Ionic equations, calculations involving concentrations, stoichiometry

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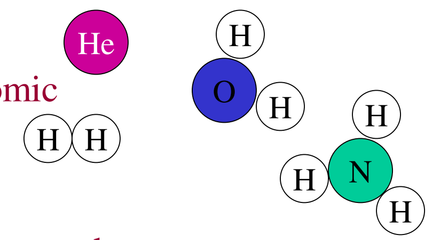
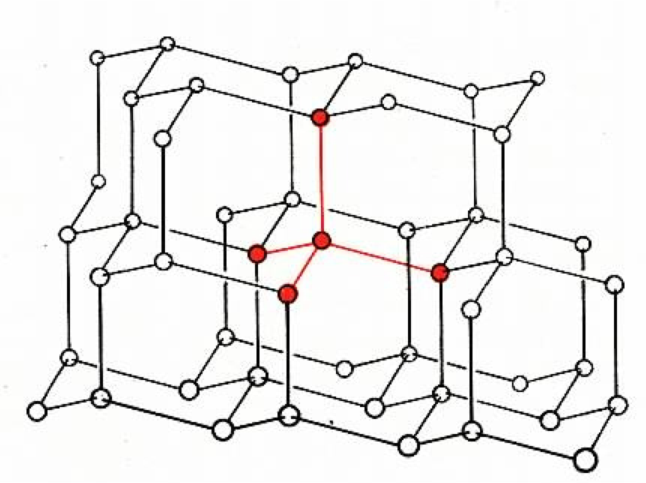
Molecule

- smallest particle of a substance having its chemical properties
- Atoms connected via covalent bonds
- Examples:
  - noble gases: monoatomic
  - other gases: diatomic
  - H_2O, NH_3 etc.
  - molecular crystals: diamond
  - ...many thousands of atoms in proteins and nucleic acids



Molecular crystal of diamond

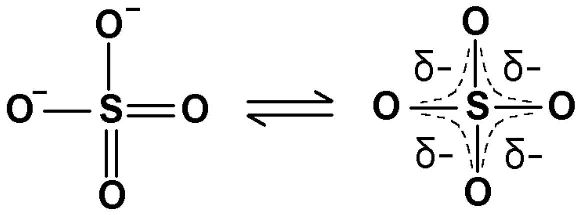


Ion

- atom or molecule with non zero charge (number of electrons does not match number of protons)
- tendency to form ions depends on **electronegativity** of element
- cations (+) or anions (-)
- monoatomic: Na^+, Cl^-, H^+, Fe^{2+}
- molecular: NO_3^- , SO_4^{2-}
- complex: $[Fe(CN)_6]^{4-}$

Molecular ions of oxo-acids:

e.g. sulfate, SO_4^{2-} :



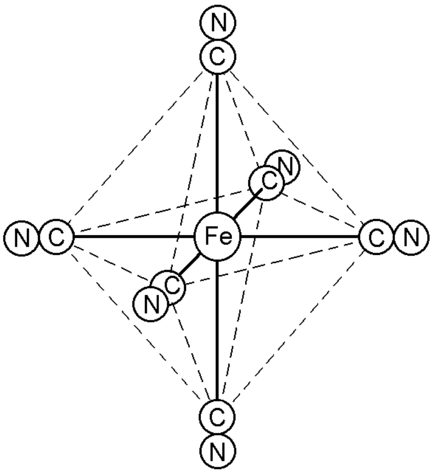
resonance stabilization of sulfate ion

..similar is nitrate NO_3^-, phosphate PO_4^{3-}, carbonate CO_3^{2-}, etc.

Coordination (complex) ions

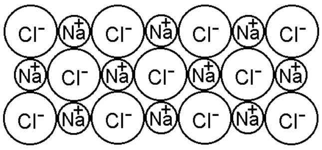
- central atom of transition metal providing empty orbitals+ ligands providing free electron pairs
- coordinate covalent bond: ligand donates <u>both</u> bonding electrons
- Number of ligands is usually 4 or 6

e.g. $[Fe(CN)_6]^{4-}$

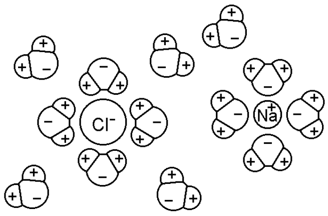


Ionic salts: no true molecule

- **Crystal lattice of NaCl:**

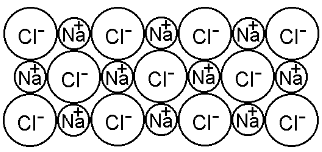


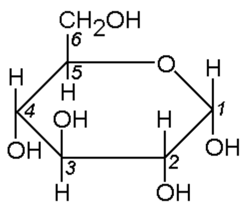
- **Dissolution of NaCl in water: electrolytic dissociation producing hydrated independent ions Na^+, Cl^-**



Chemical formulas

- Stoichiometric (empirical)
  - e.g.: sodium chloride NaCl
  - e.g.: glucose CH_2O
- Molecular
  - e.g.: sodium chloride NaCl
  - e.g.: glucose $C_6H_{12}O_6$
- Structural





IONIC EQUATIONS

Reaction I

Stoichiometric equation:

$$AgNO_3 + KCl \longrightarrow AgCl + KNO_3$$

Ionic equation:

$$Ag^+ + NO_3^- + K^+ + Cl^- \longrightarrow AgCl + K^+ + NO_3^-$$

Net ionic equation:

$$Ag^+ + \cancel{NO_3^-} + \cancel{K^+} + Cl^- \longrightarrow AgCl + \cancel{K^+} + \cancel{NO_3^-}$$

$$\boxed{\mathbf{Ag^+ + Cl^- \longrightarrow AgCl}}$$ white ppt

Also possible:

$$AgNO_3(aq) + KCl(aq) \longrightarrow AgCl(s) + KNO_3(aq)$$

$$\boxed{\mathbf{Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)}}$$

(aq)	... aqueous
(s)	... solid
(l)	... liquid
(g)	... gaseous

Reaction II

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$

ionic:

$$Cu^{2+} + SO_4^{2-} + 2Na^+ + 2\,OH^- \longrightarrow Cu(OH)_2 + SO_4^{2-} + 2\,Na^+$$

net ionic:

$$Cu^{2+} + \cancel{SO_4^{2-}} + \cancel{2Na^+} + 2\,OH^- \longrightarrow Cu(OH)_2 + \cancel{SO_4^{2-}} + \cancel{2\,Na^+}$$

$$\boxed{\mathbf{Cu^{2+} + 2\,OH^- \longrightarrow Cu(OH)_2}}$$

pale blue ppt

Reaction III

$$2\ NaOH + (NH_4)_2SO_4 \longrightarrow 2\ NH_3 + Na_2SO_4 + 2H_2O$$

ionic:

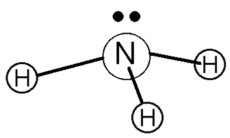
$$2Na^+ + 2OH^- + 2NH_4^+ + SO_4^{2-} \longrightarrow 2NH_3 + 2Na^+ + SO_4^{2-} + 2H_2O$$

net ionic:

$$\cancel{2Na^+} + \cancel{2}OH^- + \cancel{2}NH_4^+ + \cancel{SO_4^{2-}} \longrightarrow \cancel{2}NH_3 + \cancel{2Na^+} + \cancel{SO_4^{2-}} + \cancel{2}H_2O$$

$$\boxed{\mathbf{OH^- + NH_4^+ \longrightarrow NH_3 + H_2O}}$$

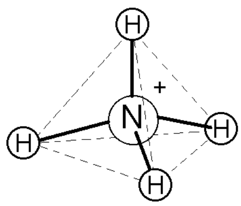
Ammonia gas: NH_3, $NH_3(g)$



Aqueous ammonia: $NH_3(aq)$, $NH_3.H_2O$, NH_4OH

$$\mathbf{NH_3.H_2O \longleftrightarrow NH_4OH}$$

$$\mathbf{NH_4OH \longleftrightarrow NH_4^+ + OH^-}$$



$\cancel{\mathbf{NH_4^+OH^-}}$

Reaction IV

$$CuSO_4 + 4\,NH_4OH \longrightarrow [Cu(NH_3)_4]SO_4 + 4H_2O$$

ionic:

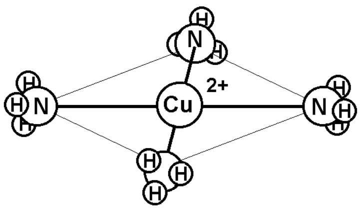
$$Cu^{2+} + \cancel{SO_4^{2-}} + 4NH_4OH \longrightarrow [Cu(NH_3)_4]^{2+} + \cancel{SO_4^{2-}} + + 4H_2O$$

net ionic:

$$Cu^{2+} + 4NH_4OH \longrightarrow [Cu(NH_3)_4]^{2+} + 4H_2O$$

tetraammincupric cation,
tetraammincopper(II)

(dark blue complex)



Writing Ionic equations: Summary

1. write correct and balanced stoichiometric equation first
2. rewrite to ionic: write separately any species that exist separately and indicate its charge if present, but write together what exists joined (usually a precipitate of insoluble salt, or a soluble coordination complex)
3. Cancel out all species not involved in the reaction
4. Check that the equation is still balanced

What combinations of cations and anions are insoluble?

- All nitrates (NO_3^-) and acetates ($CH3COO^-$) are soluble
- All salts of Na, K, Li, and NH_4^+ are soluble
- All chlorides, bromides and iodides are soluble except salts of Pb^{2+}, Ag^+, and Hg_2^{2+}
- Most sulfate salts are soluble except $BaSO_4$, $PbSO_4$, $HgSO_4$, and $CaSO_4$.
- Most hydroxides are insoluble. Soluble are only NaOH and KOH. $Ba(OH)_2$, and $Ca(OH)_2$ are marginally soluble.
- Most sulfides (S^{2-}), carbonates (CO_3^{2-}) and phosphates (PO_4^{3-}) are insoluble.

Calculations involving concentration, stoichiometry

Mole

- Unit of amount of substance
- **the amount of substance containing as many particles (atoms, ions, molecules, etc.) as present in 12 g of the carbon isotope ^{12}C**
- this amount equals 6.02×10^{23} particles (**Avogadro's Number**)

(Relative) Atomic Weight

- atomic mass unit (u): 1/12 of the mass of one atom of the carbon isotope ^{12}C

  $1\ u = 1.66057 \times 10^{-27}$ kg
- relative atomic mass (atomic weight, AW): mass of an atom expressed in u
- molecules: (relative) molecular mass (molecular weight, MW)
- substances that do not form true molecules (ionic salts etc.):

  (relative) formula weight (FW)

Molar Mass

- mass of one mole of given substance
- expressed in g/mol
- **The molar mass of a substance in grams has the same numerical value as its relative atomic (molecular) weight**

Molar Volume

one mole of any gaseous substance occupies the same volume at the same temperature and pressure

..22.414 litres at 101.325 kPa, 0 °C (273.15 K)

(Avogadro's Law)

$P . V = n . R . T$

P: pressure in kPa

V: volume in dm^3 (l)

n: number of moles

R: universal gas constant (8.31441 $N.m.mol^{-1}.K^{-1}$)

T: temperature in K

Example: what is volume of one mole of gas at 101.325 kPa and 25 °C ?

$$P.V = n.R.T$$

$$V = \frac{n.R.T}{P} = \frac{1 \times 8.31441 \times (273.15+25)}{101.325} =$$

= 24.465 dm^3

Solution

- homogeneous dispersion system of two or more chemical entities whose relative amounts can be varied within certain limits
- solvent + solute(s)
- gaseous (e.g. air)
- liquid (e.g. saline, NaCl dissolved in water)
- solid (e.g. metal alloy)

Concentration of a solution

- mass concentration: grams of substance per litre of solution
- molar concentration: moles of substance per litre of solution
- in %:
  - **% (w/v):** weight per volume, grams of substance per 100 ml of solution
  - **% (v/v)** volume per volume, ml of substance per 100 ml of solution

Conversion from mass to molar

Example: Calculate molar concentration of Na_2HPO_4 solution c = 21 g /l.
(AW of Na: 23, P: 31, O: 16, H: 1)

FW of Na_2HPO_4 : 46+1+31+4x16 = 142

Molar concentration = Mass conc. (g/l) / FW

= 21 / 142 = 0.15 mol/l

Conversion from molar to mass

Example: Calculate how many g of $KClO_4$ is needed for preparation of 250 ml of 0.1 M solution.
(AW of K: 39, Cl: 35.4, O: 16)

FW of $KClO_4$: 39 + 35.4 + 4x16 = 138.4

Mass conc. = molar conc. x FW

we need 138.4 x 0.1 x 0.25 = 3.46 g $KClO_4$

Conversions between mass and molarity: Summary

- Always distinguish between amount of substance in moles (grams) and concentration of substance in mol/l (g/l)
- For conversion from mass to molarity divide the mass (g or g/l) with molar mass (relative AW/MW/FW)
- For conversion from molarity to mass multiply the molarity (mol or mol/l) with molar mass (relative AW/MW/FW)

Conversion from % to molarity

Example: The physiological saline is NaCl 0.9 % (w/v)
What is molar concentration of NaCl in this solution?
(AW of Na: 23, Cl: 35.5)

FW of NaCl : 23+35.45 = 58.5

0.9 % (w/v) is 0.9 g/100 ml = Mass conc. 9 g/l

Molar concentration = Mass conc. (g/l) / FW

= 9/58.5 = 0.154 mol/l

Diluting solutions

Example: How many ml of water should be added to 100 ml of NaCl 1 mol/l, in order to get 0.15 mol/l ('physiological saline') ?

$$c_1 \, . \, v_1 = c_2 \, . \, v_2$$

$$1 \times 100 = 0.15 \times v_2$$

$$v_2 = 100/0.15 = 666.67 \text{ ml}$$

Volume that needs to be added:

666.67 ml - 100 ml = **566.67 ml**

Diluting solutions

Example II: You need to prepare 1 liter of 0.1 M HCl. How many ml of concentrated HCl (12 M) do you need to take ?

$$c_1 \, . \, v_1 = c_2 \, . \, v_2$$

$$12 \times v_1 = 0.1 \times 1000$$

$$v_1 = 100/12 = \mathbf{8.33 \text{ ml}}$$

What is molarity of pure water?

Molar concentration: moles of substance per liter of solution

1 liter of water weighs 997 g at 25 °C

FW of H_2O: 2+16=18

997 g H_2O is 997/18 = 55.4 moles

Molarity of pure water is **55.4 mol/l**

Titration

- Reaction: A + B $\rightarrow$ C
- **Substance A:** unknown concentration, amount (solution volume) known
- **Substance B:** known concentration, is used to determine concentration of A
  - added gradually to A untill the reaction is just complete, and the consumed amount is recorded
  - an **indicator** is needed to show that the reaction has reached completion

Types of titration

- **Neutralisation reaction (acid-base titration)**

$$\mathbf{HCl + NaOH \rightarrow NaCl + H_2O}$$

ionic: $\mathbf{H^+ + OH^- \rightarrow H_2O}$

indicator e.g. phenolphthalein (in acid colourless, but violet in alkali

- **Precipitation reaction**
- **Redox reaction**

Titration calculations

Example: An unknown sample of sulfuric acid H_2SO_4 was titrated with the known KOH solution. It was found that 12 mL of the KOH c=0.1 mol/L was needed for just complete neutralisation of 10 mL H_2SO_4 unknown sample.

What is concentration of sulfuric acid in the sample?

Equation: $H_2SO_4 + 2\,KOH \rightarrow K_2SO_4 + 2\,H_2O$

Calculation: H_2SO_4 KOH

$$c_1 \cdot v_1 = c_2 \cdot v_2$$

$$c_1 = c_2 \cdot v_2 / v_1$$

$$c_1 = 0.1 \cdot 12 / 10 = 0.12$$

Including stoichiometry : $c(H_2SO_4) = 0.12/2 =$ **0.06 mol/L**

Calculations with molar volume

Example: What is weight (in grams) of 1 liter of oxygen at atmospheric pressure and ambient temperature ?

(AW of O: 16)

Molar volume at 101.325 kPa and 25 °C: 24.5 l/mol

1 liter of oxygen is 1/24.5 = 0.040816 mol

Conversion to mass: 0.040816 x 32 = **1.306 g**

Stoichiometric calculations

Example: In the reaction between barium nitrate and sodium sulfate, how many grams of barium sulfate can be prepared from 10 ml of 10 % (w/v) barium nitrate? Take into account that about 5% of the product is lost.
(AW of barium: 137.3, sulfur: 32.1, nitrogen: 14.0, oxygen: 16.0)

equation: $Ba(NO_3)_2 + Na_2SO_4 \rightarrow BaSO_4 + 2NaNO_3$

FW $Ba(NO_3)_2$: 261.3 FW $BaSO_4$: 233.4

10 ml of 10% (w/v) $Ba(NO_3)_2$: 1 g ... 1/261.3 = 0.003827 moles

amount of $BaSO_4$ formed: 0.003827 moles ....

... 0.003827 x 233.4 = 0.8932 g (theoretical yield, 100%)

Actual yield: 0.8932 x 0.95 = **0.849 g**