Chem 232: Quantitative Analysis Lecture Notes

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Topic

SI units: French system 180 years old

Base Units

dimension	unit	symbol
length	meter	m
mass	kilogram	kg
time	second	s
electrical current	ampere	A
temperature	Kelvin	K
Amount of substance	mole	mol

derived from SI base units

dimension	unit	symbol	SI equivalent
Frequency	Hertz	Hz	$\frac{1}{s}$
force	Newton	N	$\frac{mkg}{s^2}$
pressure	Pascal	Pa	$\frac{N}{m^2}$ or $\frac{kg}{ms^2}$

SI Units are base 10 (mostly):

Conversion to common units is simplified

What is an exception?

Time, which is base 60, 24, 365.25

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SI Units Prefixes:

Prefixes can be used to simplify numbers

table 1-3 in book (big)

prefix	abbreviation	10^N where N =
yotta	Y	24
zetta	Z	21
exa	E	18
peta	P	15
tera	T	12
giga	G	9
mega	M	6
kilo	k	3
hecto	h	2
deca	da	1
unit		

SI Unit Prefixes:

table 1-3 in book (small)

prefix	abbreviation	10^N where N =
unit		
deci	d	-1
centi	c	-2
milli	m	-3
micro	μ	-6
nano	n	-9
pico	p	-12
femto	f	-15
atto	a	-18
zepto	z	-21
yocto	y	-23

Example: usage of prefixes in SI

$0.17 \times 10^4 m \rightarrow 1.7 km$

and how do you know this?

$$0.17 \times 10^4 m \frac{1km}{1000m} = 1.7km$$

Concentration units and conversions:

Concentration units and conversions: Here comes the definitions!

Definition: solution

solution:

a homogeneous mixture of two or more substances

Definition: solute

solute:

minor species in a solution

Definition: solvent

solvent:

major species in a solution

NOTE in aqueous solutions the solvent is water

written as (aq) in chemical reactions. For example

$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$

NOTE can also be a system of chemicals (methanol and water)

Definition: analyte

analyte:

species of interest in a mixture (implies a measurement)

Definition: concentration

concentration:

The ratio of solute contained in a given volume or mass of solution or solvent

Definition: mole

mole:

number of carbon atoms with mass of 0.012 kg = $6.022141415 \times 10^{23}$

Example Problem: learing about the mole

	donut	carbon atoms	molecules of acetic acid
single			

Example Problem: learing about the mole

	donut	carbon atoms	molecules of acetic acid
single	1		

Example Problem: learing about the mole

	donut	carbon atoms	molecules of acetic acid
single	1	1	

Example Problem: learing about the mole

	donut	carbon atoms	molecules of acetic acid
single pair	1	1	1

Example Problem: learing about the mole

	donut	carbon atoms	molecules of acetic acid
single	1	1	1
pair	2		

Example Problem: learing about the mole

	donut	carbon atoms	molecules of acetic acid
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Example Problem: learing about the mole

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gross	144	144	144
mole			

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Definition: Avogadro's Number

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Definition: Atomic Mass

Molar Atomic Mass:

number of grams of an element containing N_a atoms

Definition: Molar Mass

Molar Mass:

sum of the atomic masses of all the atoms in a molecule
abreviated MM herein.

Definition: Molarity

Molarity:

number of molecules or atoms or ions of a substance in moles per liter of solution

$$\text{Molarity} = \frac{\text{moles of substance}}{\text{Liters of solution}}$$

square bracket notation

[H_3O^+] these square brackets mean concentration in mole/liter

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Example Problem: mass to molarity

Seawater contains 2.7g of NaCl per 100 mL of seawater. What is the molarity of NaCl in the ocean?

Have		Need
Mass of NaCl and volume of solution	$\rightarrow$	$\mathrm{mol/L}$

- Determine Molar Mass (MM) of NaCl

$$\begin{array}{r} 22.989768\mathrm{g/mol}(\text{MM of Na}) \\ +35.4527\mathrm{g/mol}(\text{MM of Cl}) \\ \hline 58.442468\mathrm{g/mol} \end{array}$$

- Use MM to determine the moles of 2.7g NaCl

$$\text{moles of NaCl} = 2.7\mathrm{g}\left(\frac{1\mathrm{molNaCl}}{58.442468\mathrm{gNaCl}}\right) = 0.046\mathrm{mol}$$

Example Problem: mass to molarity (Continued)

Seawater contains 2.7g of NaCl per 100 mL of seawater.

- Use the moles of NaCl and volume of solution to determine molarity

$$\text{Molarity of NaCl} = \frac{0.046 \text{ mol NaCl}}{100 \times 10^{-3} \text{ L solution}} = 0.46\text{M}$$

Example Problem: Molarity to mass

$MgCl_2$ has a concentration of 0.045 M in the ocean. How many grams of $MgCl_2$ are present in 25 mL of seawater?

- First:

$$\text{Molar mass of } MgCl_2 = \begin{array}{l} 24.305 \text{ g/mole Mg} \\ 2(35.453 \text{ g/mole Cl}) \\ \overline{\hspace{3cm}} \\ 95.211 \text{ g/mole } MgCl_2 \end{array}$$

- second:

$$\text{grams of } MgCl_2 \text{ in 25 mL of seawater} = (0.045 \text{ moles/L})(95.211 \text{ g/mole})(25 \times 10^{-3} L) = 0.11\text{g}$$

Definition: Electrolyte

Electrolyte:

a substance that dissociates into ions in solution

strong: mostly disassociates

weak: partially dissociates

Example: of electrolytes

$MgCl_2$ is a strong electrolyte in water

$$70\%\ \text{of}\ MgCl_2 \quad Mg^{2+} + 2\,Cl^-$$
$$30\%\ \text{of}\ MgCl_2 \quad MgCl^+ + Cl^-$$

- NOTE there is, in reality, very little $MgCl_2$ in the solution

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70\% \text{ of } MgCl_2 & Mg^{2+} + 2\,Cl^- \\
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\end{array}
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- NOTE there is, in reality, very little $MgCl_2$ in the solution

Definition: Formal Concentration

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molarity of electrolyte solutions

- So when we say concentration of $MgCl_2$ in water is 0.054 M, what we really mean is that the formal concentration is 0.054M.

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Definition: Formula Mass

Formula Mass:

sum of all the atomic masses in the formula

why have this?

the molecular mass (MM) does not make sense for electrolytes because

- in water the molecule has broken up into ions
- in the solid form the molecules are often not pure but crystallized with water molecules
  - this is called hydrated and the number of water molecules is called the hydration number
- Example:

$NaNO_3 \cdot 5\,H_2O$

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Definition: Coulomb's Law

Coulomb's Law:

opposite charges are attracted, same charges are repelled

Definition: Electronegativity

electronegativity:

- scale of nuclear (positive) pull on electrons (negative).
- bonds formed by atoms of different electronegativity result in polar bonds

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$$\delta^{+} \qquad\qquad \delta^{-}$$

$$\mathrm{H} \text{———} \mathrm{F}$$

$$2.1 \qquad\qquad 4.0$$

Definition: Molality

Molality (m):

- concentration unit in
  - $m = \frac{\text{moles of solute}}{\text{kg of solvent}}$

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why:

molarity changes with temp because volume changes with temp

Definition: v %

Percent by Volume:

$$v\% = \frac{\text{volume of solute}}{\text{volume of total solution or mixture}} \times 100$$

Example: Everclear is 95 v % ethanol

$$95 \text{ v } \% = \frac{95 \text{ mL ethanol}}{100 \text{ mL Everclear}} \times 100\%$$

Definition: wt%

Percent by Weight:

$$wt\% = \frac{\text{mass of solute}}{\text{mass of total solution or mixture}} \times 100$$

Example Problem: wt% to molarity and molality

Find the molarity and molality of a 37.0 wt% solution of HCl in water whose density is 1.19 g/mL.

Have	want	
density, wt%	moles/L	moles/kg solvent
other info	M.M. =	36.46 g/mole

- Definition of Molarity

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

- Definition of wt %

$$wt\% = \frac{\text{g of HCl}}{\text{g of solution}} \times 100\% = 37.0wt\% = \frac{0.37\text{g HCl}}{\underbrace{1.00g \text{ solution}}_{arbitrary}} \times 100\%$$

Example Problem: wt% to molarity and molality (continued)

Find the molarity and molality of a 37.0 wt% solution of HCl in water whose density is 1.19 g/mL.

- convert g of solution → L of solution

$$\underbrace{\left(\frac{0.37\text{g HCl}}{1.00\text{g sol.}}\right)}_{\text{from definition above}} \underbrace{\left(\frac{1.19\text{g sol.}}{1.00\text{mL sol.}}\right)}_{\textit{density}} \left(\frac{1000\text{ mL}}{1\text{ L}}\right) = 440.3\frac{\text{g HCl}}{\text{L sol.}}$$

- convert g of HCl → to moles of HCl

$$\text{Molarity} = \left(440.3\frac{\text{g of HCl}}{\text{L of solution}}\right)\left(\frac{1\text{ mole HCl}}{36.46\text{g HCl}}\right) = 12.1M$$

Example Problem: wt% to molarity and molality (continued2)

- Find Molality of the same solution
  remember the definition of molaity

$$\text{molality} = \frac{\text{moles of HCl}}{\text{kg of water}}$$

- pick a mass of solution (because one is not given, it can be any convenient mass) such as 1 g of solution. Therefore,
  1 g of solution = 0.37 g of HCl + X g of water.
  where
  X = 1 g - 0.37 g = 0.63 g of water.
- convert g of HCl → to moles of HCl

$$\text{molality} = 0.37\text{g HCl}\left(\frac{1 \text{ mole HCl}}{36.46 \text{ g HCl}}\right) = 0.010148 \text{ moles HCl}$$

$$\text{molality} = \left(\frac{0.010148\text{moles HCl}}{0.63 \times 10^{-3}\ kg}\right) = 16.1m$$

Definition: ppm and ppb

ppm or ppb:

$$ppm = \frac{\text{mass of solute}}{\text{mass of sample}} \times 10^6 \ (\mu g/g)$$
$$ppb = \frac{\text{mass of solute}}{\text{mass of sample}} \times 10^9 \ (ng/g)$$

note: similarity between wt % (pph) and ppm and ppb

Assumption: ppm and ppb in water solutions are very low concentrations

- the density of the solution is therefore very close to the density of pure water
- so with density 1.0 g/mL

Derivation of ppm and ppb:

$$\text{ppm} = \left(\frac{\mu g}{g}\right) \underbrace{\left(\frac{1.00g}{mL}\right)}_{\text{assumed density}} \left(\frac{1000mL}{L}\right) \left(\frac{mg}{1000\mu g}\right) = \frac{1mg}{L}$$

$$\text{ppb} = \frac{\mu g}{L}$$

Derivation of ppm and ppb:

$$\text{ppm} = \left(\frac{\mu\text{g}}{\text{g}}\right) \underbrace{\left(\frac{1.00\text{g}}{m\text{L}}\right)}_{\text{assumed density}} \left(\frac{1000m\text{L}}{\text{L}}\right)\left(\frac{mg}{1000\mu\text{g}}\right) = \frac{1mg}{\text{L}}$$

$$\text{ppb} = \frac{\mu\text{g}}{\text{L}}$$

Example Problem: ppb to molarity

Find the concentration in molarity of 34 ppb hexane in water ($MM_{\text{hexane}} = 86$ g/mole)

- Remember your definition of ppb. $34\text{ppb} = \frac{34\mu\text{g}}{\text{L}}$
- convert µgto moles

$$34\mu\text{g}\left(\frac{1g}{10^6\mu\text{g}}\right)\underbrace{\left(\frac{1\text{mol}}{86\text{g}}\right)}_{MM_{\text{hexane}}} = 3.95 \times 10^{-7} M$$

or 0.395 µM

preparing solutions:

The reason that we have molarity as a concentration unit is because of the way that solutions are prepared using Volumetric Flasks.

Example: How to use a Volumetric Flask to make a solution from a solid

flask

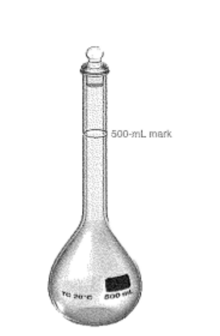

Figure: Volumetric Flask

task

You need 500 mL solution containing 10 mM Ca^{2+}. In your stockroom you have a kilogram of calcium nitrate pentahydrate ($Ca(NO_3)_2 \cdot 5\,H_2O$).

Here are your steps

- Calculate the mass needed
- weigh out close to that amount (record actual mass)
- make solution

Example: How to use a volumetric flask to make solution from a solid

- determine the number of moles of Ca^{+2} needed.

$$10mM\ \mathrm{Ca}^{+2}\left(\frac{1M}{10^3 mM}\right) = 0.01M$$

$$\frac{0.01\ mole}{L}0.500L = 5.0\times 10^{-3} moles\ \mathrm{Ca}^{+2}$$

- Determine how many moles of $Ca(NO_3)_2 \cdot 5\,H_2O$ are needed from the dissociation reaction.

$$\mathrm{Ca(NO_3)_2\cdot 5\,H_2O(s)} \rightleftharpoons \mathrm{Ca}^{+2} + 2\,\mathrm{NO_3(aq)} + 5\,\mathrm{H_2O}$$

$$5.0\times 10^{-3} moles\ \mathrm{Ca}^{+2}\left(\frac{1 mole\ \mathrm{Ca(NO_3)_2\cdot 5\,H_2O}}{1 mole\ \mathrm{Ca}^{+2}}\right) = 5.0\times 10^{-3} moles\ \mathrm{Ca(NO_3)_2\cdot 5\,H_2O}$$

Example: How to use a volumetric flask to make solution from a solid

- Determine the number of grams needed.

$$5.0 \times 10^{-3} \textit{moles } \mathrm{Ca(NO_3)_2 \cdot 5\,H_2O} \underbrace{\left(\frac{254.08g}{mole}\right)}_{FW} = 1.27g$$

- Measure (weigh) out close to that amount (record actual mass).

Let's pretend it is 1.3000 g of $Ca(NO_3)_2 \cdot 5\,H_2O$.

- make solution

Example: How to use a Volumetric Flask to make a solution from a solid

- Finally, calculate the actual concentration (remember that you measured 1.3000 g)

$$1.3000g\,\mathrm{Ca(NO_3)_2{\cdot}5\,H_2O}\left(\frac{1}{FW}\right)\left(\frac{1\ mole}{1\ mole}\right) = 5.1165\times10^{-3}\ moles\ \mathrm{Ca}^{2+}$$

$$\left(\frac{5.1165\times10^{-3}\ moles\ \mathrm{Ca}^{2+}}{0.500\mathrm{L\ sol.}}\right) = 0.0102M$$

Example: How to use a volumetric flask to make a more dilute solution from a more concentrated solution.

Ex. you have a solution of 12.1 M HCl, but you need 1 L of 0.100 M HCl.

- use the dilution equation

$$C_i V_i = C_f V_f$$

- make a table

$$\begin{aligned} C_i &= 12.1 \text{ M} \\ V_i &= ? \\ C_f &= 0.100 \text{ M} \\ V_f &= 1 \text{ L} \end{aligned}$$

- you do not know V_i, so solve the dilution equation for V_i

$$V_i = \frac{C_f V_f}{C_i} = \frac{(0.1M)(1L)}{12.1M} = 8.264 \times 10^{-3} \text{ L}$$

Example: solution dilution (continued)

so you take 8 mL out of your 12.1 M HCl solution and put it in a volumetric flask.

Next you fill the flask to about 1 cm from the fill line with your solvent

mix the sample

fill to the line with your solvent

now you need to calculate the actual concentration of your

diluted solution, because you actually only transferred 8 ml of concentrated HCl.

Example: solution dilution (continued)

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Example: solution dilution continued

- make a table

$$\begin{aligned} C_i &= \quad 12.1 \text{ M} \\ V_i &= \quad 8 \text{ mL} \\ C_f &= \quad ? \\ V_f &= \quad 1 \text{ mL} \end{aligned}$$

- you do not know C_f, so solve the dilution equation for C_f

$$C_f = \frac{C_i V_i}{V_f} = \frac{(12.1M)(8mL)}{1000mL} = 0.097 \text{ M}$$

Analytical Calculations based upon stoichiometry:

Generally, this is the application of limiting reagent.

Example: Gravimetric Analysis

What is the concentration of lead in the solution?

Sodium chloride is added to a solution of $\{Pb^{+2}\}$. Assuming that the following reaction is the only one, and that the reaction goes to completion, what was the concentration in ppm of lead(II) in the solution?

Given the RXN

$$Pb^{+2} + 2\,Cl^- \longrightarrow PbCl_2(s)$$

you filter out the ppt and the solid weighs 0.0004g.

Example: Gravimetric Analysis (continued)

$$Pb^{+2} + 2\,Cl^{-} \longrightarrow \underbrace{PbCl_2(s)}_{\text{mass} = 0.0004\text{ g}}$$

What was the concentration of lead in the solution before the addition of Cl^{-} in a sample whose volume was of 250 mL.

$$0.0004g\,PbCl_2 \underbrace{\left(\frac{1\ mole\ PbCl_2}{278.068\ g\ PbCl_2}\right)}_{\text{FW of } PbCl_2} = 1.43834\times10^{-6}\ moles\ PbCl_2$$

$$1.43834\times10^{-6}\ moles\ PbCl_2 \left(\frac{moles\,Pb^{+2}}{moles\,PbCl_2}\right) = 1.43834\times10^{-6}\ moles\ Pb^{+2}$$

$$1.43834\times10^{-6}\ moles\ Pb^{+2} \underbrace{\left(\frac{207.19g\ Pb^{+2}}{mole\ Pb^{+2}}\right)}_{\text{MM of } Pb^{+2}} = 2.98012\times10^{-4} g\,Pb^{+2}$$

Example: Gravimetric Analysis (continued)

- remember

$$\text{ppm} = \frac{\mu\text{g}}{\text{L}}$$

$$2.98012 \times 10^{-4} g\text{Pb}^{+2} \left(\frac{10^6\ \mu\text{g}}{g}\right)\left(\frac{1}{0.250\text{L}}\right) = 1192 ppm$$

or 1.2×10^3 ppm