing the reactants has no observable effect
- Reactions that favour products very strongly; where the percent reaction is greater than 99%. These reactions are observed to be quantitative reactions. These reactions are typically written with an arrow that has only one direction, to show that their reverse reaction is negligible
- Reactions that achieve noticeable equilibrium; the percent reaction lies somewhere between 1% and 99%. Only occurs in a closed system. If the percent reaction is less than 50%, reactants are favoured; if the percent reaction is more than 50%, the products are favoured
- An ICE table, standing for initial, change, and equilibrium, is useful for calculating stoichiometry involving dynamic equilibrium

EQUILIBRIUM CONSTANT

A ratio involving equilibrium constants between the reactants and products has a constant value, independent of how the equilibrium is reached. The ratio can be derived using the BCE. This ratio is called the equilibrium constant expression and denoted by K_{eq} .

In the hypothetical reaction



The value for K_{eq} , determined **empirically**, is given mathematically as

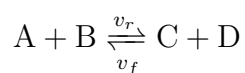
$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Where the exponents are the same as the coefficients in the BCE.

- When calculating the equilibrium conditions for homogeneous equilibrium, the expression is very straight forward. However, many equilibria involve more than one phase and are called heterogeneous
- **Homogeneous equilibria:** equilibria in which all entities are in the same phase
- **Heterogeneous equilibria:** equilibria in which reactants and products are in more than one phase
- When writing the equilibrium constant expression, it is essential to note that the position of the equilibrium **does not depend on the amounts of solid or liquid components present**. This is because, fundamentally, the “concentrations” of pure solids and liquids do not change. Therefore, the “concentrations” of these components are not included in the equilibrium constant expression
- In other words, since solids and liquids generally do not change concentrations, they are **not included** in the equilibrium constant equation

Derivation of the Equilibrium Constant

Given equilibrium equation



Where v_f is the rate of the forward reaction and v_r is the rate of the reverse reaction, we can derive two equations

$$v_f = k_f[A][B]$$

$$v_r = k_r[C][D]$$

During equilibrium, the forward reaction rate is equivalent to the reverse reaction rate. That is, $v_f = v_r$

$$\begin{aligned} v_f &= v_r \\ k_f[A][B] &= k_r[C][D] \\ \frac{k_f}{k_r} &= \frac{[C][D]}{[A][B]} \\ K &= \frac{[C][D]}{[A][B]} \end{aligned}$$

Of course, this applies to the case where the reactants have different coefficients as well

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

THE REACTION QUOTIENT

Equilibrium Establishment

- When the reactants and products for a particular chemical reaction are combined, it is useful to know whether the mixture is at equilibrium or not. When it is not, it is necessary to know how the system will change in order to establish equilibrium
- This change in equilibrium is typically referred to as a *shift*
- A shift **to the right** means that the concentration of the **products** will increase to reach equilibrium
- A shift **to the left** means that the concentration of the **reactants** will increase to reach equilibrium

Determining the *shift* in position is very simple if the concentration of any one of the reactants or products is 0:

- The system must shift in the direction of the missing component(s)
- This is because it is impossible to reach equilibrium if one of the components is missing

The Reaction Quotient

- When all of the initial concentrations are non-zero, then the reaction quotient, denoted by Q , is used to determine the shift that is required to establish equilibrium
- The reaction quotient uses the equilibrium constant expression for the reaction; however, the **initial concentrations** are used in the equation, rather than the equilibrium concentrations

For instance, in the reaction $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)}$

$$Q = \frac{[\text{NH}_3]_o^2}{[\text{N}_2]_o[\text{H}_2]_o^3}$$

Where the subscripted o denotes that it is the **initial concentration**.

Recalling that Q and K measure the ratio between the concentrations of the products to reactants, we can compare the values of Q to K to assert the following

- When $Q > K$
 - The initial concentration ratio between products to reactants is **too large**
 - Some products will be consumed to form reactants in equilibrium
 - The system shifts **left** to reach a state of equilibrium
- When $Q < K$
 - The initial concentration ratio between products to reactants is **too little**
 - Some reactants will be consumed to form products in equilibrium

- The system shift **right** to reach a state of equilibrium
- When $Q = K$
 - The initial concentration represents a system that is already in a state of equilibrium
 - The system will undergo no shift

Sample: For the synthesis of ammonia at 500°C , the equilibrium constant is $K = 6.0 \times 10^{-2}$. Predict the direction that the system must shift in order to establish equilibrium for the following “initial concentration” scenarios.

Experiment	$[\text{N}_2]$	$[\text{H}_2]$	$[\text{NH}_3]$
1	1.0×10^{-5}	2.0×10^{-3}	1.0×10^{-3}
2	1.5×10^{-5}	3.54×10^{-1}	2.0×10^{-4}
3	5.0	1.0×10^{-2}	1.0×10^{-4}

Answer: For experiment 1, the value for Q is

$$\begin{aligned}
 Q &= \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \\
 &= \frac{(1.0 \times 10^{-3})^2}{(1.0 \times 10^{-5})(2.0 \times 10^{-3})^3} \\
 &= 1.25 \times 10^7
 \end{aligned}$$

Since $Q > K$, the reaction shifts to the left.

For experiment 2, the value for Q is

$$\begin{aligned}
 Q &= \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \\
 &= \frac{(2.0 \times 10^{-4})^2}{(1.5 \times 10^{-5})(3.54 \times 10^{-1})^3} \\
 &= 0.06
 \end{aligned}$$

Since $Q \approx K$, the reaction has no shift.

For experiment, 3, the value for Q is

$$\begin{aligned}
 Q &= \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \\
 &= \frac{(1.0 \times 10^{-4})^2}{(5.0)(1.0 \times 10^{-2})^3} \\
 &= 0.002
 \end{aligned}$$

Since $Q < K$, the reaction will shift right.

QUALITATIVE CHANGES IN EQUILIBRIUM SYSTEMS

Le Chatelier's Principle

When a chemical system at equilibrium is disturbed by a change in property, the system adjusts in a way that opposes the change.

- **Equilibrium shift:** movement of a system at equilibrium, resulting in a change in the concentrations of reactants and products
- Keep in mind that any increase/decrease in concentration is **gradual**

Le Chatelier's Principle and Concentration Changes

- In most industrial chemical processes, we want to ensure that equilibrium is not achieved. That is, the reverse reaction is not allowed to occur, for maximum efficiency and profit. For instance, the synthesis of ammonia in the Haber process
- To ensure the maximum efficiency, reactants are constantly added while products are simultaneously removed to utilize Le Chatelier's Principle in order to minimize the reverse reaction
- When you add particles to a reaction system, the rates at the new equilibrium state will be greater than before, because the system now contains a large number of particles. Likewise, if particles were removed, the rates at the new equilibrium state will be less than before

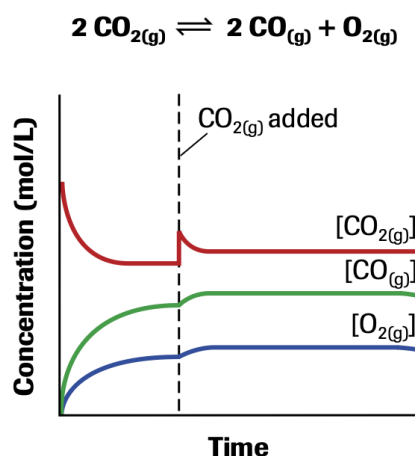


Figure 4: In this case, because reactants are being added, to achieve equilibrium, there will be a shift to the right to produce more products. This results in a concentration increase (till eventual decrease until equilibrium) in $[\text{CO}_{2(g)}]$ and a slight increase in $[\text{CO}_{(g)}]$ and $[\text{O}_{2(g)}]$. Initially, the forward reaction rate is significantly faster than the reverse reaction rate, until they eventually equal once they reach a state of equilibrium once the reverse reaction rate begins to speed up.

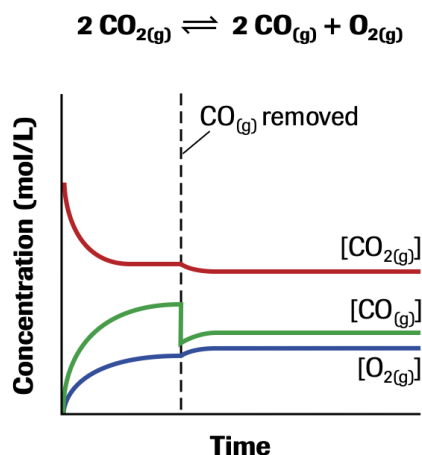


Figure 5: In this case, because products are being removed, to achieve equilibrium, there will be a shift to the right to produce more products. This results in a concentration decrease in $[\text{CO}_{2(g)}]$ and a slight increase in $[\text{CO}_{(g)}]$ and $[\text{O}_{2(g)}]$. Initially, the forward reaction rate is significantly faster than the reverse reaction rate, until they eventually equal once they reach a state of equilibrium once the reverse reaction rate begins to speed up.

Figure 4

Disturbing the iron(III) thiocyanate equilibrium

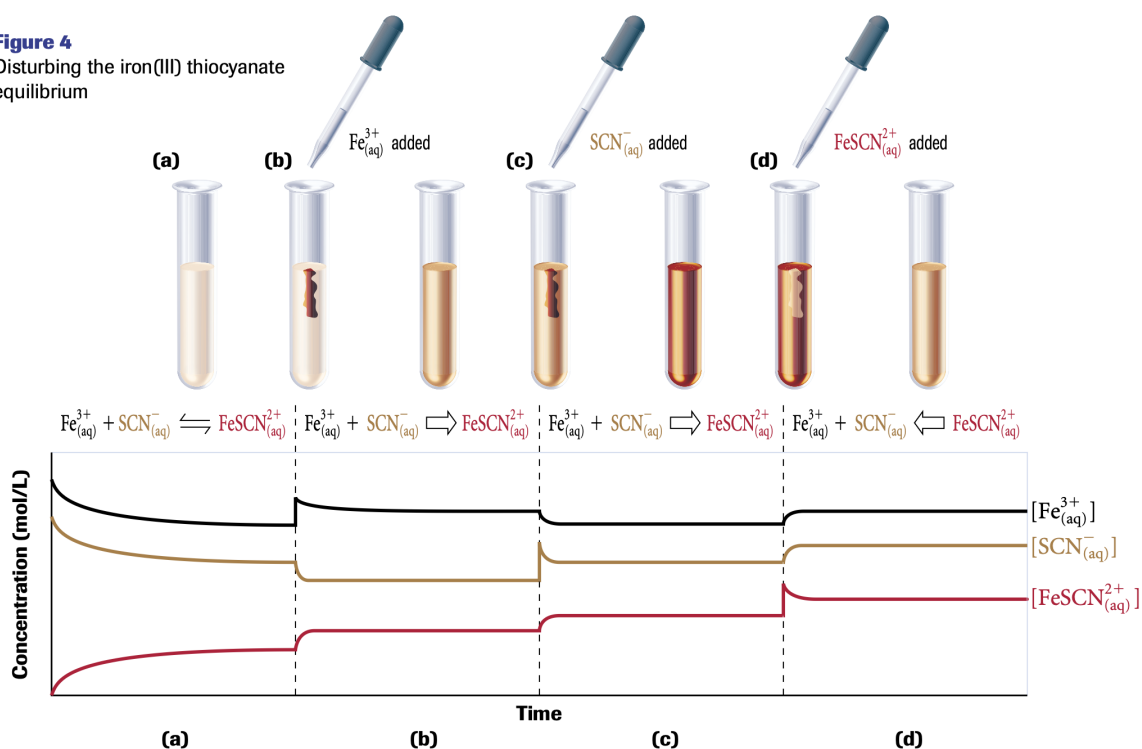


Figure 6: An example of the effects of concentration change on equilibrium shift.

Le Chatelier's Principle and Temperature Changes

The two types of reactions to consider are endothermic and exothermic reactions

endothermic reaction: reactants + energy \rightleftharpoons products

exothermic reaction: reactants \rightleftharpoons products + energy

- Energy can be added or removed to a system by heating or cooling the container. The

equilibrium shifts, according to Le Chatelier's Principle, to minimize the changes

- If the system is **cooled**, the system tries to **warm itself up** by shifting the equilibrium in a direction that produces heat. If heat is added, the equilibrium position will shift such that heat is absorbed by the system
- For instance, in the decomposition of dinitrogen tetroxide



When the system at equilibrium is heated, the reaction shifts to the right, increasing the concentration of $\text{NO}_{2(g)}$. This is made visible by the intensification of the reddish-brown colour. You can almost think of energy as a **chemical entity** partaking in the reaction

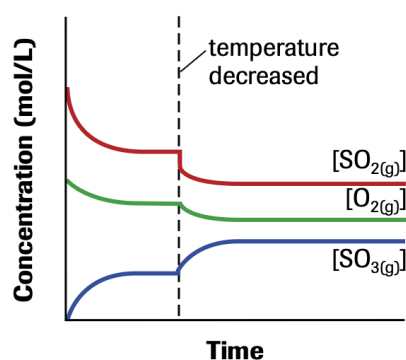
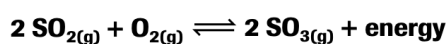


Figure 7: In this example, when the temperature is cooled, the system will counteract this change according to Le Chatelier's Principle by producing more heat. Thus, a right shift is observed by increasing the products via the consumption of reactants. Note that the forward rate is faster than the reverse rate initially, so that the system can produce more heat to counteract the decrease in temperature until equilibrium is achieved.

Important. Temperature change is the only factor that will **change the equilibrium constant value**. This is because the equilibrium constant depends on the fact that the closed system has constant temperature and pressure.

Le Chatelier's Principle and Gas Volume Changes

- According to Boyle's Law, the volume and pressure are inversely proportional. That is, if the volume decreases by half, the pressure increases by a factor of two
- Changing the volume of any equilibrium system **may** cause a shift in the equilibrium. If all the reactants and products are aqueous, then the shift in equilibrium is negligible. However, if there are chemical entities in the gaseous state, then a shift in equilibrium will be observed

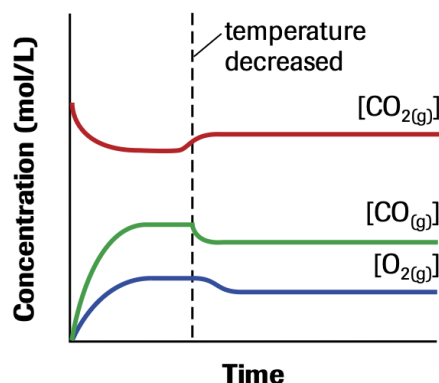
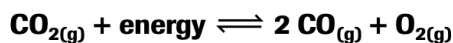


Figure 8: In this example, when the temperature is cooled the system will counteract this change by consuming less heat. Thus, a left shift is observed. Note that the reverse rate is faster than the forward rate initially, so that the system consumes less heat to counteract the decrease in temperature until equilibrium is achieved.

- For instance, consider $\text{N}_{2(g)} + 3 \text{H}_{2(g)} \rightleftharpoons 2 \text{NH}_{3(g)}$. On the reactants side, there are a total of 4 moles molecules, while on the product side, there are a total of 2 moles of molecules. When there is an increase in pressure, Le Chatlier's Principle suggests that the system will counteract the increase in pressure by reducing the pressure. In this case, the equilibrium will shift to the right, since there will be less moles of molecules in the system
- A system with equal number of gas molecules on each side of the equation will not have an equilibrium shift
- Particles in the **solid, liquid, or aqueous state** are not of significance when it comes to determining equilibrium shift. This is because substances in these condensed states are virtually incompressible, and so reactions involving them cannot counteract pressure change
- Kinetic theory explains the effects of a decrease in volume by assuming that both the forward and reverse reaction rates increase because the concentrations (partial pressures) of reactants and products increase. However, the forward reaction rate increases more than the reverse reaction rate because there are more particles involved in the forward reaction. The shift causes concentration changes that eventually increase the reverse rate and decrease the forward rate until they become equal

Common Ion Effect

The solubility of an ionic solids dissolved in pure water differs from a solution that contains a common ion to the ionic solid. For instance, consider dissolving sodium chloride in pure water versus dissolving it in sodium hydroxide solution. In the latter case, there is already an abundance of sodium ions before adding in the sodium chloride, which will affect the equilibrium position.

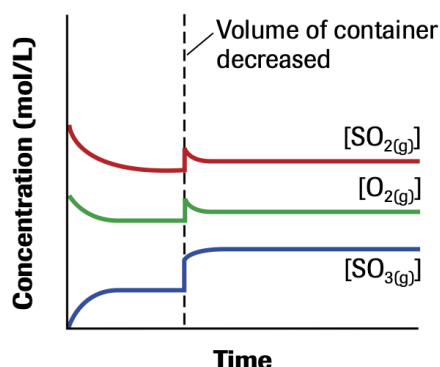
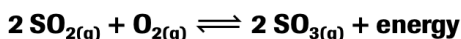


Figure 9: The equilibrium is disturbed by a decrease in volume. The equilibrium shifts forward to counteract the increase in pressure.

Important. Regardless of whether there are pre-existing common ions in the solution or not, the solubility product of the salt, K_{sp} , remains the same. The K_{sp} expression does not specify ions FROM that specific salt, but rather the entire concentration of ions.

The common ion effect is the expression used to describe the lowering of the solubility of a salt because the solvent into which it is being dissolved already contains ion(s) common to the salt.

Changes That Do Not Affect The Position of Equilibrium Systems

- **Adding Catalysts**

- The presence of a catalyst in a chemical reaction system lowers the activation energy for both forward and reverse reactions by an equal amount, so the equilibrium state is established much quicker but at the **same position** as it would without a catalyst
- Forward and reverse reaction rates are increased equally
- The value of catalysts in industrial processes is to decrease the time required for equilibrium shifts to occur, allowing a more rapid overall production of the desired product

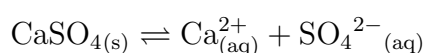
- **Adding Inert Gases**

- Adding inert gases, such as noble gases, which will not partake in the reaction of the system, does not affect the equilibrium position
- It may, however, affect the speed at which the equilibrium position is established, similar to the catalyst
- According to kinetic theory, the presence of inert gas changes the probability of a successful collision for both the reactants and products equally, resulting in no shift in the equilibrium system

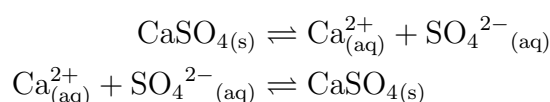
THE SOLUBILITY PRODUCT CONSTANT

- **Solubility:** the concentration of a saturated solution of a solute in a particular solvent at a particular temperature; solubility is a specific maximum concentration
- **Solubility product constant:** denoted by K_{sp} , this is the value obtained from the equilibrium law applied to a saturated solution
- **Trial ion product:** the reaction quotient applied to the ion concentrations of a slightly soluble salt. This is denoted by Q , or the reaction quotient
- **Supersaturated solution:** a solution whose solute concentration exceeds the maximum equilibrium concentration

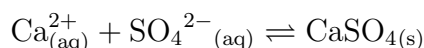
Solid ionic compounds dissociate to form anions and cations in an aqueous solution



When the solid salt is initially added to water, there are no calcium or sulfate ions present. However, as the reaction proceeds, the concentration of ions begins to increase. Therefore, it becomes more likely that they ions will collide with each other and reform the solid phase



Eventually, in a closed system, equilibrium is reached



At equilibrium, it would appear that no more solids are dissolving because the solution is **saturated**. However, the reality is that the forward reaction rate equals the reverse reaction rate. The equilibrium constant for this specific type of reaction is the **solubility product constant**, denoted by K_{sp} .

Important. Excess solids must be present in the saturated solution in order to establish this equilibrium.

In our example, the solubility product constant would be

$$K_{sp} = [\text{Ca}_{(aq)}^{2+}][\text{SO}_{4(aq)}^{2-}]$$

Note that there is no denominator in this case because the reactants are solids.

Solubility Product vs. Solubility

- The **solubility product** for a given reaction is an *equilibrium constant*. Therefore, it has only one value at a specific temperature
- The term **solubility** refers to the amount of a particular substance that is able to dissolve in solution, measured as a concentration

Important. Determining the solubility is useful for ensuring that no reactants are wasted, since there is no point adding reactants beyond the maximum saturation of the solution.

Sample: copper(I) bromide has a measured solubility of $2.0 \times 10^{-4} \text{ mol L}^{-1}$ at 25°C . Calculate the solubility product constant.

Answer: The BCE is



Therefore, the concentration of $\text{Cu}_{(aq)}^{1+}$ and $\text{Br}_{(aq)}^{1-}$ ions are the same as the solubility of $\text{CuBr}_{(aq)}$

$$\begin{aligned} K_{sp} &= [\text{Cu}_{(aq)}^{1+}][\text{Br}_{(aq)}^{1-}] \\ &= (2.0 \times 10^{-4})(2.0 \times 10^{-4}) \\ &= 4.0 \times 10^{-8} \end{aligned}$$

Sample: Calculate the solubility product constant for bismuth sulfide, Bi_2S_3 , if it has a measured solubility of $1.0 \times 10^{-15} \text{ mol L}^{-1}$ at 25°C .

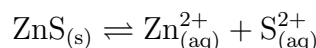
Answer: The BCE is



$$\begin{aligned} K_{sp} &= [\text{Bi}_{(aq)}^{3+}]^2[\text{S}_{(aq)}^{2+}]^3 \\ &= (2.00 \times 10^{-15})^2(3.00 \times 10^{-15})^3 \\ &= 1.08 \times 10^{-73} \end{aligned}$$

Sample: The solubility product constant for zinc sulfide is 6.1×10^{-24} at 25°C . Determine the individual ion concentrations.

Answer: The BCE is



Since we do not know the concentrations of the ions, let them both be denoted x , since they have the same coefficients

$$\begin{aligned} K_{sp} &= [\text{Zn}_{(aq)}^{2+}][\text{S}_{(aq)}^{2-}] \\ 1.6 \times 10^{-24} &= (x)(x) \\ x^2 &= 1.6 \times 10^{-24} \\ x &= 1.26 \times 10^{-12} \text{ mol L}^{-1} \end{aligned}$$

Sample: The K_{sp} for copper(II) iodate, $\text{Cu}(\text{IO}_3)_2$, is 1.4×10^{-7} at 25°C . Calculate its solubility at this temperature.

Answer: The BCE is



Similar to the last sample, we let x equal the solubility of $\text{Cu}(\text{IO}_3)_2$

$$\begin{aligned} K_{\text{sp}} &= [\text{Cu}_{(\text{aq})}^{2+}][\text{IO}_3^{-}(\text{aq})]^2 \\ 1.4 \times 10^{-7} &= (x)(2x)^2 \\ x &= \left(\frac{1.4 \times 10^{-7}}{4}\right)^{\frac{1}{3}} \\ &= 3.24 \times 10^{-3} \text{ mol L}^{-1} \end{aligned}$$

Precipitation

The K_{sp} value can also be used to predict whether or not a precipitate will form when two solutions are mixed. Calculate the reaction quotient, Q , and compare it to K_{sp} .

- If $Q < K_{\text{sp}}$, the solution is unsaturated; therefore, **no precipitate**
- If $Q > K_{\text{sp}}$, the solution is saturated; therefore, there **is precipitate**
- If $Q = K_{\text{sp}}$, the solution is exactly at the saturation point; therefore, **no precipitate**

Sample: Will a precipitate form if 25.0 mL of 0.00400 M aluminum hydroxide solution mixed with 25.0 mL of 0.0150 M calcium nitrate solution? K_{sp} for $\text{Ca}(\text{OH})_2$ is 6.5×10^{-6} .

Answer: Note that this is a double displacement reaction, which is why we are given the K_{sp} for $\text{Ca}(\text{OH})_2$. To determine if a precipitate will form, we need to calculate for Q and compare it with K_{sp} . To calculate Q , we need to determine $[\text{Ca}_{(\text{aq})}^{2+}]$ and $[\text{OH}_{(\text{aq})}^{-}]$. One important thing to keep in mind is that the combined volume of the two solutions is 50 mL. For $\text{Al}(\text{OH})_3$

$$\begin{aligned} C_1V_1 &= C_2V_2 \\ C_2 &= \frac{C_1V_1}{V_2} \\ &= \frac{(0.004 \text{ M})(25 \text{ mL})}{50 \text{ mL}} \\ &= 0.002 \text{ M} \end{aligned}$$

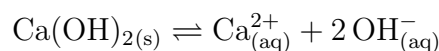
For $\text{Ca}(\text{NO}_3)_2$

$$\begin{aligned} C_1V_1 &= C_2V_2 \\ C_2 &= \frac{C_1V_1}{V_2} \\ &= \frac{(0.015 \text{ M})(25 \text{ mL})}{50 \text{ mL}} \\ &= 0.0075 \text{ M} \end{aligned}$$

Therefore, the concentrations we need are

$$\begin{aligned}[\text{OH}^-_{(\text{aq})}] &= 3[\text{Al}(\text{OH})_3] = 3(0.002 \text{ M}) = 0.006 \text{ M} \\ [\text{Ca}^{2+}_{(\text{aq})}] &= [\text{Ca}(\text{NO}_3)_2] = 0.0075 \text{ M}\end{aligned}$$

The BCE for the dissociation reaction is



Therefore, the Q value is

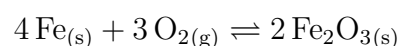
$$\begin{aligned}Q &= [\text{Ca}^{2+}_{(\text{aq})}][\text{OH}^-_{(\text{aq})}]^2 \\ &= (0.0075)(0.06)^2 \\ &= 2.70 \times 10^{-7}\end{aligned}$$

Since $Q < K_{\text{sp}}$, the solution is unsaturated, and no precipitate is formed.

SPOTANEITY, ENTROPY, AND GIBB'S FREE ENERGY

Spontaneous Reactions

- A **spontaneous** process is one that occurs in a system left to itself. Once started, no action from the outside system is necessary to make the process continue
- A **non-spontaneous** process, on the other hand, will not occur unless some external action is continuously applied
- Example: the rusting of an iron pipe exposed to the atmosphere. Although the process occurs quite slowly, it does so continuously. Consequently, the amount of iron decreases and the amount of rust increases as time elapses. Therefore, the reaction below is spontaneous



The reverse reaction on the other hand is non-spontaneous

We can make the following general statements:

- If a reaction is **spontaneous**, then its reverse reaction is **non-spontaneous**
- Both spontaneous and non-spontaneous reactions are possible; however, only the spontaneous reaction will occur **naturally**
- Although most exothermic reactions are spontaneous, there are some endothermic reactions that are also spontaneous (such as the evaporation of water); therefore, we cannot base spontaneity based on enthalpy change

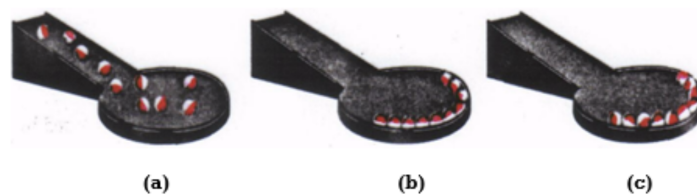


Figure 10

Entropy - Spontaneity and Disorder

Consider the analogy in Figure 10, where 10 half red half white coloured balls are released. If we were to release the balls, which setup would be most likely?

- Arrangement (a) is **not possible**, since the potential energy has not reached a minimum
- The disorder of (c) makes it more likely than the ordered arrangement in (b)

Consider a situation in which two identical bulbs are filled with ideal gases A and B. Each bulb has a pressure of 1.00 atm. This is shown in Figure 11

- A stopcock valve joins the two bulbs. When the valve is opened, assuming the two gases do not react, then each gas is going to expand into the bulb, containing the other gas and will continue mixing until the partial pressure of each gas is 0.500 atm in each bulb

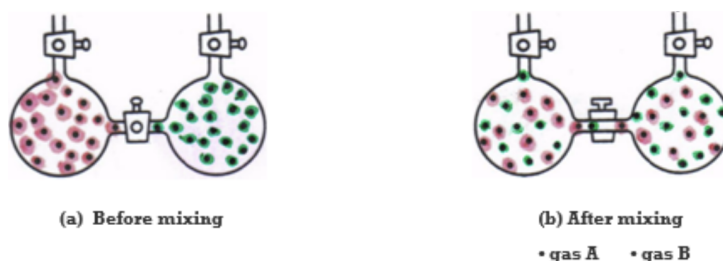


Figure 11

Important. One of the characteristics of an ideal gas is that its internal energy (E) and enthalpy (H) depend only on temperature and NOT on pressure or volume. Recall there are no IMF between gases A and B, when these two ideal gases mix at a constant temperature, $\Delta E = PV + \Delta H \approx \Delta H = 0$, recalling that $PV \approx 0$. Therefore, enthalpy is NOT the driving force behind the spontaneous mixing of gases. The driving force is simply the tendency of molecules to arrange themselves in the most random or **disordered** manner.

What is **entropy**?

- **Entropy**, denoted by S , is the thermodynamic property related to the degree of disorder in a system. The greater the degree of randomness or disorder in a system the greater its entropy

- Like internal energy and enthalpy, entropy is a *function of state*. Entropy has a unique value for a system whose temperature, pressure, and composition are specified
- The **entropy change**, ΔS , is the difference in entropy between two states and also has a unique value
- The formula for standard entropy change is

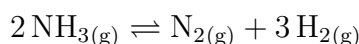
$$\Delta S^\circ = \sum n_p S^\circ_{\text{products}} - \sum n_f S^\circ_{\text{reactants}}$$

In general, a system will experience an increase in entropy ($\Delta S > 0$) if:

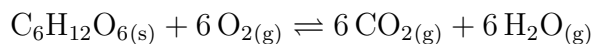
- The volume of the gaseous system increases
- The temperature of the system increases
- The physical state of a system changes from solid to liquid or gas, or liquid to gas ($S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$)

In chemical reactions, entropy increases ($\Delta S > 0$) when:

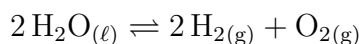
- Fewer moles of reactant molecules form a greater number of moles of product molecules. For instance, the reverse reaction of the Haber process



- Complex molecules are broken down into simpler subunits



- Solid reactants become liquid or gaseous products (or liquids become gases)



Free Energy

- Gibbs concluded that the spontaneity of a reaction depends on both enthalpy and entropy
- Gibbs Free Energy is the energy available to do work and is calculated as

$$G = H - TS$$

- The free energy change is

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

- When $\Delta G < 0$, the reaction is **spontaneous**
- When $\Delta G > 0$, the reaction is **non-spontaneous**
- When $\Delta G = 0$, the reaction is at equilibrium

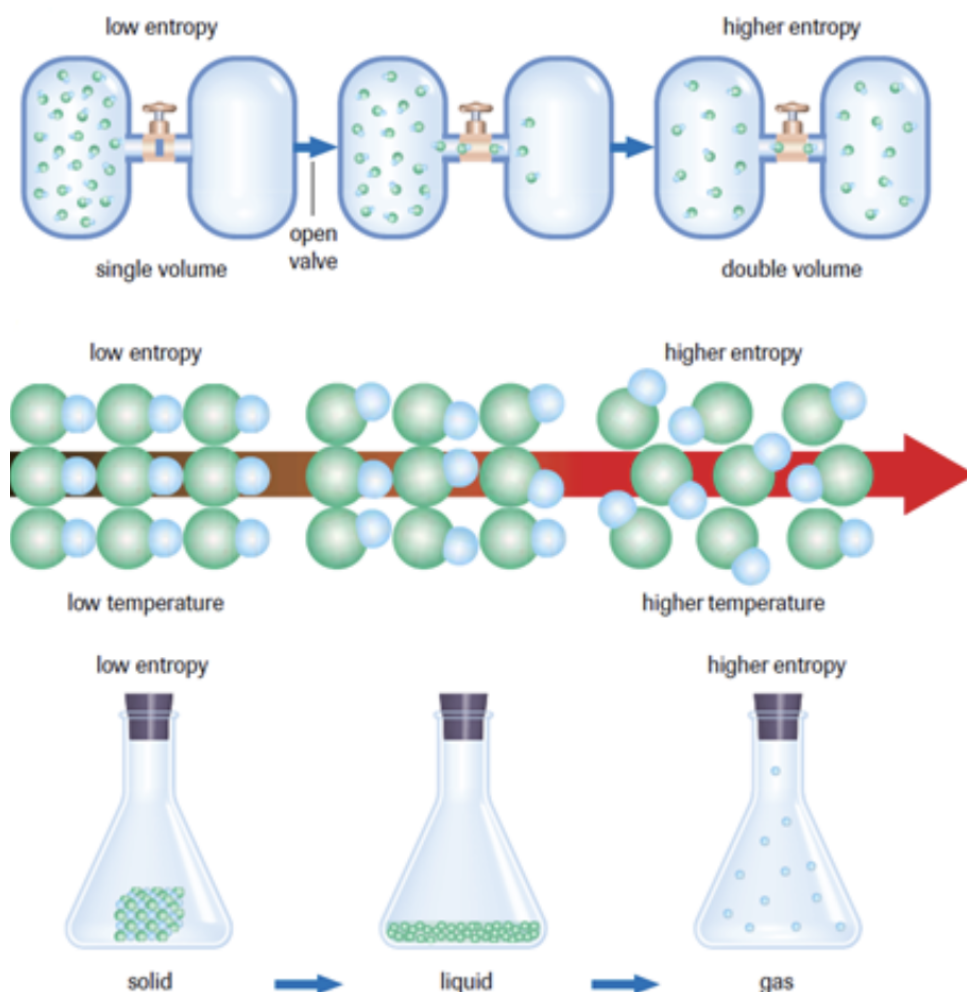


Table 0.1: We can use the end behaviour with respect to temperature, T

ΔG	ΔH	ΔS	$\Delta G = \Delta H - T\Delta S$
always spontaneous	negative	positive	negative at all temperatures
spontaneous at high temperatures	positive	positive	negative at high temperatures
spontaneous at low temperatures	negative	negative	negative at low temperatures
always non-spontaneous	positive	negative	positive at all temperatures

Important. Note that the entropy change is measured in units $\text{J mol}^{-1} \text{K}^{-1}$, while enthalpy is measured in units kJ mol^{-1} . Keep an eye out for joules vs kilojoules.

For instance, in an exothermic reaction, we can calculate the Gibbs free energy to determine the spontaneity of the reaction. In an exothermic reaction, $\Delta H < 0$, due to it releasing energy. Furthermore, $\Delta S > 0$, since the entropy of the system is greater by either forming more moles of product or forming all gas products. Therefore, $\Delta G < 0$ no matter what temperature, hence an exothermic reaction is spontaneous.

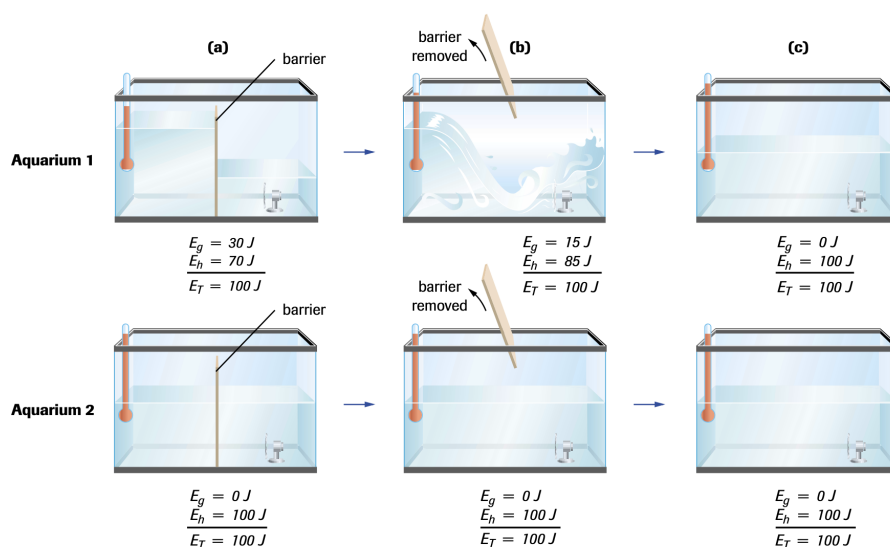


Figure 12: In (a), $G > 0$ and $\Delta G = 0$ (ordered); the reaction is non-spontaneous, external action needs to be applied for the process to occur. In (b), $G > 0$ and $\Delta G < 0$ (disordered); the reaction is spontaneous, no external action needs to be applied for the process to occur. In (c), $G = 0$ and $\Delta G = 0$ (equilibrium).

First Law of Thermodynamics

The total amount of energy in the universe is constant. Energy can be neither created nor destroyed, but can be transferred from one object to another, or transformed from one form to another.

Second Law of Thermodynamics

All changes either directly or indirectly increase the entropy of the universe. Mathematically

$$\Delta S_{\text{universe}} > 0$$

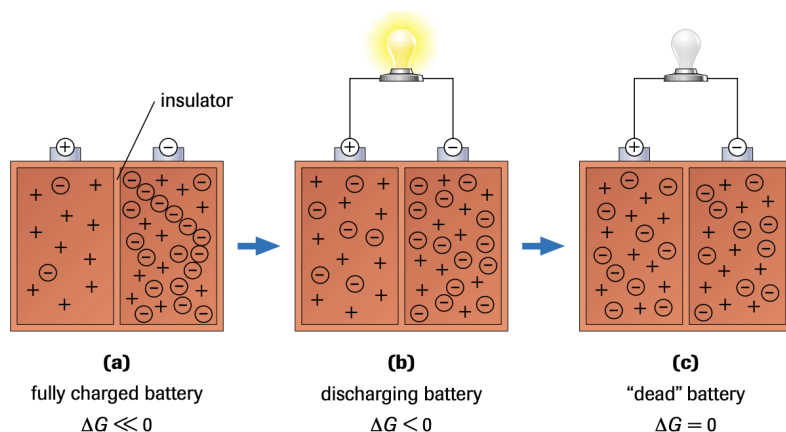
Third Law of Thermodynamics

The entropy of a perfectly ordered pure crystalline substance is 0 at absolute zero. Mathematically

$$S = 0 \quad \text{at} \quad T = 0\text{ K}$$

Equilibrium and ΔG

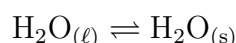
Consider Figure 13. When fully charged, the unequal distribution of charge on two sides of an insulator is maximal and the value of ΔG for the system is large and negative. When a conductor is connected between the two terminals, charges **spontaneously** flow from the negative terminal to the positive terminal, generating current and hence voltage. However, this flow increases the value of ΔG and releases free energy that is able to perform useful work, in this case lighting the lightbulb. When the electrical charges become equally distributed between the two compartments, dynamic equilibrium is achieved and the value of $\Delta G = 0$. No net movement of charge is possible, and no more work can be extracted from the system.


Figure 10

- (a)** A charged battery contains an unequal distribution of charges across the internal insulator. The value of ΔG is large and negative.
- (b)** A discharging battery releases free energy as the value of ΔG decreases. The free energy released is used to perform useful work.
- (c)** A "dead" battery has a ΔG value of zero. The system is in a state of dynamic equilibrium. The system has no more free energy to release and can do no work.

Figure 13

For instance, consider liquid water being cooled to a temperature below its freezing point at 101.3 kPa of pressure



Above 0°C , $\Delta G > 0$ and freezing is nonspontaneous ($\Delta H \leq 0$ and $\Delta S < 0$), thus the water remains liquid. At exactly 0°C , the system is in a state of dynamic equilibrium as an ice-water mixture: slush. The water remains as slush as long as the temperature is 0°C , and the water becomes ice once the temperature is below 0°C ($\Delta G < 0$)

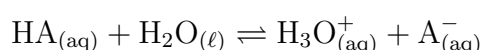
ACID AND BASE DISSOCIATION CONSTANTS

Water undergoes **autoionization**. Roughly, there are 1 in a billion successful collisions in pure water at SATP.

$$\begin{aligned}
 K_w &= 1.4 \times 10^{-14} \\
 [\text{H}_3\text{O}_{(\text{aq})}^+] &= 1.0 \times 10^{-7} \\
 [\text{OH}_{(\text{aq})}^-] &= 1.0 \times 10^{-7}
 \end{aligned}$$

Similar to the solubility product constant, the acid and base dissociation constants are calculated via writing the balanced dissociation equation and plugging in the concentrations.

Keep in mind that strong acids have a percent reaction $>99\%$, thus we do not consider equilibrium. For a weak acid however, because their percent reaction $<99\%$, we can consider their equilibrium. For a weak acid $\text{HA}_{(\text{aq})}$

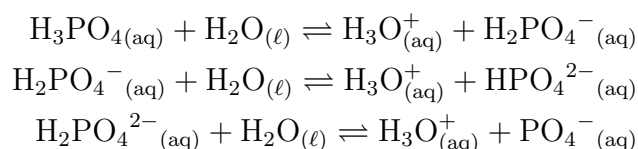


The acid dissociation constant is

$$K_a = \frac{[\text{H}_3\text{O}_{(\text{aq})}^+][\text{A}_{(\text{aq})}^-]}{[\text{HA}_{(\text{aq})}]}$$

Important. Fluoric acid, $\text{HF}_{(\text{aq})}$, is actually a **strong acid**. This is because fluorine is extremely electronegative.

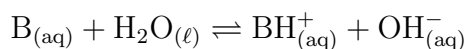
Keep in mind that for polyprotic acids, they actually undergo a series of equilibrium reactions. Consider for instance the weak acid $\text{H}_3\text{PO}_{4(\text{aq})}$, which is triprotic and actually undergoes three different equilibrium reactions simultaneously, which each successive reaction become weaker than the previous.



In most cases, the latter 2 reactions are negligible since the acid gets progressively weaker. Furthermore, there is a $\text{H}_3\text{O}_{(\text{aq})}^+$ **common ion effect**, promoting the reverse reaction even more. Thus, in polyprotic acids, we mainly only consider the first equilibrium reaction. In this case, the acid dissociation constant is

$$K_a = \frac{[\text{H}_3\text{O}_{(\text{aq})}^+][\text{H}_2\text{PO}_{4(\text{aq})}^-]}{[\text{H}_3\text{PO}_{4(\text{aq})}]}$$

The base dissociation is exactly the same as the acid dissociation constant. Given a weak base $\text{B}_{(\text{aq})}$



The dissociation constant is

$$K_b = \frac{[\text{BH}_{(\text{aq})}^+][\text{OH}_{(\text{aq})}^-]}{[\text{B}_{(\text{aq})}]}$$

Important. Given K_a and K_b , their product equals K_w . Keep in mind that a and b should be the acid and conjugate base, or conjugate acid and base, respectively.

$$(K_a)(K_b) = K_w$$

For instance, consider acetic acid

$$\begin{aligned}(K_a)(K_b) &= \left(\frac{[\text{H}_3\text{O}_{(\text{aq})}^+][\text{CH}_3\text{COO}_{(\text{aq})}^-]}{[\text{CH}_3\text{COOH}_{(\text{aq})}]} \right) \left(\frac{[\text{CH}_3\text{COOH}_{(\text{aq})}][\text{OH}_{(\text{aq})}^-]}{[\text{CH}_3\text{COO}_{(\text{aq})}^-]} \right) \\ &= [\text{H}_3\text{O}_{(\text{aq})}^+][\text{OH}_{(\text{aq})}^-] \\ &= K_w\end{aligned}$$

ACID AND BASE PROPERTIES OF SALTS

A **salt** is simply another name for an ionic compound. Different salts can produce ions that can act as acids or bases, or **neither**.

Salts that Produce Neutral Salts

In general, **strong acids and strong bases** have no effect on the pH. This is due to the strong acid having a weak affinity for hydronium ions (hence it can fully dissociate) and the strong base not being able to attract the hydronium ions.

The conjugate base of a strong acid has virtually no affinity for protons when compared to the affinity of water molecules; this is why strong acids completely dissociate in aqueous solutions.

For instance, the conjugate bases $\text{Cl}^-_{(\text{aq})}$ and $\text{NO}_3^-_{(\text{aq})}$ (from strong acids) do not combine with the $\text{H}_3\text{O}^+_{(\text{aq})}$, and as a result, have no effect on the pH. In other words, strong acids have no effect on the pH.

Cations such as $\text{K}^+_{(\text{aq})}$ and $\text{Na}^+_{(\text{aq})}$ (from strong bases) have no affinity for $\text{H}^+_{(\text{aq})}$ nor can they produce $\text{H}^+_{(\text{aq})}$. They have no effect on pH either. In other words, strong bases have no effect on the pH.

Since in both cases there is no change in the number of $\text{H}_3\text{O}^+_{(\text{aq})}$ ions, there will be no shift in equilibrium of $\text{H}_2\text{O}_{(\ell)} \rightleftharpoons \text{H}_3\text{O}^+_{(\text{aq})} + \text{OH}^-_{(\text{aq})}$, thus no change in $\text{OH}^-_{(\text{aq})}$ concentration is observed either.

Important. Salts that consist of the cations of strong bases and the anions of strong acids have no effect on the pH of a solution whose solvent is water.

Salts that Produce Basic Solutions

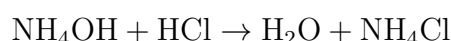
For any salt whose cation has neutral properties and whose anion is the conjugate base of a weak acid produces a basic solution.

For instance, in an aqueous solution of sodium acetate, $\text{NaCH}_3\text{COO}_{(\text{aq})}$, the major species are $\text{Na}^+_{(\text{aq})}$, $\text{CH}_3\text{COO}^-_{(\text{aq})}$, and $\text{H}_2\text{O}_{(\ell)}$. As previously discussed, the $\text{Na}^+_{(\text{aq})}$ ions has neither acid nor base properties. The acetate ion however is the conjugate base of acetic acid, a weak acid. This means that the acetate ion has a strong affinity for hydronium ions and is a base. Therefore, the acetate ions will react with the hydrogen in the hydronium ions, causing a shift in the water equilibrium, producing more $\text{OH}^-_{(\text{aq})}$ ions. Hence, the solution becomes basic.

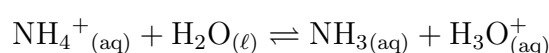
Salts that Produce Acidic Conditions

Salts whose cations are the conjugate acid of a weak base (and whose anions come from a strong acid) produce acidic conditions.

For instance



The NH_4Cl will dissociate further with the water molecules. Since Cl^- is a strong acid, it has no affinity for protons. However, ammonia does



Since $\text{NH}_4^+_{(\text{aq})}$ is a weak acid, it gives away protons and hence produces more hydronium ions. Therefore, the solution becomes acidic.

Salts that May be Acidic or Basic

There are salts where **both** the cation and anion affect the pH of the solution. For instance, ammonium acetate $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2(\text{aq})$. In such situations, we will only look at them **qualitatively** and predict whether the solution will be acidic, basic, or neutral.

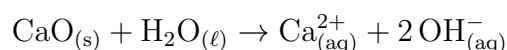
- If $K_a > K_b$, the solution will be acidic
- If $K_a < K_b$, the solution will be basic
- If $K_a = K_b$, the solution will be neutral

Hydrolysis of Metal and Nonmetal Oxides

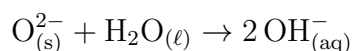
Metal and nonmetal oxides have low solubility in water. Therefore, we consider their **reaction** instead of dissociation in water instead. These reactions produce either acidic or basic solutions

- Metal oxides react with water to produce basic solutions
- Nonmetal oxides react with water to produce acidic solutions

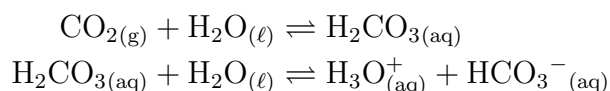
For instance, the reaction of the metal oxide calcium oxide in water



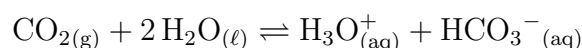
Where the oxide ions are believed to react with the water to form hydroxide ions, thus producing a basic solution



Another example is with carbon dioxide, a nonmetal oxide



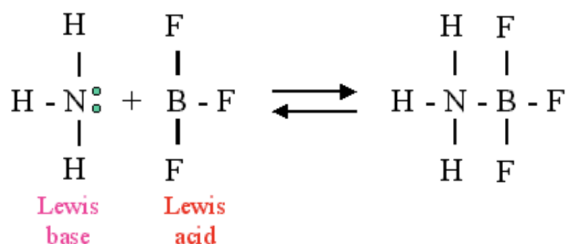
The $\text{H}_2\text{CO}_{3(\text{aq})}$ cancel out and the net equation is



Producing an acidic solution.

Lewis Acids and Bases

- **Lewis acid:** an atom, ion, or molecule that is an **electron-pair** acceptor
- **Lewis base:** an atom, ion, or molecule that is an **electron-pair** donor



BUFFERS

The most common application of acid-base solutions are **buffered solutions**. A buffer is a solution that resists change in pH when either hydroxide ions or protons are added

- A buffered solution may contain a **weak acid and a salt containing its conjugate base** (e.x. HF and NaF) or a **weak base and a salt containing its conjugate acid** (e.x. NH_3 and NH_4Cl)
- By choosing the correct components, a solution can be buffered to almost any pH
- A buffer is able to resist significant changes in pH because it has both the acid and basic components. These components neutralize added H^+ or OH^-

When the concentrations of the conjugate acid/base is the same as the base/acid, the target pH of the solution is simply the pK_a .

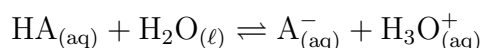
$$\begin{aligned}
 K_a &= \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \\
 &= [\text{H}_3\text{O}^+] \\
 \text{pK}_a &= \text{pH}
 \end{aligned}$$

This occurs when $[\text{A}^-] = [\text{HA}]$. At this point, this is known as the **half neutralization point**, where half of the volume of the equivalence point is required.

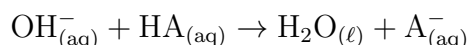
Important. The half neutralization point allows us to utilize $\text{pK}_a = \text{pH}$ which allows us to identify the acid.

How Does Buffering Work?

Suppose a buffer contains a relatively large amount of weak acid HA



When hydroxide ions are added to the solution, the weak acid is the best source of protons



The net result is that $\text{OH}^-_{(\text{aq})}$ ions do not build up in the solution, rather they are replaced by $\text{A}^-_{(\text{aq})}$ ions. Recall that the solution already contains $\text{A}^-_{(\text{aq})}$ ions, from the salt. Recall that

$$\begin{aligned}
 K_a &= \frac{[\text{H}_3\text{O}^+_{(\text{aq})}][\text{A}^-_{(\text{aq})}]}{[\text{HA}_{(\text{aq})}]} \\
 [\text{H}_3\text{O}^+_{(\text{aq})}] &= K_a \frac{[\text{HA}_{(\text{aq})}]}{[\text{A}^-_{(\text{aq})}]}
 \end{aligned}$$

If the original concentrations of $[HA]$ and $[A^-]$ are initially very large, when OH^- ions are added, the change in the ratio $[HA]:[A^-]$ will be minimal.