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Reactions in solution

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THE most common reactions happen in solution and involve cations and anions. Think, for example, when you add sugar to your coffee or how metal rusts when it gets wet. The first example involves a dissolution reaction, whereas the second a redox reaction in which electrons are being exchanged. Overall there are three main different types of reactions happening in solutions. It is not only important to be able to differentiate these reactions, but it is also important to understand the nuances between acid-base reactions, precipitation reactions, and redox reactions. It is also critical to understand the properties of solutions and learn how to quantify and compare the amount of solute in a solution. On one hand, most of you will be surprised to know that water does not conduct electricity. This is because pure water is a weak electrolyte. On the other hand, the importance of electrolytes is well known among the sports community. If you have ever played a sport, you have probably chugged a sports drink. These are electrolyte solutions. However, few know the specifics of their function. Electrolytes are salts that conduct electricity in water by separating them into positive and negative ions. To understand the properties of solutions it is important to identify and differentiate the different types of electrolytes.

GOALS

1. Identify the components of a solution
2. Carry composition calculations
3. Classify electrolytes
4. Differenciate reactions in solution
5. Balance redox reactions

1.1 Solutions and composition

Discussion: List three solutions in your household containing just a single solute. Give the chemical formula of the solute and the name of the solvent.

Solutions are homogeneous mixtures of two components. The state of the matter of both components of the mixture or their polarity affect the formation of a solution. For example, a solution will not result from mixing oil and water as they have different polar character and it will form from mixing table salt and water as both are polar chemicals. At the same time, the more solute you add to a solution the more concentrated the solution will be. This section covers polarity and the composition of solutions.

What makes a solution? Solutions are homogeneous mixtures of a solute and a solvent. Homogeneous means that if you look at the mixture you will not be able to differentiate both components and you will only see it as a whole. In a solution, the solute is the component of the mixture in less amount, whereas the solvent is the component in a larger amount. Think about mixing sugar with water. Sugar is sweet and water tasteless. When you mix both, you form a solution of sugar (solute) in water (solvent) and you will not see sugar in the solution as it is dissolved. In this particular example, sugar will be the solute in the solution, as the sugar is in less amount than water. Is important to remember that a solution is the result or mixing a solute and a solvent:

$$\text{Solution} = \text{Solute} + \text{Solvent}$$

Sample Problem 1

Identify the solute and the solvent in the following mixtures: (a) 10g of $H_2O(l)$ mixed with 3g of $KCl(s)$; (b) 10g $Cu(s)$ mixed with 3g $Zn(s)$

SOLUTION

(a) Potassium chloride is in less amount and hence will be the solute. Water, in larger quantity, will be the solvent. This is an example of an aquose-based solution. (b) Zn is in less amount and hence will be the solute, and Cu the solvent. This is a solid solution.

STUDY CHECK

Identify solute and solvent in the following mixture: (a) 10g of $H_2O(l)$ and 20g of $CH_3OH(l)$; (b) 1g of $I_2(s)$ and 100g of $CH_3CH_2OH(l)$

Types of solutions You can prepare different types of solutions by mixing a solid and a liquid, like when you mix sugar and water, or salt and water. You can create solutions as well by mixing two liquids or two solids. Examples are vinegar–a liquid solution of acetic acid (liquid) in water (liquid)–or steel– a solid solution that contains iron and carbon, both solids.

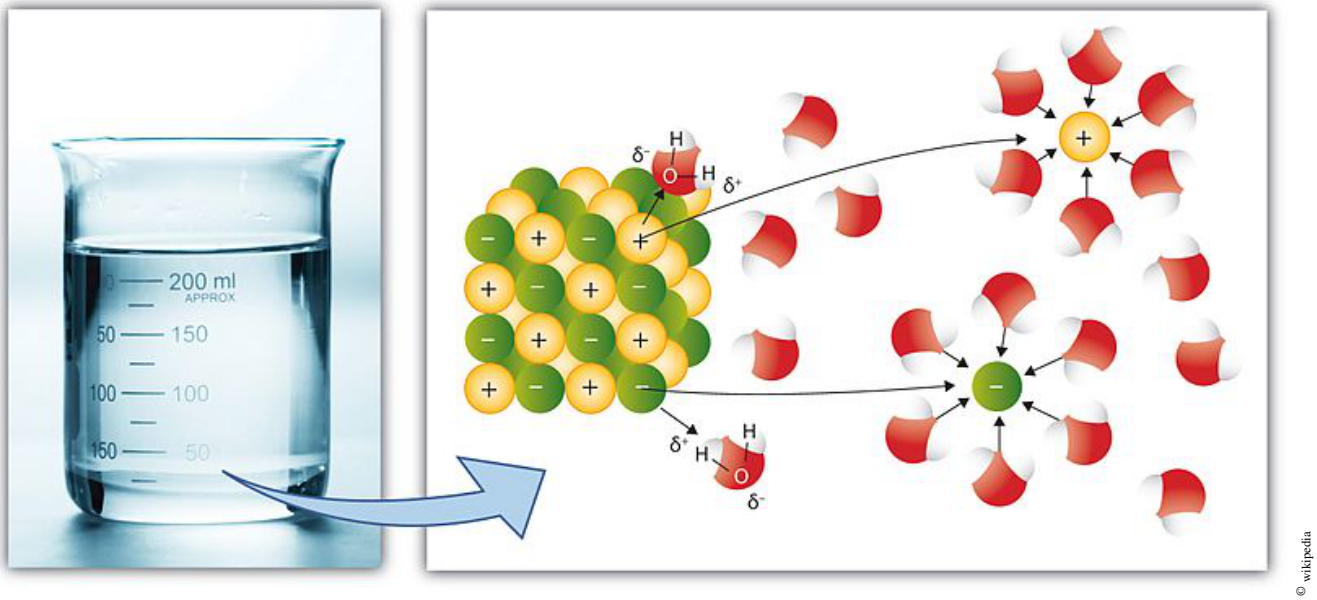

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Figure 1.1 A solution results from dissolving a solute into a solvent

Empirical rules of polarity The affinity between two chemicals is related to a concept called polarity. Molecules contain electrons and depending on the electron distribution within the molecules, molecules can be polar or non-polar. Molecules with an even electron distribution are non-polar as they have no permanent dipole moment. An example of this is H_2 molecule. Differently, HF is a polar molecule, as F concentrates more the electron density of the molecule than H. The polar nature of substances–with a permanent dipole moment–is related to miscibility and molecules with similar polar character will mingle and mix together creating a single visible phase. As an example, water (H_2O, polar) and methanol (CH_3OH, polar) will mix together. Differently, water (polar) and oil (non-polar) are immiscible due to its different polar nature and they will not mix. Even if the rules or polarity are based of the nature and

structure of the molecule, one can use very simple empirical rules to classify molecules as polar or non-polar. These rules work in general well for the case of diatomic and very large molecules:

- Diatomic molecules made of the same element (e.g. H_2) are non-polar.
- Diatomic molecules made of different elements (e.g. HI) are polar.
- Poliatomic molecules (with more than four atoms) made of C and H (e.g. CH_4) are in general non-polar.
- Poliatomic molecules (with more than four atoms) containing C, H and a different atom (e.g. CH_3F) are in general polar.

Sample Problem 2

Classify the following molecules as polar or nonpolar: H_2, HCl, CH_3CH_3, and CH_3CH_2Cl.

SOLUTION

H_2 is a non-polar molecule, being a diatomic molecule containing two atoms of the same element. Differently HCl is polar. CH_3CH_3 is a non-polar poliatomic molecule made of C and H atoms, whereas CH_3CH_2Cl is polar.

STUDY CHECK

Classify the following molecules as polar or nonpolar: HF, Cl_2, C_2H_4, and C_2H_3Cl.

Mixing and polarity A solution is formed when both the solute and the solvent mix. However, they will only mix if they have the same polarity. As an example, water (H_2O) is a polar molecule and methanol (CH_3-OH) too. Hence they will both mix and form a solution. If the elements of a mixture have different polarity they will not mix. An example is benzene (C_6H_6, nonpolar) and water, or for example oil (nonpolar) and water (polar).

Table 1.1 Polarity and mixing

Solvent	Solute	Mixing?
Polar	Polar	Yes
Polar	Nonpolar	No
Nonpolar	polar	No
Nonpolar	Nonpolar	Yes

Sample Problem 3

Use polarity arguments to indicate if the following substances will mix: (a) $H_2O_{(g)}$ and $CH_{4(g)}$; (b) $H_2O_{(g)}$ and $HCl_{(g)}$

SOLUTION

(a) Water and methane (CH_4) will not mix, as water is a polar molecule and CH_4 (methane) is nonpolar. (b) They will mix as HCl is a polar molecule and so is water.

STUDY CHECK

Use polarity arguments to indicate if the following substances will mix: (a) $H_2O_{(l)}$ and $CH_3Cl_{(l)}$; (b) $CH_3Cl_{(l)}$ and $CCl_{4(l)}$

Concentration of solutions The concentration of a solution refers to the amount of solute with respect to the amount of solution. The larger concentration the larger the number of solute particles with respect to the particles of solvent. Concentration is one of the most important properties of a solution as it affect the physical properties of a solution such as the freezing and boiling point. There are many different concentration units, such as molarity, mass percent concentration, or volume percent concentration. All these different units overall express the ration between the particles–mass or volume–of solute and solvent.

Mass percent concentration The mass percent (m/m) is the amount of solute in grams per grams of solution in percent form

$$m/m = \frac{\text{g of solute}}{\text{g of solution}} \times 100$$

Sample Problem 4

A NaCl solution is prepared by mixing 4g of NaCl with 50g of H_2O. Calculate the percent (m/m) of the solution.

SOLUTION

We need the grams of solute and the grams of solution. The grams of solute are given (4g of NaCl), whereas the grams of solution result from adding the grams of solvent and solute: 54 g of solution. Using the formula for the percent (m/m), he have:

$$m/m = \frac{4 \text{ g of solute}}{54 \text{ g of solution}} \times 100 = 7.4\%$$

This means that by mixing 4g of NaCl with 50g of H_2O you prepare a 7.4% (m/m) solution.

STUDY CHECK

A KCl solution is prepared by mixing 5g of KCl with 200g of H_2O. Calculate the percent (m/m) of the solution.

Volume percent concentration The volume percent concentration (v/v) is the volume of solute per volume of solution in percent form

$$v/v = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100$$

Mass/volume percent concentration The mass/volume percent concentration (m/v) is the mass of solute per mL of solution in percent form.

$$m/v = \frac{\text{g of solute}}{\text{mL of solution}} \times 100$$

Molarity concentration The molarity (M) is the moles of solute per L of solution.

$$M = \frac{\text{moles of solute}}{\text{L of solution}}$$

Sample Problem 5

A NaCl solution is prepared by mixing 4g of NaCl (MW=58.4g/mol) with 50 g of water until a final volume of 52mL of solution. Calculate: (a) the mass percent (m/m) concentration; (b) the molarity.

SOLUTION

(a) to calculate the mass percent (m/m) we just need the grams of solute and the grams of solution–that is four plus fifty. Both numbers are already given:

$$m/m = \frac{\text{g of solute}}{\text{g of solution}} \times 100 = \frac{4 \text{ g of solute}}{54 \text{ g of solution}} \times 100 = 9.2\%$$

(b) To calculate molarity we need the moles of solute and the liters of solution.

We have the mL of solution, that can be converted to L: 52mL$= 5.2 \times 10^{-2} L$. To calculate the moles of solute, we will use the grams of solute and the molar mass to convert this value into moles: $4g/58.4g/mol$ =0.068moles. Plugging all values into the molarity formula:

$$M = \frac{\text{moles of solute}}{\text{L of solution}} = \frac{0.068 \text{ moles of solute}}{5.2 \times 10^{-2}\text{L of solution}} = 1.31M$$

STUDY CHECK

(a) A solution is prepared by mixing 8g of NaCl (MW=$74g/mol$) with 250mL of H_2O. Calculate the molarity; (b) A KCl solution is prepared by mixing 45g of KCl with 200g of H_2O. Calculate the percent (m/m) of the solution.

Concentration units as conversion factors Each of the different concentration units–molarity, mass percent, volume percent, mass/volume percent–can be used in a conversion factor form. For example, if the molarity of a solution is 3M, this means that in the solution there is 3 moles of solute every one litter of solution.

$$3\text{M} \quad \text{or} \quad \frac{3 \text{ mol of solute}}{1 \text{ L of solution}} \quad \text{or} \quad \frac{1 \text{ L of solution}}{3 \text{ mol of solute}}$$

Similarly, if the mass percent of a solution is 5% this means that there is 5 grams of solute every 100 grams of solution. We often use concentration units as conversion factors when we need to transform between on unit on top (bottom) of the conversion factor and the unit on the bottom (top).

Sample Problem 6

How much volume of a 4M solution do you need to provide 5 moles of solute.

SOLUTION

We will use the conversion factor of Molarity using the volume on top and the moles on the bottom in order to cancel the units:

$$5\cancel{\text{moles of solute}} \times \frac{1 \text{ L of solution}}{4\cancel{\text{moles of solute}}} = 1.25\text{L}$$

This means that 1.25L of a 4M solution will provide 5 moles of solute.

STUDY CHECK

How many grams of a 6% (m/m) solution do you need to provide 5 grams of solute.

Dilution Dilution is the process for preparing a diluted solution from a more concentrated solution. Solutions are often times stored in a stock room in concentrated form. These stocks should be diluted before use. In order to dilute a solution we need to take a certain amount of the concentrated solution and add water. When adding water, the number of moles of solute does not change, and the concentration always decreases. We have a concentrated solution (c_1) and we need to prepare a certain volume (V_2) of a more diluted solution (c_2). The question is how much volume of the concentrated solution (V_1) we need to take. In order to answer this we should use the following formula:

$$c_1 \cdot V_1 = c_2 \cdot V_2$$

Sample Problem 7

How many liters of a 3M NaCl solution are required to prepare 2L of a 1M diluted NaCl solution.

SOLUTION

We have a concentrated solution of 3M molarity and we want to prepare a more dilute solution. In particular 2L of a 1M. Hence: $c_1 = 3$ and $c_2 = 1M$ and $V_2 = 2L$. Using the dilution formula:

$$3M \cdot V_1 = 1M \cdot 2L$$

Solving for V_1 we have a volume of 0.66L.

STUDY CHECK

How many liters of a 5M NaCl solution are required to prepare 3L of a 3M diluted NaCl solution.

Molarity calculation involving grams As molarity is just the ration between the moles of solute and the litters of solution, we can use this property to calculate the mass of solute contained in a certain volume of solution. We will proceed by first calculating the number of moles in that volume to then convert moles into grams.

1.2 Electrolytes and insoluble compounds

On one hand, electrolytes are compounds that conduct the electricity once dissolved in water. Differently, nonelectrolytes are compounds that do not conduct the electricity once dissolved in water. On the other hand, insoluble compounds are not soluble in water, whereas soluble compounds can be dissolved in water. This section covers the properties of electrolytes and insoluble (and soluble) compounds. At the end of this section, you should be able to classify a chemical in terms of its electrolyte type and solubility character.

Soluble and insoluble salts Soluble compounds dissolve in water, whereas insoluble compounds do not. For example, barium chromate ($BaCrO_{4(s)}$) is an insoluble salt. How do we know that? The Table bellow will help you predict the solubility of a salt. In order to do this, you need to start by assess the right ion (the anion, CrO_4^{2-}) located on the left column of the Table below. After that you need to assess the left ion (the cation, Ba^{2+}) located on the right column. If you follow this, you will see that chromate is insoluble and barium is not part of any exception. Let us predict for example the soluble/insoluble nature of $CaSO_4$, calcium sulfate. We start by looking for SO_4^{2-} in the left column to find out is soluble. Next we continue in the same line as SO_4^{2-} and look for the ion in the left Ca^{2+}. In conclusion, even when SO_4^{2-} is soluble, when combined with Ca^{2+}, we have that $CaSO_4$ is insoluble, and overall $CaSO_{4(s)}$ is insoluble.

Sample Problem 8

Predict the soluble/insoluble nature of the following compounds: (a) K_2CO_3, (b) $NaNO_3$ and (c) $Ca(OH)_2$.

SOLUTION

(a) $K_2CO_{3(aq)}$ is soluble, as $CO_3{}^{-2}$ is insoluble but when combined with K^+ the salt becomes soluble. (b) All nitrates are soluble without exceptions. (c)

$Ca(OH)_{2(aq)}$ is soluble.

STUDY CHECK

Predict the soluble/insoluble nature of the following compounds: (a) Li_3PO_4 (b) Na_2S (c) AgCl

Table 1.2 Soluble and insoluble compounds

Ions that form *soluble* compounds...	... **except** when combined with
Group I ions (Na^+, Li^+, K^+, etc)	no exceptions
Ammonium (NH_4^+)	no exceptions
Nitrate (NO_3^-)	no exceptions
Acetate (CH_3COO^-)	no exceptions
Hydrogen carbonate (HCO_3^-)	no exceptions
Chlorate (ClO_3^-)	no exceptions
Halide (F^-, Cl^-, Br^-)	Pb^{2+}, Ag^+ and Hg_2^{2+}
Sulfate (SO_4^{2-})	Ag^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Hg_2^{2+} and Pb^{2+}
Ions that form *insoluble* compounds...	**... except when combined with**
Carbonates (CO_3^{2-})	group I ions (Na^+, Li^+, K^+, etc) or ammonium (NH_4^+)
Chromates (CrO_4^{2-})	group I ions (Na^+, Li^+, K^+, etc) or Ca^{2+}, Mg^{2+}or ammonium (NH_4^+)
Phosphates (PO_4^{3-})	group I ions (Na^+, Li^+, K^+, etc) or ammonium (NH_4^+)
Sulfides (S^{2-})	group I ions (Na^+, Li^+, K^+, etc) or ammonium (NH_4^+)
Hydroxides (OH^-)	group I ions (Na^+, Li^+, K^+, etc) or Ca^{2+}, Mg^{2+}, Sr^{2+}or ammonium (NH_4^+)

Strong electrolytes Strong electrolytes completely dissociate in water. Hence, in a solution of a strong electrolyte you will only have ions and never molecules. Strong electrolytes are typically ionic compounds such as $MgCl_2$ or NaCl (table salt). We represent the dissociation of a strong electrolyte with a single arrow, meaning that the reaction proceeds to completion and for the example below, in the solution we will only have ions ($Mg^{2+}_{(aq)} + 2\,Cl^-_{(aq)}$) and not molecules ($MgCl_{2(s)}$):

$$MgCl_{2(s)} \xrightarrow{H_2O} Mg^{2+}_{(aq)} + 2\,Cl^-_{(aq)}.$$

Weak electrolytes Weak electrolytes partially dissociate in water, and this is indicated by means of a chemical reaction with a double arrow. Hence in a solution of a weak electrolyte you will have ions as well as molecules at the same time. Examples of weak electrolytes are hydrofluoric acid, water, ammonia or acetic acid. The dissociation of hydrochloric acid (HF) proceeds as:

$$HF_{(l)} \xrightleftharpoons{H_2O} H^+_{(aq)} + F^-_{(aq)}$$

Acetic acid (CH_3COOH) is an important weak electrolyte and its dissociation proceeds somehow in a peculiar way:

$$CH_3COOH_{(l)} \xrightleftharpoons{H_2O} CH_3COO^-_{(aq)} + H^+_{(aq)}$$

Nonelectrolytes Nonelectrolytes do not dissociate in water. Hence a solution of a nonelectrolyte will only contains molecules and not ions. Examples of nonelectrolytes are carbon-based chemicals such as methanol, ethanol, urea or sucrose. The dissociation of urea for example CH_4N_2O proceeds as:

$$CH_4N_2O_{(s)} \xrightarrow{H_2O} CH_4N_2O_{(aq)}$$

Identify the electrolyte character of a chemical You can use the Table below to identify the electrolyte character of a chemical. Ionic compounds are in general strong electrolytes, and most acids as well. There is four important weak electrolytes: water, acetic acid, ammonia and hydrofluoric acid. Covalent compounds are in general nonelectrolytes. Organic compounds, compounds based on carbon atoms (e.g. $C_{12}H_{22}O_{11}$) are in general nonelectrolytes.

Table 1.3 Different types of electrolytess

Electrolyte Type	Dissociation	Particles in solution	Examples
Strong	Fully	Mostly ions	Ionic Compounds and most acids and bases (hydroxides): NaCl, NaOH, HCl, $MgCl_2$, H_2SO_4, etc
Weak	Partially	Ions & molecules	NH_3, CH_3COOH (acetic acid), HF, H_2O
Nonelectrolytes	No	molecules	Most covalent compounds: CH_3OH (methanol), CH_3CH_2OH (ethanol), $C_{12}H_{22}O_{11}$ (sucrose), CH_4NO_2 (urea)

Breaking down electrolytes into ions Electrolytes–in particular strong electrolytes–dissociate producing ions. This way, a solution of for example NaCl does not contain NaCl molecules but $Na^+_{(aq)}$ cations and $Cl^-_{(aq)}$ anions. Hence it is important to correctly break down electrolytes into ions. In order to do this, you need to revert the combination of ions that produce a given chemical while making sure the charges are balanced. For example, let us beak magnesium chloride $MgCl_{2(aq)}$ into ions. This is a strong electrolytes formed by magnesium cations and chloride anions. The valence of magnesium is +II and the valence of chlorine is -I. The $MgCl_2$ formula also tells us we have one magnesium and two chlorines. The overall process is:

$$MgCl_{2(aq)} \longrightarrow Mg^{2+}_{(aq)} + 2\,Cl^-_{(aq)}$$

Another example, magnesium nitrate $Mg(NO_3)_2$. This strong electrolyte–as this is an ionic salt–is made of magnesium with valence +II and nitrate with valence -I. The formula indicated we have one $Mg^{2+}_{(aq)}$ and two $NO_3{}^-{}_{(aq)}$. Hence:

$$Mg(NO_3)_{2(aq)} \longrightarrow Mg^{2+}_{(aq)} + 2\,NO_3{}^-{}_{(aq)}$$

Sample Problem 9

For the following chemicals indicate whether you will have in the solution (a) only ions, (b) ions and some molecules, or (c) molecules: NH_3, KOH, and $C_{12}H_{22}O_{11}$.

SOLUTION

Ammonia (NH_3) is a weak electrolyte and a solution of ammonia will contain ions and well as ammonia molecules. Differently KOH is a strong electrolyte and in solution you would find only ions (K^+ and OH^-). Sucrose ($C_{12}H_{22}O_{11}$) is a nonelectrolyte and in solution you will find molecules.

STUDY CHECK

For the following chemicals indicate whether you will have in the solution only ions, ions and some molecules, or molecules: (a) H_2SO_4, HNO_3 and CH_3OH.

Sample Problem 10

Break down the following chemicals into ions, if possible:

Chemical	Particles in solution
$K_2CrO_{4(aq)}$	
$Ba(NO_3)_{2(aq)}$	
$BaCrO_{4(s)}$	
$KNO_{3(aq)}$	

SOLUTION

We can only break down into ions ionic compounds and oxosalts that are not solid. From the list of chemicals in the example, we will not be able to break down $BaCrO_{4(s)}$ into ions as it is a solid. From the other chemicals, $K_2CrO_{4(aq)}$ is named potassium chromate and contains $2K^+_{(aq)}$ and ${CrO_4}^{2-}{}_{(aq)}$ ions. Barium nitrate–$Ba(NO_3)_{2(aq)}$–will produce $Ba^{2+}_{(aq)}$ and $2{NO_3}^-{}_{(aq)}$. Finally, potassium nitrate– $KNO_{3(aq)}$–will produce $K^+_{(aq)}$ and ${NO_3}^-{}_{(aq)}$. In the table:

Chemical	Particles in solution
$K_2CrO_{4(aq)}$	$2K^+_{(aq)} + {CrO_4}^{2-}{}_{(aq)}$
$Ba(NO_3)_{2(aq)}$	$Ba^{2+}_{(aq)} + 2{NO_3}^-{}_{(aq)}$
$BaCrO_{4(s)}$	$BaCrO_{4(s)}$
$KNO_{3(aq)}$	$K^+_{(aq)} + {NO_3}^-{}_{(aq)}$

STUDY CHECK

Break down the following chemicals into ions, if possible: $H_2O_{(l)}$, $NH_{3(l)}$, $AgNO_{3(aq)}$.

1.3 An introduction to reactions in solution

There are three different reactions in solution: acid-base reactions, precipitation reaction and redox reactions. The key to identify acid-base reactions is in the reactants, as an acid-base reaction results from the reaction between and acid and a base. Precipitation reactions are reactions that produce a precipitate. Hence, the key to identify a precipitation reaction is in the products. Precipitation reactions always contains a solid as a product. Redox reactions contain two elements with different redox number in the reactants and products. The key to identify redox reactions is to be able to spot elements with different oxidation state, for example: Cu and Cu^{2+} or H^+ and H_2. In the following we will describe more about the three different types of reactions in solution. The goal of this section is for you to be able to identify each type.

Acid–base reactions Acid-base reactions result from the reaction of an acid with a base. Both they produce water and another chemical. An example is:

$$HBr_{(aq)} + KOH_{(aq)} \longrightarrow KBr_{(aq)} + H_2O_{(l)} \text{ (acid-base reaction)}$$

Hydrobromic acid (HBr) is an acid and potassium hydroxide (KOH) a base. The result of an acid-base reaction is always water and an ionic compound, in this case KBr.

Precipitation reactions Precipitation reactions result in an insoluble chemical, that is, results in a solid chemical. An example would be:
$K_2CrO_{4(aq)} + Ba(NO_3)_{2(aq)} \longrightarrow BaCrO_{4(s)}\downarrow + 2\,KNO_{3(aq)}$ (precipitation reaction)
The chemical $BaCrO_{4(s)}$ is a solid that precipitates in the solution, hence the name of the type of reaction. The symbol on $BaCrO_{4(s)}\downarrow$ represents the precipitation process. The solubility of a given solute such as $BaCrO_{4(s)}$ is the amount of solute (in grams) that can be dissolve in a given mass of solvent (in particular 100 g of solvent). A solute with a low solubility will be hard to dissolve. Think about cacao and water. The solubility of cacao is low and hence by simply adding cacao powder to water you will not be able to make a solution. However, solubility depends on the solute and solvent combination, but also on the temperature and by warming up a solvent you can increase solubility and fit more solute in the same amount of solvent. This section covers different aspects of solubility.

Redox reactions Redox reaction are different than acid-base or precipitation reaction. They contain the same chemical element in two different states resulting from the loss or win of electrons. Look for example:

$$2\,Al_{(s)} + 3\,Cu^{+2}_{(aq)} \longrightarrow 2\,Al^{+3}_{(aq)} + 3\,Cu_{(s)} \text{(redox reaction)}$$

We have that neither $Al_{(s)}$ or $Cu_{(aq)}{}^{+2}$ are an acid or a base, therefore this is not an acid-base reaction. Also there is no insoluble product, hence this is not a precipitation reaction. Indeed, this is a redox reaction, as we have Al in two different states: as metallic $Al_{(s)}$ and as ionic $Al_{(aq)}{}^{+3}$, which result from the loss of three electron. Therefore in redox reaction there is always elements in the chemicals that lose electrons. In redox reactions there is also an element that wins electrons. For example, $Cu_{(s)}$ and $Cu_{(aq)}{}^{+2}$ have different redox number. In particular, $Cu_{(aq)}{}^{+2}$ is the result of removing three electrons from $Cu_{(s)}$. At this point, we have that this reaction is redox as it contains an element that gains electrons and an element that loses electrons. Sometimes, the redox state of the elements is not that obvious. Look at this example:

$$Fe_{(s)} + CuSO_{4(aq)} \longrightarrow FeSO_{4(aq)} + Cu_{(s)} \text{(redox reaction)}$$

This is a redox reaction as you can find iron and copper in two states, metallic and also ionic. Therefore, these two metals have two different redox numbers in the reaction.

Sample Problem 11

Classify the following reactions as acid-base, redox or precipitation.
(a) $Fe_{(s)} + Cu^{+2}_{(aq)} \longrightarrow Fe^{+2}_{(aq)} + Cu_{(s)}$
(b) $AgNO_{3(aq)} + NaCl_{(aq)} \longrightarrow AgCl_{(s)} + NaNO_{3(aq)}$
(c) $2\,HCl_{(aq)} + Ca(OH)_{2(aq)} \longrightarrow CaCl_{2(aq)} + 2\,H_2O_{(l)}$

SOLUTION

The first reaction is a redox reaction. This is because we can find two different oxidation states for Cu and also for Fe. That means one of these elements lost electrons and the other won electrons. The second reaction is a precipitation reaction as it produces a solid. The last reaction is an acid base, as the reactants are an acid and a base.

STUDY CHECK

Classify the following reactions as acid-base, redox or precipitation.
(a) $HNO_{2(aq)} + NaOH_{(aq)} \longrightarrow NaNO_{2(aq)} + H_2O_{(l)}$
(b) $2\,Na_{(s)} + Cl_{2(g)} \longrightarrow 2\,NaCl_{(s)}$

(c) $MgCl_{2(aq)} + 2\,AgNO_{3(aq)} \longrightarrow 2\,AgCl_{(s)} + Mg(NO_3)_{2(aq)}$

1.4 Precipitation reactions and acid-base reactions

This section deal with two important types of reactions in solution. Precipitation reactions are characterized by the products and acid-base by the reactants. In an acid-base reaction, the reactants are an acid and a base, and they react to produce water and other chemical. Precipitation reactions produce a precipitate, that is, a solid.

Solubility formula Solubility (s) is the grams of a solute per 100 g of solvent:

$$s = \frac{\text{g of solute}}{\text{100 g of solvent}}$$

A saturated solution can be achieved when you fit the maximum amount of solute in the solvent. If you continue adding solute to a saturated solution it will precipitate and solid will form.

Acid–base reactions Acid-base reactions result from the reaction of an acid with a base. Both they produce water and another chemical. An example is:

$$HBr_{(aq)} + KOH_{(aq)} \longrightarrow KBr_{(aq)} + H_2O_{(l)} \text{ (acid-base reaction)}$$

Hydrobromic acid $HBr_{(aq)}$ is an acid and potassium hydroxide a base.

Precipitation reactions Precipitation reactions result in an insoluble chemical. An example would be:
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The chemical $BaCrO_{4(s)}$ is a solid that precipitates in the solution. The solubility of a given solute such as $BaCrO_{4(s)}$ is the amount of solute (in grams) that can be dissolve in a given mass of solvent (in particular 100 g of solvent). A solute with a low solubility will be hard to dissolve. Think about cacao and water. The solubility of cacao is low and hence by simply adding cacao powder to water you will not be able to make a solution. However, solubility depends on the solute and solvent combination, but also on the temperature and by warming up a solvent you can increase solubility and fit more solute in the same amount of solvent. This section covers different aspects of solubility.

Formula equations, ionic equations and net ionic equations Electrolytes in solutions contains ions–cations and anions–however, when we write chemical formulas we barely show those ions. Differently, we just write the formulas and that is the reason that chemical equations are referred as *formula equation*. Look for example:

$$K_2CrO_{4(aq)} + Ba(NO_3)_{2(aq)} \longrightarrow BaCrO_{4(s)}\downarrow + 2\,KNO_{3(aq)} \text{ (formula equation)}$$

In this equation, $K_2CrO_{4(aq)}$ is actually in the form of ions: $2K^+_{(aq)}$ and ${CrO_4}^{2-}{}_{(aq)}$. At the same time, $Ba(NO_3)_{2(aq)}$ in the form of ions results in $Ba^{2+}_{(aq)}$ and $2{NO_3}^-{}_{(aq)}$. Also, $2KNO_{3(aq)}$ contains $2K^+_{(aq)}$ and $2{NO_3}^-{}_{(aq)}$. Finally, $Ba(CrO_4)_{(s)}$ does not produce any ions in solution, as it is a solid. Ionic equations result from writing all ions in a formula equation:

$$2\,K^+_{(aq)} + {CrO_4}^{2-}{}_{(aq)} + Ba^{2+}_{(aq)} + 2\,{NO_3}^-{}_{(aq)} \longrightarrow$$
$$BaCrO_{4(s)}\downarrow + 2\,K^+_{(aq)} + 2\,{NO_3}^-{}_{(aq)} \text{ (ionic equation)}$$

However, the ionic equation contains repeated ions. Look for example the previous equation with $2\,K^+_{(aq)}$ on the left and on the right of the equation. If we simplify the repeated ions

$$\cancel{2\,K^+_{(aq)}} + {CrO_4}^{2-}{}_{(aq)} + Ba^{2+}_{(aq)} + \cancel{2\,{NO_3}^-{}_{(aq)}} \longrightarrow$$
$$BaCrO_{4(s)} + \cancel{2\,K^+_{(aq)}} + \cancel{2\,{NO_3}^-{}_{(aq)}}$$

we obtain what is called as the *net ionic equation*:

$${CrO_4}^{2-}{}_{(aq)} + Ba^{2+}_{(aq)} \longrightarrow BaCrO_{4(s)}\downarrow \text{ (net ionic equation)}$$

Overall, we have that the formula equation, ionic equation and net ionic equation are just three different ways to express the same chemical equation. The first form includes only molecules whereas the second included all ions produced by each chemical. The last form, includes only ions that are not repeated in both sides of the equation.

Sample Problem 12

Write down the ionic equation and net ionic for the following formula equation:

$$HBr_{(aq)} + KOH_{(aq)} \longrightarrow KBr_{(aq)} + H_2O_{(l)}$$

SOLUTION

Mind we can only break down strong electrolytes. Hence, water will not be expressed in the form or ions as it is a weak electrolyte. If we break down the other chemicals we have the ionic equation:

$$H^+_{(aq)} + Br^-_{(aq)} + K^+_{(aq)} + OH^-_{(aq)} \longrightarrow K^+_{(aq)} + Br^-_{(aq)} + H_2O_{(l)}$$

If we eliminate the ions that are repeated in both sides:

$$H^+_{(aq)} + \cancel{Br^-_{(aq)}} + \cancel{K^+_{(aq)}} + OH^-_{(aq)} \longrightarrow \cancel{K^+_{(aq)}} + \cancel{Br^-_{(aq)}} + H_2O_{(l)}$$

we have the net ionic equation:

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)}$$

STUDY CHECK

Write down the ionic equation and net ionic for the following formula equation:

$$AgNO_{3(aq)} + NaBr_{(aq)} \longrightarrow AgBr_{(s)}\downarrow + NaNO_{3(aq)}$$

1.5 Redox reactions

Redox reaction are different than acid-base or precipitation reaction. They contain the same chemical element in two different states resulting from the loss or win of electrons. For example:

$$2\,Al_{(s)} + 3\,Cu^{2+}_{(aq)} \longrightarrow 2\,Al^{3+}_{(aq)} + 3\,Cu_{(s)} \text{ (redox reaction)}$$

We have that neither $Al_{(s)}$ or $Cu^{2+}_{(aq)}$ are an acid or a base. Also there is no product precipitate. Hence, this reaction is not an acid-base reaction or a precipitation reaction. This is a redox reaction, as we have Al in two different states: as metallic $Al_{(s)}$ and as ionic

$Al^{3+}_{(aq)}$, which result from the loss of an electron. In redox reaction there is always elements in the chemicals that lose electrons and chemicals winning electrons.

Oxidation state or redox number The redox number, also called oxidation number or oxidation state helps compare elements that have lost (or gained) different charge. When comparing two elements with different redox numbers, the larger this number the more electrons the element has lost. Similarly, the smaller this number the smaller this number the more electrons the element has won.

Rules to calculate redox numbers We indicate redox numbers with roman number on top of the element. For example the redox number of manganese in this compound is $+7$: $\underline{Mn}^{VII}O_4{}^-$. The redox number can be a non integer number. There is five rules to identify the redox number of an element.

- **Rule 1** Single atoms or elements have zero redox number. Examples are Na or H_2, both with redox zero.
- **Rule 2** Monoatomic ions have redox number equal to their charge. Examples are Na^+ or Cl^- with redox $+1$ and -1, respectively.
- **Rule 3** The redox number of fluorine is -1
- **Rule 4** The redox number of hydrogen on its covalent (e.g. H_2O) compounds is $+1$.
- **Rule 5** The redox number of oxygen in normal oxides (e.g. MgO) is normally -2, with the exception of peroxides (e.g. H_2O_2) in which is -1.

Calculating the redox number How do we calculate the redox number for example of manganese in this chemical: $\underline{Mn}O_4{}^-$, permanganate. In order to do this, we need to set up a formula so that the redox numbers of all elements in the molecule–taking into account the number of atoms in the molecule–equals to the charge. In the case of permanganate, let us call x to the redox number of manganese. We know the redox of oxygen is -2 and we have four oxygens in the molecule. We also know the charge of the ion is -1. Therefore we have:

$$x + 4 \cdot (-2) = -1$$

If we solve for x we obtain a redox number of manganese of VII.

Sample Problem 13

Calculate the redox number of the elements underlined in the following molecules: (a) $K_2\underline{C}O_3$ and (b) $H_2\underline{C}O$.

SOLUTION

Let us set up the redox equation for the first compound, knowing that the redox of oxygen is -2 and potassium $+1$. The unknown variable x represents the redox number of the underlined element. We have:

$$2 \cdot (+1) + x + 3 \cdot (-2) = 0$$

Mind we have two potassium and three oxygens hence we need to time the redox of K by two and the redox of O by three. If we solve for x we obtain a redox number for carbon of IV. The redox equation for the second example is:

$$2 \cdot (+1) + x + (-2) = 0$$

Mind that according to the redox rules, the redox number of oxygen is $+1$. Solving for x we have a redox number of zero.

> **STUDY CHECK**
> Calculate the redox number of the elements underlined in the following molecules: (a) $\underline{Cr_2}O_7^{2-}$ and (b) $\underline{Cr_2}O_3$

Redox means oxidation and reduction By comparing the redox number of the same element in two different compounds we can figure out in what compound the element has lost or gained electrons. Look for example the case of $\underline{Cr^{VI}}_2O_7^{2-}$ and $\underline{Cr^{III}}_2O_3$. The same element in two different molecules has two different redox numbers. In the case of dichromate, the redox of Cr is VI, whereas in the case of chromium(III) oxide the redox of Cr is III. The larger the redox number the more oxidized is an element, and that means the element has lost electrons. The smaller the redox number the more reduced is the element and that means it has gained electrons. If we compare both case, we have that Cr in dichromate is oxidized–it lost electrons–and Cr in chromium(III) oxide is reduced–it gained electrons.

Redox numbers in chemical reactions The goal is to identify the element that undergoes oxidation and reduction in a chemical reaction. We can reach this goal by using the half-reaction method. Every redox reaction is composed of two process, a reduction and the oxidation. These two processes can be separated into two half-reactions so that the combination of both half-reactions lead to the balanced redox. Let us work on a simple unbalanced redox reaction:

$$Al_{(s)} + {Cu_{(aq)}}^{+2} \longrightarrow {Al_{(aq)}}^{+3} + Cu_{(s)}$$

Solid $Al_{(s)}$ on the reactant side has zero redox number, whereas ionic ${Al_{(aq)}}^{+3}$ on the product side has redox number equal to III. Al has undergone oxidation as its redox number increases from zero to three. Al has lost three electrons. We can write the oxidation half-reaction:

$$Al_{(s)} \longrightarrow {Al_{(aq)}}^{+3} + 3\,e^- \text{ (oxidation)}$$

Mind that electrons have negative charge and we add electrons to compensate the charge of ${Al_{(aq)}}^{+3}$. Now let us compare the redox number of Cu. In the reactant side we have ${Cu_{(aq)}}^{+2}$ with redox of II. In the product side we have $Cu_{(s)}$ with zero redox number. Cu has undergone reduction as its redox number has decreases. This means it has gained electrons, in particular two electrons:

$${Cu_{(aq)}}^{+2} + 2\,e^- \longrightarrow Cu_{(s)} \text{ (reduction)}$$

Balancing simple redox reactions The goal here is to balance a redox chemical reaction by combining two half-reactions. In the example above the oxidation and reaction involve different number of electrons. Hence in order to be able to add both redox we need to time each half-reaction by a number so that the number of electrons cancel out. As the first reaction involved three electrons and the second two, we will do:

$$\begin{array}{ll} 2\cdot\left(\ Al_{(s)} \longrightarrow {Al_{(aq)}}^{+3} + 3\,e^-\ \right) & \text{(oxidation)} \\ 3\cdot\left(\ {Cu_{(aq)}}^{+2} + 2\,e^- \longrightarrow Cu_{(s)}\right) & \text{(reduction)} \\ \hline 2\,Al_{(s)} + 3\,{Cu_{(aq)}}^{+2} + \cancel{6\,e^-} \longrightarrow 2\,{Al_{(aq)}}^{+3} + 3\,Cu_{(s)} + \cancel{6\,e^-} & \text{(redox)} \end{array}$$

The overall balanced redox equation is:

$$\overset{\text{Oxidation:}-3e^-}{\overbrace{2\,\overset{0}{Al}(s) + 3\,\overset{II}{Cu}^{2+}(aq) \longrightarrow 2\,\overset{III}{Al}^{3+}(aq)}} + 3\,\overset{0}{Cu}(s)$$

$$\underbrace{\phantom{2\,Al(s) + 3\,Cu^{2+}(aq) \longrightarrow 2\,Al^{3+}(aq) + 3\,Cu(s)}}_{\text{Reduction:}+2e^-}$$

Balancing redox reactions in acidic medium Redox reactions happen in either basic or acidic medium. Here we will go over how to balance redox reactions in acidic medium. In order to do this we will first separate the reaction in two half-reactions. In each semi-reaction we will balance all elements but hydrogen and oxygen. When all elements are balanced, we will proceed to balance O by adding H_2O molecules and we will balance H by adding H^+. Finally, we all add electrons to compensate the charge of the reaction. Let us work on an example:

$$MnO_{4(aq)}{}^- + Fe_{(aq)}{}^{2+} \longrightarrow Mn_{(aq)}{}^{2+} + Fe_{(aq)}{}^{3+}$$

One of the semi-reactions involve Manganese whereas the other involves Iron. The redox number of Mn in permanganate is VII hence Manganese is being reduced, as its redox number decreases from VII to II, whereas Iron is being oxidized as its redox number increases from II to III. The oxidation half-reaction does not contain hydrogen or oxygen hence we will only have to balance the charger with one electron:

$$Fe_{(aq)}{}^{2+} \longrightarrow Fe_{(aq)}{}^{3+} + e^- \text{ (oxidation)}$$

The reduction half-reaction contains oxygen. Hence, we will have to add H_2O molecules to balance oxygen and H^+ to balance hydrogen. In particular, we will need two water molecules–as $MnO_4{}^-$ has four oxygens and we will have to add eight protons as we are adding four molecules of water. Finally, we need to add three electrons to equalize the charge:

$$MnO_{4(aq)}{}^- + 8\,H_{(aq)}{}^+ + 5\,e^- \longrightarrow Mn_{(aq)}{}^{2+} + 4\,H_2O_{(l)} \text{ (reduction)}$$

As the oxidation involves one electron and the reduction three, we need to time the oxidation by three:

$$5 \cdot \left(Fe_{(aq)}{}^{2+} \longrightarrow Fe_{(aq)}{}^{3+} + e^- \right) \qquad \text{(oxidation)}$$

$$MnO_{4(aq)}{}^- + 8\,H_{(aq)}{}^+ + 5\,e^- \longrightarrow Mn_{(aq)}{}^{2+} + 4\,H_2O_{(l)} \qquad \text{(reduction)}$$

$$+$$

$$5\,Fe_{(aq)}{}^{2+} + MnO_{4(aq)}{}^- + 8\,H_{(aq)}{}^+ + \cancel{5\,e^-} \longrightarrow 5\,Fe_{(aq)}{}^{3+} + Mn_{(aq)}{}^{2+} + 4\,H_2O_{(l)} + \cancel{5\,e^-} \qquad \text{(redox)}$$

$$8\,H^+(aq) + \overset{VII}{Mn}O_4(aq) + 3\,\overset{II}{Fe}^{2+}(aq) \longrightarrow 3\,\overset{III}{Fe}^{3+}(aq) + \overset{II}{Mn}^{2+}(aq) + 4\,H_2O(l)$$

$$\text{Oxidation:}-1e^-$$

$$\text{Reduction:}+5e^-$$

Sample Problem 14

Balance the following redox in acidic medium:

$$Cr_2O_7^{2-} + SO_3^{2-} \longrightarrow Cr^{3+} + SO_4^{2-}$$

SOLUTION

We locate the same element in both sides of the reaction with different redox number. We found Chromium in the form of dichromate ($Cr_2O_7^{2-}$) with redox number VI and Chromium in the product side with redox III. Therefore Chromium is being reduced, as its redox number decreases. Differently, we found sulphur in the reactants side in the form of sulfite (SO_3^{2-}) with redox number of IV and in the product side with redox number of VI. Therefore Sulphur is being oxidized. We will first set up the oxidation half-reaction knowing that we have different amounts of Cr in both side and that we will have to add water molecules to balance O and protons to balance H. As we have seven oxygens in $Cr_2O_7^{2-}$ we will have to add seven water molecules. Also, as we add seven water molecules we will have to add fourteen protons. We will need six electrons to compensate the charge:

$$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O \text{ (reduction)}$$

For the reduction half-reaction, we have a difference of one oxygen atoms and hence we will need one water molecule and two protons; we will need two electrons to compensate the charge:

$$SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2\,H^+ + 2\,e^- \text{ (oxidation)}$$

In order to add both half-reactions as the reduction involves two electrons and the oxidation six, we will have to multiply the reduction half-reaction by three:

$$1 \cdot \left(Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O \right) \quad \text{(reduction)}$$
$$3 \cdot \left(SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2\,H^+ + 2\,e^- \right) \quad \text{(oxidation)}$$

$$Cr_2O_7^{2-} + 14\,H^+ + 3\,SO_3^{2-} + 3\,H_2O + \cancel{6e^-} \longrightarrow 2\,Cr^{3+} + 7\,H_2O + 3\,SO_4^{2-} + 6\,H^+ + \cancel{6e^-} \quad \text{(redox)}$$

After we cancel the electrons and eliminate protons and water molecules, the balanced reaction is:

$$8\,H^+(aq) + \overset{VI}{Cr_2O_7}^{2-}(aq) + 3\,\overset{IV}{SO_3}^{2-}(aq) \longrightarrow 3\,\overset{VI}{SO_4}^{2-}(aq) + 2\,\overset{III}{Cr}^{3+}(aq) + 7\,H_2O_{(l)}$$

Oxidation: $-2e^-$ (IV → VI)

Reduction: $+3e^-$ (VI → III)

STUDY CHECK

Balance the following redox in acidic medium:

$$Cr_2O_7{}^{-2}{}_{(aq)} + NO_2{}^-{}_{(aq)} \longrightarrow Cr^{3+}_{(aq)} + NO_3{}^-{}_{(aq)}$$

Balancing redox reactions in basic medium In order to balance a redox in basic medium we need first to balance the reaction in acidic medium. After, we will compensate all H^+ with OH^- in both sides of the reaction. Mind that when combining

H^+ with OH^- we obtain H_2O. For example, in order to balance the following reaction in basic medium:

$$3\,Fe_{(aq)}{}^{2+} + MnO_{4(aq)}{}^{-} + 4\,H_{(aq)}{}^{+} \longrightarrow 3\,Fe_{(aq)}{}^{3+} + Mn_{(aq)}{}^{2+} + 2\,H_2O_{(l)}$$

we will add four OH^- in both sides:

$$3\,Fe_{(aq)}{}^{2+} + MnO_{4(aq)}{}^{-} + 4\,H_{(aq)}{}^{+} + 4\,OH_{(aq)}{}^{-} \longrightarrow 3\,Fe_{(aq)}{}^{3+} + Mn_{(aq)}{}^{2+} + 2\,H_2O_{(l)} + 4\,OH_{(aq)}{}^{-}$$

And after cancelling the four protons with the four hydroxyls, we have:

$$3\,Fe_{(aq)}{}^{2+} + MnO_{4(aq)}{}^{-} + 4\,H_2O_{(l)} \longrightarrow 3\,Fe_{(aq)}{}^{3+} + Mn_{(aq)}{}^{2+} + 2\,H_2O_{(l)} + 4\,OH_{(aq)}{}^{-}$$

Now we have four water molecules in the left and two in the right. We will cancel two molecules from each side in order not to report water molecules twice:

$$3\,Fe_{(aq)}{}^{2+} + MnO_{4(aq)}{}^{-} + 2\,H_2O_{(l)} \longrightarrow 3\,Fe_{(aq)}{}^{3+} + Mn_{(aq)}{}^{2+} + 4\,OH_{(aq)}{}^{-}$$