

CHAPTER 4
**Solution Chemistry
 and the Hydrosphere**

Earth: The Water Planet

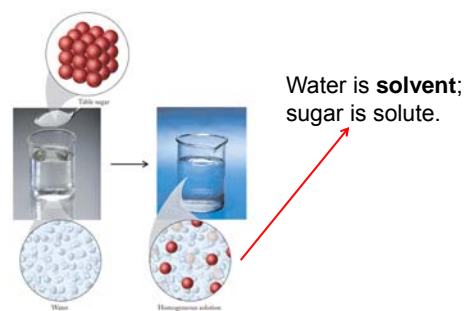
- Earth's surface ~ 75% covered by water; depressions in earth's crust filled with 1.5×10^{21} L of $H_2O(l)$.
- Properties of water responsible for life on Earth, and many geographical features.
- All natural waters (fresh or saltwater) have ionic and molecular compounds dissolved in them.
- A large proportion of the living systems is water.

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Solutions

- Solutions:
 - **Homogeneous mixtures** of two or more substances:
 - » **solvent** = substance present in the greatest quantity
 - » **solutes** = substances dissolved in the solvent (*i.e.*, the other components or substances in the mixture)
- Aqueous solutions → water is solvent.



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Concentration Units

- Define the amount of solute in a solution:

$$\frac{\text{amount of solute}}{\text{amount of solvent}} \text{ or } \frac{\text{amount of solute}}{\text{amount of solution}}$$
- Most common concentration units based on:
 - Mass or moles of solute
 - Volume of solvent.
 - g/L or mol/L.

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- Molarity (M):

$$M = \frac{\text{moles of solute } (n)}{\text{volume of solution } (L)}$$

Since $n = (\text{grams})/(\text{molar mass})$:

$$M = \frac{(\text{grams of solute}) / (\text{molar mass of solute})}{\text{liters of solution}}$$

- For small concentrations:
 Use *milli-* ($10^{-3} M$) or *micro-* ($10^{-6} M$) molarity

- Parts per million ($1\text{ ppm} = 1\text{g}/10^6\text{ g}$ of solution):

$$\text{ppm} = \left(\frac{\text{grams of solute}}{10^6 \text{ grams of solution}} \right), \text{ or}$$

$$\text{ppm} = \left(\frac{\text{mass of solute}}{\text{mass of solution}} \right) \times 10^6$$

- Equivalent to (mg solute/kg solvent).
- Useful for very small concentrations of solute.
- Parts per billion (ppb) = ($1\text{g}/10^9\text{ g}$).

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Molarity as Conversion Factor

To find the amount of solute (moles or grams) in a given volume of solution:

$$\text{Molarity} = \frac{\text{\# of moles of solute}}{\text{\# of liters of solution}}$$

- Rearrange to solve for # moles:
moles solute; $n = (\text{molarity})(\text{\# liters of solution})$.
 $n = M \times \text{volume}$ (in liters).
Once n is known, can use MW to calculate g .

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Dilution of Concentrated Solutions

Stock Solution: **Concentrated** solution (*i.e.*, high solute-to-solvent ratio).

Dilution: Preparation of **dilute** solution (*i.e.*, low solute-to-solvent ratio) by adding solvent to a given volume of stock solution.

Number of moles of solute remains constant!

$$n = (\text{\# moles solute})_{\text{stock}} = (\text{\# moles solute})_{\text{dilute}}$$

$$M_s \times V_s = M_d \times V_d \quad \text{Dilution Formula}$$

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Practice: Calculating Molarity

What is the molarity of an aqueous solution prepared by adding 36.5 g of barium chloride to enough water to make 750.0 mL of solution?

Practice: Mass of Solute

How many grams of aluminum nitrate are required to make 500.0 mL of a 0.0525 M aqueous solution?
($MM = 150.99\text{g/mol}$)

What is the molarity of nitrate ion in a 0.0525 M solution of aluminum nitrate?

Dilutions



a) Obtain known volume of stock.

b) Transfer to volumetric glassware.

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Practice: Diluting Stock Solutions

Hydrochloric acid is obtained in 12.0 M stock solution. What volume of stock solution is required to make 500.0 mL of a 0.145 M dilute solution?

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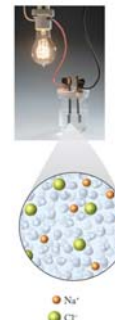
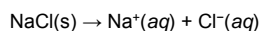
Electrolytes

- **Strong Electrolytes:**

Nearly 100% dissociated into ions. (ionic compounds)

Conduct electric current efficiently.

- Examples: Solutions of NaCl, HNO₃, HCl



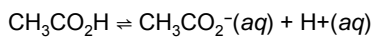
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- **Weak Electrolytes:**

Only partially dissociate into ions.
(predominantly covalent bonds)

Slightly conductive.

Examples: Vinegar (aq. solution of acetic acid);



<5% dissociation

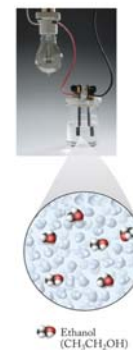


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Non-electrolytes

- Substances in which no ionization occurs. There is no conduction of electrical current.

- Examples: Aqueous solutions of sugar, ethanol, ethylene glycol.



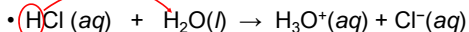
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Acid-Base Reactions

- Brønsted-Lowry definitions:

- Acids = proton (H⁺) donors.

- Bases = are proton acceptors.



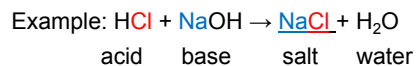
Proton donor (acid) Proton acceptor (base)

- Free H⁺ ions don't exist in water—they strongly associate with water molecules to create hydronium ions (H₃O⁺).

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Neutralization: Reaction between an acid and a base to produce a solution of a salt and water.

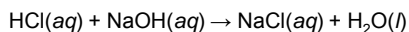
Salt: Ionic compound containing an anion from an acid and a cation from a base.



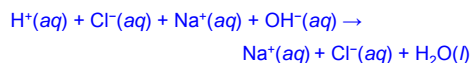
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Types of Equations

Molecular Equations: Reactants/products written disregarding dissociation of substances /molecules:



Ionic Equations: Electrolytes shown as dissolved ions:



Full Ionic Equation

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Strong Acids and Bases

Strong Acids/Bases:
Completely ionized
in aqueous solution
(i.e., strong electrolytes).

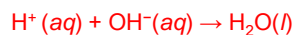
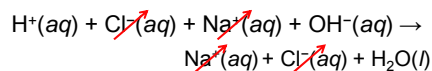
See Table 4.3.

All other acids assumed to be weak.

Acid	Molecular Formula
Hydrochloric acid	HCl
Hydrobromic acid	HBr
Hydroiodic acid	HI
Nitric acid	HNO ₃
Sulfuric acid	H ₂ SO ₄
Perchloric acid	HClO ₄

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Net Ionic Equations: Remove **spectator** ions (ions present in same form on both reactants and products side of chemical equation.) dissolved ions.

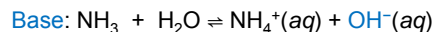
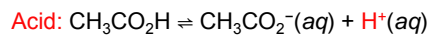


The actual reaction occurring is shown by the net ionic reaction/equation.

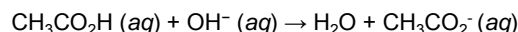
Weak Acids and Bases

Weak acids/bases dissociate only partially (weak electrolytes).

Use double arrow (\rightleftharpoons) to indicate **incomplete dissociation** to form all ions.



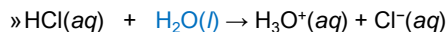
Net ionic equation for neutralization reaction the same for weak acids and **strong bases**:



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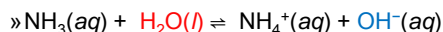
Water: Acid or Base?

- Water as a base:



Proton donor (acid) Proton acceptor (base)

- Water as an acid:



Proton acceptor (base) Proton donor (acid)

- Amphiprotic: Acts as an **acid** or a **base**.

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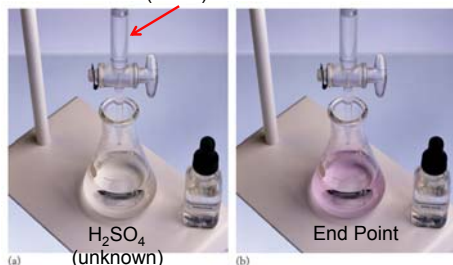
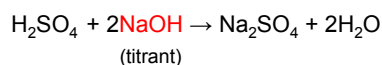
Key Titration Terms

Titration: A volumetric method to determine the concentration of an unknown substance by reacting it with a standard solution.

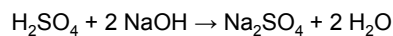
Standard solution: A solution of known concentration (also called the **titrant**).

Equivalence point: In a titration, when enough standard solution has been added to completely react with the unknown substance.

End point: In a titration, when the indicator changes color.

Titration Example

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Stoichiometry Calculations

At the equivalence point:

$$\frac{\# \text{ moles H}_2\text{SO}_4}{\# \text{ moles NaOH}} = \frac{1}{2}$$

$$2(\# \text{ moles H}_2\text{SO}_4) = \# \text{ moles NaOH}$$

$$2M_{\text{acid}} V_{\text{acid}} = M_{\text{base}} V_{\text{base}}$$

$$M_{\text{acid}} = \frac{M_{\text{base}} V_{\text{base}}}{2V_{\text{acid}}} \quad \text{or} \quad M_{\text{base}} = \frac{2M_{\text{acid}} V_{\text{acid}}}{V_{\text{base}}}$$

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Practice: Acid-Base Titration

What is the concentration of sulfuric acid if 15.00 mL of it reacts with 18.45 mL of a 0.0973 M NaOH solution?

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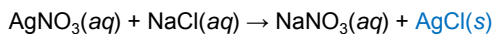
Practice: Titration

If 30.34 mL of a 0.135 M solution of hydrochloric acid (HCl) were required to neutralize 25.00 mL of a sodium hydroxide (NaOH) solution, what is the molarity of the sodium hydroxide solution?

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Precipitation Reactions

- Precipitate: **Solid product** formed from reactants in solution.



- Can predict formation of precipitates based on solubility "rules."

Precipitation reactions can be written using net ionic equations.

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Solubility Guidelines

- Soluble Cations:
 - All Group I ions (alkali metals) and NH_4^+ compounds
- Soluble Anions:
 - All NO_3^- and CH_3COO^- (acetate), ClO_4^- (perchlorate)
 - All Halides (Group 17)
 - Exceptions:** Ag^+ , Cu^+ , Pb^{2+} , Hg_2^{2+}
 - All Sulfates (SO_4^{2-})
 - Exceptions:** Pb^{2+} , Hg_2^{2+} , Ca^{2+} , Ba^{2+} , Sr^{2+}
- Combining anions/cations **not listed above** will result in formation of an **insoluble compound**.

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Insoluble Compounds

- All hydroxides (OH⁻) **except**:
 - Group 1A (e.g., NaOH); Ca(OH)₂, Sr(OH)₂, and Ba(OH)₂
- All sulfides (S²⁻) **except**:
 - Group 1A and NH₄⁺; and CaS, SrS, BaS
- All carbonates (CO₃²⁻) **except** 1A, NH₄⁺
- All phosphates (PO₄³⁻) **except** 1A, NH₄⁺

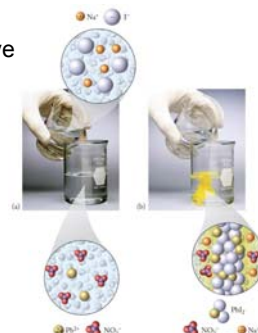
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Precipitation

Combination ions that together would not dissolve ⇒ precipitate!

Cations: ~~Na⁺~~, Pb²⁺
 Anions: ~~NO₃⁻~~, I⁻

Soluble Not soluble



Precipitate: PbI₂(s)

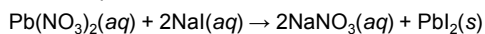
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Net Ionic Equations

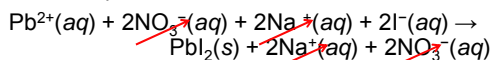
Soluble ionic compounds:

Strong electrolytes: ionize completely in aqueous solution. Can write total and net ionic equations.

Molecular Eq.:



Total Ionic Eq.:

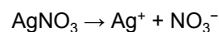
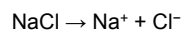


Net Ionic Eq.: $\text{Pb}^{2+}(\text{aq}) + 2\text{I}^{-}(\text{aq}) \rightarrow \text{PbI}_2(\text{s})$

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Practice: Will a Precipitate Form?

Does a precipitate form when sodium chloride is mixed with silver nitrate? If so, write the net ionic equation for the formation of the precipitate:



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Practice: Calculating Mass of Precipitate

What mass of barium sulfate is produced when 100.0 mL of a 0.100 M solution of barium chloride is mixed with 100.0 mL of a 0.100 M solution of iron (III) sulfate?

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Types of Solutions

Saturated solution:

Contains the maximum amount of solute that can dissolve in a given volume at a given temperature.

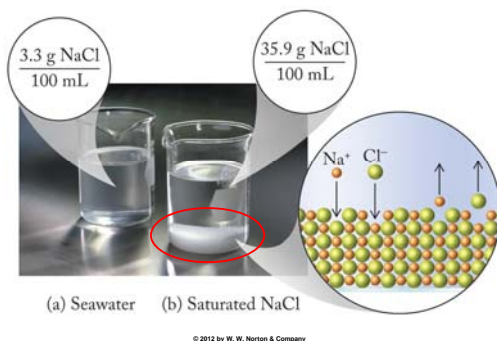
Solubility = g solute/100 mL solvent.

Supersaturated solution:

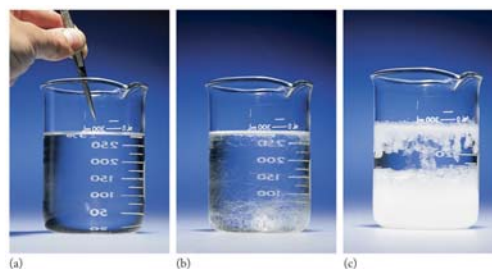
Contains more dissolved solute than a saturated at a given temperature, **unstable**.

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A Saturated Solution Example



Supersaturated Solution



Precipitates form out of a supersaturated solution.

Ion Exchange

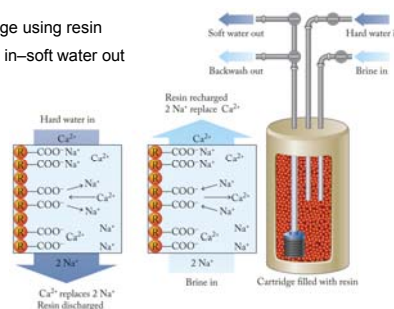
- Important in purification and softening of water.
- “Soft” metal ions (Na^+) exchanged for metals that contribute to “hard” water (Ca^{2+} , Mg^{2+}):
 - Uses ion exchange resin or zeolites:
 - $2(\text{R-COO}^- \text{Na}^+) + \text{Ca}^{2+} \rightarrow (\text{RCOO}^-)_2 \text{Ca}^{2+} + 2\text{Na}^+$

Exchange resin

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Ion Exchange: Water Softeners

- Ion exchange using resin
- Hard water in—soft water out



Zeolites: Natural Minerals as Ion Exchangers

- Rigid, porous 3-dimensional cage-like structures.
- Good materials for adsorption and/or exchange of ions or small molecules (H_2O , NH_3).



Oxidation-Reduction Reactions

Oxidation-Reduction Reactions (Redox):

Characterized by gain or loss of electrons by atoms involved in the reaction.

Oxidation:

Reaction involving combination with O_2 .

Loss of electrons: $\text{Na(s)} \rightarrow \text{Na}^+ + \text{e}^-$

Reduction:

Reaction involving loss of O or gain of H atoms.

Gain of electrons: $\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-$

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Oxidation number

The oxidation number of an element indicates the number of electrons lost, gained, or shared as a result of chemical bonding. The change in the oxidation state of a species lets you know if it has undergone oxidation or reduction.

Oxidation can be defined as "an increase in oxidation number".

Reduction can be defined as "a decrease in oxidation number".

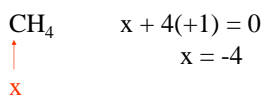
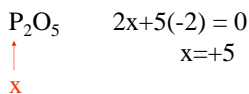
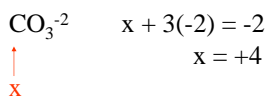
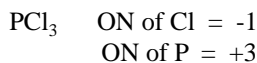
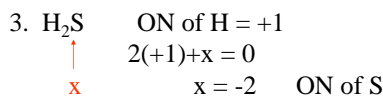
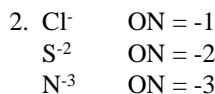
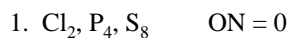
Assigning Oxidation States/Numbers

1. The oxidation number of elements in a neutral molecule sum to zero or sum to charge of the ion in an ion.
2. Oxidation state of an atom in an element = 0.
3. Oxidation state of monatomic ion = charge.
4. Fluorine = -1 in all compounds.
5. Hydrogen = +1, oxygen = -2 in most compounds (except in peroxides where oxygen = -1).
6. Unless combined with O or F, the halogens are -1.

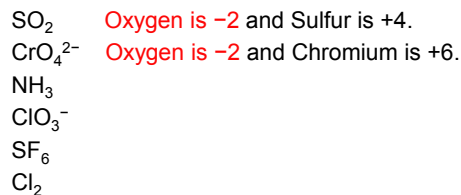
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General rules of ON of atoms:

1. Elemental atom ON = 0
2. Monoatomic ion ON = charge
3. Binary compound.
More nonmetallic atom ON = negative
4. Sum of all ON in a species = actual charge
5. In a compound; F -1 (always)
H +1 (except metal hydrides)
O -2 (except super and peroxides)
O, S, Se, Te -2; *except when combined with O and halogens*
halogens -1

Practice: Assigning Oxidation Numbers

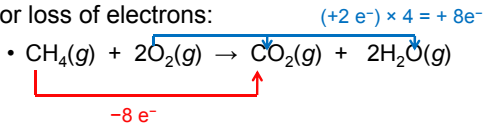
Assign oxidation numbers to each element in the following compounds. (The first two are provided as examples.)



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Redox Reactions: Electron Transfer

- Change in oxidation states results from gain or loss of electrons:

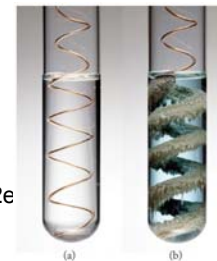
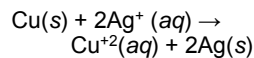


OXIDATION NUMBERS			
Atoms in Reactants		Atoms in Products	
C in CH ₄	-4	C in CO ₂	+4
H in CH ₄	+1	H in H ₂ O	+1
O in O ₂	0	O in CO ₂	-2
		O in H ₂ O	-2

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Oxidation-Reduction Half-Reactions

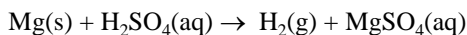
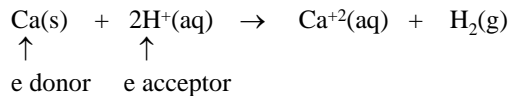
Copper wire immersed in silver nitrate solution:



Can split the overall redox reaction into half-reactions:

- Oxid: $\text{Cu}(s) \rightarrow \text{Cu}^{2+}(aq) + 2e^-$
- Red: $\text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s)$

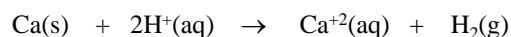
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*Terminology:*

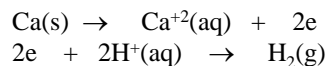
oxidizes reduces oxidized reduced

reducing oxidizing
agent agent

reductor oxidizer

Half Reaction:

split the overall reaction to an oxidation half - and a reduction half;

Oxidation and reduction - necessarily simultaneous.Balancing Redox Reactions: Half-Reaction Method

- Write separate reduction, oxidation half-reactions.
- For each half-reaction:
 - Balance elements (except H, O).
 - Balance O using H₂O.
 - Balance H using H⁺.
 - Balance charge using electrons.

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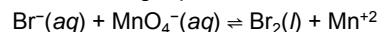
- Balance electrons by multiplying each half-reaction by an integer to equalize electron counts.
- Add half-reactions.
- Check that elements and charges are balanced.
- If in acid solution use H^+ if necessary to balance O by forming water.
- If in basic solution, add OH^- to neutralize to form water

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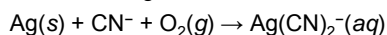
Practice: Balancing Redox Reactions in Acid Solution

Balance the following equation in acid solution:



Practice: Balancing Redox Reactions in Basic Solution

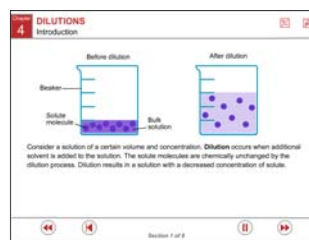
Balance the following reaction in basic solution:



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ChemTour: Dilution



[Click here to launch this ChemTour](#)

Students are introduced to the concept of dilution and making standard solutions from a stock solution. Students arrange a series of solutions in order of increasing concentration based upon the intensity of their color. Using the ordered series of solutions with concentrations given, students predict the concentration of unknown solutions.

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ChemTour: Migration of Ions in Solution



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A simple conductivity apparatus is used to show the macroscopic results of ion movement in a solution. An idealized microscopic view of the solution is used to show that cations are attracted to the negative electrode and anions are attracted to the positively charged electrode. Students classify substances based on their conductivity.

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ChemTour: Saturated Solutions



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This ChemTour explains the dynamics of saturated solutions. *Concept Test*: True or False?: Unsaturated solutions are static, while saturated solutions are dynamic.

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Sample Exercise 4.1

The average concentration of chloride ion in seawater is 19.353 g Cl⁻/kg solution. The World Health Organization recommends that the concentration of Cl⁻ ions in drinking water not exceed 250 ppm. How many times as much chloride ion is there in seawater than in the maximum concentrations allowed in drinking water?

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Sample Exercise 4.2

PVC pipes are only used for drain pipes, never for pipes bringing water into a building. The maximum concentration of vinyl chloride (CH₂CHCl) allowed in drinking water in the United States is 0.002 mg CH₂CHCl/L solution. What molarity is this?

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Sample Exercise 4.3

A water sample from the Great Salt Lake in Utah contains 83.6 mg of Na⁺ per 1.000 g of water. What is the molarity of Na⁺ if the density of the water is 1.160 g/mL?

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Sample Exercise 4.4

In setting up a saltwater aquarium, you need an aqueous solution called Kalkwasser, which has a calcium hydroxide concentration of 0.0225 M. How many grams of Ca(OH)₂ do you need to make 500.0 mL of Kalkwasser?

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- **Solve:** Equation 4.2 gives us the mass of Ca(OH)₂ needed:

$$\begin{aligned} \text{Grams Ca(OH)}_2 &= M \times V \times M \\ &= \frac{74.10 \text{ g}}{\text{mol}} \times 0.5000 \text{ L} \times \frac{0.0225 \text{ mol}}{\text{L}} = 0.834 \text{ g} \end{aligned}$$

Figure 4.6 shows the technique for making this solution. A key feature is that we dissolve 0.834 g of solute in 200–300 mL of water and then add additional water until the final solution has the volume specified.

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Sample Exercise 4.5

The solution used in hospitals for intravenous infusion—called physiolo or saline solution—is 0.155 M in NaCl. It is typically prepared by diluting solution, the concentration of which is 1.76 M, with water. What volume solution is required to prepare 60.0 L of physiological saline?

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Sample Exercise 4.6

Write the balanced (a) molecular, (b) overall ionic, and (c) net ionic equations that describe the reaction that takes place when an aqueous solution of sulfuric acid is neutralized by an aqueous solution of potassium hydroxide.

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Sample Exercise 4.7

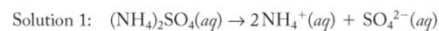
Commercial vinegar must contain no less than 4 grams of acetic acid per 100 mL of vinegar. Suppose the titration of a 25.00 mL sample of vinegar requires 11.20 mL of a 5.95 M solution of NaOH. What is the molarity of the vinegar? Could this be a commercial sample of vinegar?

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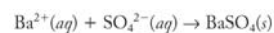
Sample Exercise 4.8

A precipitate forms when aqueous solutions of ammonium sulfate and barium chloride are mixed. Write the net ionic equation for the reaction.

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Sample Exercise 4.8 (cont.)▪ **Solve:**

The new combinations are BaSO₄ and NH₄Cl. Table 4.5 indicates that all ammonium salts are soluble, and so the ammonium and chloride ions remain dissolved. Barium sulfate is insoluble, however, and that salt precipitates. The net ionic equation describes the formation of the precipitate:



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Sample Exercise 4.10

To determine the concentration of chloride ion in a 100.0 mL sample of groundwater, a chemist adds a large enough volume of a solution of AgNO₃ to the sample to precipitate all the Cl⁻ as AgCl. The mass of the resulting AgCl precipitate is 71.7 mg. What is the chloride concentration in milligrams of Cl⁻ per liter of groundwater?

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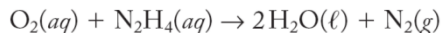
Sample Exercise 4.11

What is the oxidation number of sulfur in (a) SO₂, (b) Na₂S, and (c) CaSO₄?

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Sample Exercise 4.12

The reaction of oxygen with hydrazine:



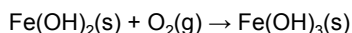
is used to remove dissolved oxygen gas from aqueous solutions, and the combustion of hydrazine produces enough energy that the substance is used as a rocket fuel. Identify the species oxidized, the species reduced, the oxidizing agent, the reducing agent, and the number of electrons transferred in the balanced chemical equation.

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Sample Exercise 4.14

Wetland soil is blue-gray due to $\text{Fe}(\text{OH})_2(s)$, while well-aerated soils are often orange-red due to the presence of $\text{Fe}(\text{OH})_3(s)$. Give the balanced equation for the reaction of $\text{O}_2(g)$ with $\text{Fe}(\text{OH})_2(s)$ in soil that produces $\text{Fe}(\text{OH})_3(s)$ in basic solution.

- **Collect and Organize:** can write the unbalanced equation:



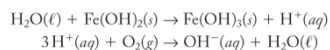
Balance the equation; both mass and charge.

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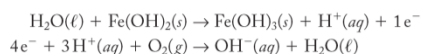
2b. Balance O by adding water as needed.



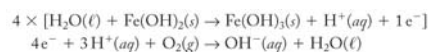
2c. Balance H by adding $\text{H}^+(aq)$ as needed



3. Balance charge.



4. Balance numbers of electrons.



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Sample Exercise 4.13

Iodine is slightly soluble in water and dissolves to make a yellow-brown solution of $\text{I}_2(aq)$. When colorless $\text{Sn}^{2+}(aq)$ is dissolved in it the solution turns colorless as $\text{I}^-(aq)$ forms and $\text{Sn}^{2+}(aq)$ is converted into $\text{Sn}^{4+}(aq)$. (a) Is this a redox reaction? (b) Balance the equation that describes the reaction.

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Analyze: oxidation half-reaction is clear: iron(II) hydroxide oxidized to iron(III) hydroxide; reduction half-reaction, O_2 must be converted into the additional OH^- ion in the iron(III) hydroxide product.

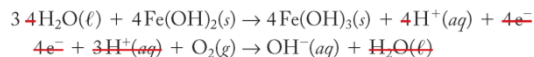
Solve: 1. Separate the equations.



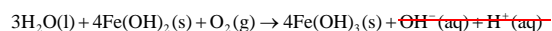
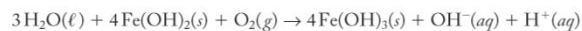
2a. Balance all masses except H and O. This step is not needed because the only mass not attributed to H and O is Fe, which is balanced.

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5. Add the two equations.



This gives us the balanced equation:



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