Review of Chemical Concepts
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2. Can Wastewater Effluent be Directly Used as a Source of Drinking Water?
3. Harvesting the Wind: A 21st Century Fairytale
4. Is Nuclear Energy the Key to Reducing Carbon Emissions?
5. The Truth About Endocrine Disruptors
6. What Constitutes Sustainable Environmental Engineering Design?

Periodic Table of the Elements
Makeup of an Atom

- An atom is made up of the following components (Neils Bohr):
  - Nucleus
    - Positive charged particles called Protons
  - Neutrons that have no charge
  - Shell
    - Negative charged particles called Electrons
- An atom has no charge when the number of protons equals the number of electrons.

Definitions

- **Atomic weight**: is the mass of the atom measured in atomic mass units (amu); where 1 amu is 1/12th the mass of a carbon atom.
- **Atomic number**: is the number of protons in the nucleus.
- **Isotopes**: atoms having the same number of protons, but differing numbers of neutrons. Therefore, they have different atomic weights.
- **Molecular weight**: is the sum of all the atomic weights of a molecule.

Calculating AW and MW

<table>
<thead>
<tr>
<th>Element of compound</th>
<th>Symbol</th>
<th>AW or MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>N</td>
<td>14.01</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg</td>
<td>24.31</td>
</tr>
<tr>
<td>Arsenic</td>
<td>As</td>
<td>74.92</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu</td>
<td>63.55</td>
</tr>
<tr>
<td>Potassium chloride</td>
<td>KCl</td>
<td>39.10 + 35.35 = 74.45</td>
</tr>
<tr>
<td>Ammonium sulfate</td>
<td>(NH₄)₂SO₄</td>
<td>(14.01 + 4(1.01) + 32.07 + 4(16.00)) = 132.17</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>Na₂CO₃</td>
<td>22.99 + 2 + 12.01 + 3(16.00) = 84.99</td>
</tr>
</tbody>
</table>

Molarity

\[
M = \frac{\text{moles of solute}}{\text{volume of solution}} = \frac{\text{moles}}{L}
\]

1 mole of a substance is equal to the atomic mass of the substance in grams.
Molarity Example

Determine the grams of potassium chloride that must be added to a 1-Liter volumetric flask to make a 0.5 M solution.

\[ KCl = 39.10 + 35.35 = 74.45 \text{ g KCl mole} \]

\[ M = \frac{\text{moles}}{L} = 0.5 \text{ M} = \frac{X \text{ g KCl}}{74.45 \text{ g KCl/mole}} \]

\[ X = 0.5 \frac{\text{moles}}{L} \times 74.45 \text{ g KCl/mole} = 37.23 \text{ g} \]

Normality

\[ N = \frac{\text{equivalents of solute}}{\text{volume of solution}} = \frac{\text{eq}}{L} \]

\[ EW = \frac{AW}{z} = \frac{MW}{z} \]

EW = equivalent weight

\[ N = z \times M \]

z = charge or valence or number of hydrogen ions that react

z = number of electrons transferred during oxidation/reduction

Equivalents react with Equivalents

\[ N_1 \Psi_1 = N_2 \Psi_2 = \text{equivalents} \]

N= Normality of solution

\[ \Psi = \text{Volume of solution} \]

Calculating EW

<table>
<thead>
<tr>
<th>Compound</th>
<th>Products</th>
<th>EW = MW/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>H⁺ + Cl⁻</td>
<td>(1.01 + 35.45)/1 = 36.46 g/eq</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>H⁺ + HSO₄⁻</td>
<td>(1.01 + 32.07 + 45.06)/1 = 88.24 g/eq</td>
</tr>
<tr>
<td>H₂SO₃</td>
<td>2H⁺ + SO₃⁻</td>
<td>(1.01 + 32.07 + 45.06)/2 = 49.05 g/eq</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>H⁺ + H₂PO₄⁻</td>
<td>(1.01 + 31.01 + 45.06)/1 = 87.08 g/eq</td>
</tr>
<tr>
<td>H₂PO₄</td>
<td>2H⁺ + HPO₄⁻</td>
<td>(1.01 + 31.01 + 45.06)/2 = 43.54 g/eq</td>
</tr>
<tr>
<td>H₃PO₃</td>
<td>3H⁺ + PO₄⁻</td>
<td>(1.01 + 31.01 + 45.06)/3 = 32.17 g/eq</td>
</tr>
<tr>
<td>Fe(OH)₃</td>
<td>Fe³⁺ + 3 OH⁻</td>
<td>(55.85 + 3(16.00 + 1.01))/3 = 35.63 g/eq</td>
</tr>
</tbody>
</table>
### Chemical Reactions

\[ a \, A + b \, B \xrightarrow{k_f} c \, C + d \, D \]

- \( a, b, c, \) and \( d \) = molar coefficients
- \( A, B, C, \) and \( D \) = concentration of constituents \( A, B, C, \) and \( D \)
- \( k_f \) = rate constant in the forward direction
- \( k_r \) = rate constant in the reverse direction

### Equilibrium Constant (\( K \))

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

- \( K \) = equilibrium constant, units depend on the specific reaction
- \( A, B, C, \) and \( D \) = molar concentrations of \( A, B, C, \) and \( D \)

### pH

\[ \text{pH} = -\log\left[ \text{H}^+ \right] \]

- \( \left[ \text{H}^+ \right] \) = hydrogen ion concentration in moles/L
- pH scale shown in the literature ranges from 0 to 14
- The pH however, can be lower or higher

### pH Estimates of Household Items

![pH Scale Diagram]
pOH

pOH = −log[OH⁻]

[OH⁻] = hydroxide ion concentration in moles/L

pH + pOH = 14

Brønsted-Lowry Theory

HA + B⁻ ⇌ A⁻ + HB

Acid−Base

Acid-conjugate base pairs

Acid: donates a H⁺ or proton to another substance.
Base: accepts a H⁺ or proton from another substance.

Amphoteric Substances

H₂O + H₂O ⇌ HO⁻ + H₃O⁺

Water is an amphoteric substance since it acts both as an acid or a base.

When water donates a proton, it forms the conjugate base, OH⁻.
When water accepts a proton, it forms the conjugate acid, H₂O⁺.

Water is a Weak Acid/Base

H₂O ⇌ H⁺ + OH⁻

K_{equilibrium} = \frac{[H⁺][OH⁻]}{H₂O} = 1.8 \times 10^{-16} @ 25°C
Example 1

- Calculate the hydrogen ion concentration, hydroxide ion concentration, pOH, and hydrogen ion concentration expressed in terms of CaCO₃ if the pH of an aqueous solution is 7.5

Solution

$$\text{pH} = -\log\left[\text{H}^+\right]$$

$$\left[\text{H}^+\right] = 10^{-\text{pH}} = 10^{-7.5} = 3.16 \times 10^{-8} \text{ moles/L}$$

Example 1 Continued

$$\text{pH} + \text{pOH} = 14$$

$$\text{pOH} = 14 - \text{pH} = 14 - 7.5 = 6.5$$

$$\left[\text{OH}^-\right] = 10^{-\text{pOH}} = 10^{-6.5} = 3.16 \times 10^{-7} \text{ moles/L}$$

$$K_w = [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$$

$$\left[\text{OH}^-\right] = \frac{K_w}{[\text{H}^+]} = \frac{1 \times 10^{-14}}{10^{-7.5}} = 3.16 \times 10^{-7} \text{ moles/L}$$

Example 1 Continued

$$\left[\text{H}^+\right] = 10^{-\text{pH}} = 10^{-7.5} = 3.16 \times 10^{-8} \text{ moles/L}$$

$$\left[\text{H}^+\right] = 3.16 \times 10^{-8} \frac{\text{moles}}{\text{L}} \left( \frac{1 \text{ g H}^+}{1 \text{ mole H}^+} \right) \left( \frac{1 \text{ eq H}^+}{1 \text{ g H}^+} \right) \left( \frac{50 \text{ g CaCO}_3}{1 \text{ eq CaCO}_3} \right)$$

$$\left[\text{H}^+\right] = 1.58 \times 10^{-6} \frac{\text{g}}{\text{L}} \left( \frac{1000 \text{ mg}}{\text{g}} \right) = 1.58 \times 10^{-3} \frac{\text{mg}}{\text{L}}$$
**Acid Dissociation**

\[ \text{HA} \rightleftharpoons \text{H}^+ + \text{A}^- \]

\[ K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \]

\[ pk_a = - \log K_a \]

Strong acids when \( pk_a < 1 \)

**Base Dissociation**

\[ \text{BOH} \rightleftharpoons \text{B}^+ + \text{OH}^- \]

\[ K_b = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]} \]

\[ pk_b = - \log K_b \]

Strong bases when \( pk_b < 1 \)

### Table 3.2

<table>
<thead>
<tr>
<th>Acid</th>
<th>Base</th>
<th>( pk_a )</th>
<th>( pk_b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>Cl^-</td>
<td>3.0</td>
<td>17.0</td>
</tr>
<tr>
<td>HNO_3</td>
<td>NO_3^-</td>
<td>3.3</td>
<td>10.5</td>
</tr>
<tr>
<td>HSO_4^-</td>
<td>SO_4^2-</td>
<td>2.4</td>
<td>12.0</td>
</tr>
<tr>
<td>HF</td>
<td>F^-</td>
<td>3.44</td>
<td>10.9</td>
</tr>
<tr>
<td>HNO_2</td>
<td>NO_2^-</td>
<td>4.2</td>
<td>9.3</td>
</tr>
<tr>
<td>H_2SO_3</td>
<td>HSO_3^-</td>
<td>3.6</td>
<td>5.7</td>
</tr>
<tr>
<td>HCO_3^-</td>
<td>CO_3^2-</td>
<td>6.3</td>
<td>12.3</td>
</tr>
<tr>
<td>H_2S</td>
<td>HS^-</td>
<td>7.2</td>
<td>7.7</td>
</tr>
<tr>
<td>H_2CO_3</td>
<td>HCO_3^-</td>
<td>7.2</td>
<td>10.3</td>
</tr>
<tr>
<td>H_2PO_4^-</td>
<td>HPO_4^2-</td>
<td>12.3</td>
<td>7.2</td>
</tr>
<tr>
<td>NH_4^-</td>
<td>NH_3</td>
<td>9.3</td>
<td>4.7</td>
</tr>
<tr>
<td>HCO_3^-</td>
<td>CO_3^2-</td>
<td>5.7</td>
<td>10.3</td>
</tr>
<tr>
<td>PO_4^3-</td>
<td>PO_4^3-</td>
<td>12.3</td>
<td>7.2</td>
</tr>
<tr>
<td>OH^-</td>
<td>OH^-</td>
<td>14.0</td>
<td>14.0</td>
</tr>
</tbody>
</table>

Source: CRC, 2006

### Calculating the pH of Solutions

1. Write all pertinent chemical equations.
2. Write all appropriate equilibrium expressions.
3. Prepare a charge balance i.e. electroneutrality.
4. Write all mass balances.
5. Solve by making simplifying assumptions.
6. Check all assumptions.
Example 2: Step 1
Determine the pH of a 0.050 molar solution of hydrochloric acid (HCl).

Step 1
H₂O ⇌ H⁺ + OH⁻
HCl ⇌ H⁺ + Cl⁻
(Strong Acid: complete dissociation)

Example 2: Steps 2 & 3
Step 2
[H⁺][OH⁻] = 10⁻¹⁴

Step 3
[H⁺] = [OH⁻] + [Cl⁻] Charge Balance

Example 2: Steps 4 & 5
Step 4
[H⁺] = [Cl⁻] = 0.05M

Step 5
[H⁺] = [OH⁻] + [Cl⁻] = [OH⁻] + 0.05 M
Assume that [H⁺] >> [OH⁻]
Therefore, [H⁺] = 0.05 M pH = -log 0.05 = 1.30

Example 2: Step 6
Step 6: Check assumptions
[H⁺][OH⁻] = 10⁻¹⁴

[OH⁻] = \frac{10^{-14}}{0.05 M} = 2 \times 10^{-13} << 0.05 M
Example 3: Step 1

Determine the pH of a 1.0 molar solution of HF (hydrofluoric acid).

Step 1

\[ \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \]

\[ \text{HF} \rightleftharpoons \text{H}^+ + \text{F}^- \]

(Weak Acid: incomplete dissociation)

Example 3: Steps 2 & 3

Step 2

\[ [\text{H}^+][\text{OH}^-] = 10^{-14} \]

\[ \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = 10^{-3.4} \]

Step 3

\[ [\text{H}^+] = [\text{OH}^-] + [\text{F}^-] \]

Charge Balance

Example 3: Steps 4 & 5

Step 4

\[ \text{HF} + [\text{F}^-] = 1.0 \text{ M or } \frac{\text{HF}}{\text{F}^-} = 1.0 \text{ M} - [\text{F}^-] \]

Step 5

Assume that \[ [\text{H}^+] >> [\text{OH}^-] \] Therefore, \[ [\text{H}^+] = [\text{F}^-] \]

\[ \frac{[\text{H}^+] [\text{F}^-]}{[\text{HF}]} = 10^{-3.4} = \frac{[\text{H}^+]^2}{[\text{HF}]} \]

Example 3: Step 5 Continued

Step 5

Assume that \[ [\text{H}^+] >> [\text{OH}^-] \] Therefore, \[ [\text{H}^+] = [\text{F}^-] \]

\[ \frac{[\text{H}^+]^2}{[\text{HF}]} = \frac{[\text{H}^+]^2}{1.0 \text{ M} - [\text{H}^+]} \]

\[ [\text{H}^+]^2 + 10^{-3.4}[\text{H}^+] - 10^{-3.4} = 0 \]
Example 3: Step 5 Continued

Step 5

\[
\left[ \text{H}^+ \right]^2 + 10^{-3.4} \left[ \text{H}^+ \right] - 10^{-3.4} = 0
\]

Quadratic Equation

\[
\left[ \text{H}^+ \right] = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = 1.97 \times 10^{-2}
\]

\[
\text{pH} = -\log \left[ 1.97 \times 10^{-2} \right] = 1.70
\]

Example 3: Step 6

Step 6: Verify

\[
\left[ \text{H}^+ \right] \left[ \text{OH}^- \right] = 10^{-14}
\]

\[
\left[ \text{OH}^- \right] = \frac{10^{-14}}{\left[ \text{H}^+ \right]} = \frac{10^{-14}}{1.97 \times 10^{-2}} = 5.08 \times 10^{-13}
\]

\[
\left[ \text{OH}^- \right] = 5.08 \times 10^{-13} \ll \left[ \text{H}^+ \right] = 1.97 \times 10^{-2}
\]

Solid-Phase Equilibrium Reactions

\[ \text{A}_a \text{B}_b \rightleftharpoons a \text{A} + b \text{B} \]

The equation above shows the relationship between the solid phase of a salt or ionic compound and its dissolution species.

\[ a \text{A} \rightleftharpoons b \text{B} \]

There is no denominator in the above equilibrium expression since the solids species is assumed to remain constant. \( K_{sp} \) is the solubility product.

Example 3

Calculate the solubility product of barium sulfate (BaSO\(_4\)) at 25°C if its solubility in pure water is 1.05×10\(^{-5}\).

\[ \text{BaSO}_4 \rightleftharpoons \text{Ba}^{2+} + \text{SO}_4^{2-} \]

\[ [\text{Ba}^{2+}] = [\text{SO}_4^{2-}] = 1.05 \times 10^{-5} \]

\[ [\text{Ba}^{2+}] [\text{SO}_4^{2-}] = K_{sp} \]

\[ K_{sp} = [1.05 \times 10^{-5}] [1.05 \times 10^{-5}] = 1.10 \times 10^{-10} \]
Example 4

Calculate the solubility of calcium fluoride (CaF$_2$) if its solubility product is $4.0 \times 10^{-11}$.

$$
\text{CaF}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{F}^- \\
[\text{Ca}^{2+}] = x \quad [\text{F}^-] = 2x
$$

$$
[\text{Ca}^{2+}]^1 [\text{F}^-]^2 = K_{sp} = 4.0 \times 10^{-11}
$$

$$
x \times (2x)^2 = 2.15 \times 10^{-7} \text{ moles/L}
$$

Dalton’s Law and Partial Pressure

$$
P_T = P_1 + P_2 + P_3 + P_4
$$

$P_T$ = total system pressure

$P_i$ = partial pressure of each component

$P_i = y_iP_T$

$y_i$ = mole fraction of component i in the gas phase

$$
y_i = \frac{n_i}{n} \quad \frac{P_i}{P_T}
$$

Henry’s Law

Henry’s law relates the amount of gas that can dissolve in a liquid (at equilibrium) to the vapor pressure of the gas. There are different forms of Henry’s law and the units for the Henry’s constant will vary.

$$
P_i = k'_{hi} x_i
$$

$P_i$ = partial pressure of each component

$x_i$ = mole fraction of component i in the liquid phase

$k'_{hi}$ = Henry’s constant based on liquid-phase mole fraction, atm

Example 5

Calculate the solubility of nitrogen gas at 25°C and 1 atm assuming nitrogen is 79% by volume in the atmosphere.

$$
P_x = 1 \text{ atm} \left(\frac{79\%}{100\%}\right) = 0.79 \text{ atm}
$$

$$
P_A = k'_{hi} \quad k'_{hi} = \text{Table 3.5} = 1540 \frac{\text{L atm}}{\text{mol}}
$$

$$
A = \frac{P_A}{k'_{hi}} \quad N_1 = \frac{0.79 \text{ atm}}{1540 \frac{\text{L atm}}{\text{mol}}} = 5.13 \times 10^{-4} \text{ moles/L}
$$
Example 5 Continued

\[ N_2 = 5.13 \times 10^{-4} \text{ moles} \left( \frac{28 \text{ g N}_2}{1 \text{ mole N}_2} \right) \left( \frac{1000\text{ mg}}{1 \text{ g}} \right) \]

\[ N_2 = \frac{14.4 \text{ mg}}{\text{L}} \]

Example 6

Calculate the solubility of oxygen gas at 25°C and 1 atm assuming oxygen is 21% by volume in the atmosphere.

\[ P_o = 1 \text{ atm} \times \left( \frac{21\%}{100\%} \right) = 0.21 \text{ atm} \]

\[ P_x = k_{H}^{A} x_{A} \]

Table 3.5 \[ k_{H}^{A} = 4.26 \times 10^{4} \text{ atm} \]

\[ x_{A} = \frac{P_x}{k_{H}^{A}} \]

\[ x_{O_2} = \frac{0.21 \text{ atm}}{4.26 \times 10^{4} \text{ atm}} = 4.93 \times 10^{-6} \]

Example 6 Continued

\[ x_{O_2} = \frac{0.21 \text{ atm}}{4.26 \times 10^{4} \text{ atm}} = 4.93 \times 10^{-6} \]

\[ x_{O_2} = \frac{\text{moles of gas } n_{g}}{\text{moles of gas } n_{g} + \text{moles of water } n_{w}} \]

1 liter of water contains: \[ 1000 \text{ g} \]

\[ 18 \text{ g H}_2\text{O/mole} = 55.6 \text{ moles} \]

\[ x_{O_2} = \frac{n_{g}}{n_{g} + 55.6 \text{ moles}} = 4.93 \times 10^{-6} \]

\[ n_{g} + 55.6 \text{ moles} \times 4.93 \times 10^{-6} = n_{g} \]

\[ n_{g} \text{ O}_2 = 2.74 \times 10^{-4} \text{ moles} \]

\[ n_{g} \text{ O}_2 = 2.74 \times 10^{-4} \text{ moles} \]

\[ O_{2} = \frac{2.74 \times 10^{-4} \text{ moles}}{1 \text{ L}} \left( \frac{32 \text{ g O}_2}{1 \text{ mole O}_2} \right) \left( \frac{1000 \text{ mg}}{1 \text{ g}} \right) \]

\[ O_{2} = \frac{8.77 \text{ mg}}{\text{L}} \]
Alkalinity

Alkalinity is a water's ability to resist a change in pH when an acid is added i.e. buffering capacity. It is expressed in terms of CaCO$_3$ and measured by titration with 0.02N sulfuric acid.

\[
\text{alk} \left( \frac{\text{eq}}{\text{L}} \right) = \left[ \text{HCO}_3^- \right] + 2\left[ \text{CO}_3^{2-} \right] + \left[ \text{OH}^- \right] - \left[ \text{H}^+ \right] \]

= concentration, moles/L

\[
\left( \frac{\text{eq}}{\text{L}} \right) \left( \frac{50 \text{ g CaCO}_3}{\text{eq}} \right) = \frac{\text{g CaCO}_3}{\text{L}}
\]

Temperature Corrections

The equilibrium rate constant can be corrected for temperature variations using the following equation.

\[
\ln \frac{K_1}{K_2} = \frac{\Delta H^*}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

Snoeyink and Jenkins