

Chapter 1 Measurements

Problems 7, 8, 10, 12, 14, 22, 25, 27, 28, 29

1-1 SI Units

A review of things from week 1 freshman chem.

1. I expect you to remember these units from freshman chem.
2. common multipliers M, k, d, c, m, μ , n

1-2 Conversion Between Units

Again, you learned how to do unit conversion back in General Chem, and I expect that you can do it now.

1-3 Chemical Concentrations

We will be making up and using lots of solutions in this class, let's start by a with a gentle reminder of some terminology.

Solvent - the liquid that makes up the bulk of the solution

Solute - the minor species that is dissolved in the solvent

Concentration - refers to how much solute is contained in the solvent

There are lot's of ways of expressing concentration. The one we use most often in chemistry is:

Molarity(M)- # of moles of substance in a liter *of solution*. (You know this already)

Used in chemistry because if you know a volume you can calculate the moles of solute in that volume. Takes time to make up because you have to use a volumetric flask.

Formality(F) - Sometimes we use the term Formality instead of molarity Why?

We use Formality to take into account the fact that when electrolytes dissolve ionize, and the ions are not necessarily that same as the compound. Thus Formality is based on the Formula weight, and that is the sum of the atomic weights of the molecules in the solution.

Let's make a 1M solution of NaCl. Are there any NaCl molecules in solution? NO. We have 1M Na^+ , and 1M Cl^- , but no NaCl. Technically we have 0M NaCl. Thus we use formality to take into account the fact that once the solute is in solution its ionization state might change to something new or different than we started with.

This is also useful in solution of weak acids and weak bases. Remember the definition of a weak acid? Say we have a solution containing HF ($K_a = 6.8 \times 10^{-4}$, $\text{HF} \rightleftharpoons \text{H}^+ + \text{F}^-$) By definition, a weak acid is only partially ionized, so even if you started making this solution by putting 1 mole of HF in 1 l of

water, when the ionization is complete you now have <1M HF and some low concentration of F⁻.

Since few people take the time to calculate the true molar concentration of all the ions in this solution, the far easier way is to simply refer to the total concentration as 1F HF and ignore the molar concentration of the ions.

Molality (m)- Moles of substance in a kilogram *of solvent*. Not used too often in analytical chemistry, more often in physical chemistry.

Percent composition - Used frequently in practical labs because it is easy to make up, simply weigh out substances and mix together. Can't be used as easily for quantitative analysis

There are two kinds of % compositions

Weight % = mass of solute/total mass of solution X 100

And

Volume % = Volume of solute/total volume of solution X 100

Along these line are

parts per million(ppm)

= (mass of substance/mass of sample) x 10⁶

= grams solute/million grams of solution

= mg of solute /liter of solution

= μg of solute/gram (mL) of solution

And

parts per billion(ppb)

= (mass of substance/mass of sample) x 10⁹

= grams of solute/billion grams of solution

= mg solute/ liter of solution

= ng of solute/gram(mL) of solution

Example:

Lets say you have .25 mg of lead in 1L of drinking water, what is that in ppm or ppb

ppm

$$\begin{aligned} .25 \text{ mg}/1\text{L} \times 1\text{L}/1000\text{g} \times .001\text{g}/\text{mg} &= 2.5 \times 10^{-7} \\ &= 2.5 \times 10^{-7} \times 10^6 = 2.5 \times 10^{-1} \text{ .25 ppm} \\ &= 2.5 \times 10^{-7} \times 10^9 = 2.5 \times 10^2 = 250 \text{ ppb} \end{aligned}$$

1-4 Preparing Solutions

You prepare a solution of a given molarity we weigh out the correct mass of a substance and dissolve it in the desired volume. Often we make a solution that is more concentrated than we need, and we then need to dilute it. The dilution formula is very simple

$$\text{Dilution formula : } M_{\text{conc}} \cdot V_{\text{conc}} = M_{\text{dil}} \cdot V_{\text{dil}}$$

A simple example. We have Stock HCL that is 12.1 M and we want to make 1 L of 1.00 M HCl, How much concentrated HCl do we need?

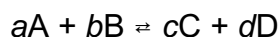
$$12.1(X) = 1000(1.000)$$

$$X = 1000/12.1$$

$$X = 82.6 \text{ mls}$$

1-5 The Equilibrium Constant

In General Chemistry you learned that if you have the reaction



You can write the equilibrium expression:

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

Remember when K represents Product/reactants so $K > 1$ means the products are favored, so the reaction goes to the right (reaction favorable), when $K < 1$ the reactants are favored, so the reaction goes to the left (is NOT favored)

Where K is a constant, a, b, c, d are the stoichiometric coefficients and $[A], [B], [C],$ and $[D]$ are the molar concentrations of the reagents. This is actually a little bit wrong.

In this class we will be a little more picky about our definition. In Chapter 11, for instance, you will learn that true equilibrium expression actually uses activities a , and NOT molar concentrations. Thus the true equilibrium expression should be:

$$K = \frac{a^c a^d}{a^a a^b}$$

In chapter 12 we will learn more about the exact meaning of activity, but for now what you need to know is that to calculate activity, you take the molar concentration, and divide it by the molar concentration of the standard state (and a little bit more - see chapter 8). (See [Handbook of Chemistry and Physics for exact definition of activity and equilibrium constant, since few texts do this well](#)).

What is the 'standard state'? Well for all solutes dissolved in a solvent the standard state is 1M.

So to make a better equilibrium expression we actually should be thinking:

$$K = \frac{\left(\frac{[C]}{[1]}\right)^c \left(\frac{[D]}{[1]}\right)^d}{\left(\frac{[A]}{[1]}\right)^a \left(\frac{[B]}{[1]}\right)^b}$$

So we have divided all of our concentrations by 1, BIG WOW. You can see why when we weren't too picky we could simply plug in the regular molar concentration. Does anybody see the other implication of this factor? This makes $[X]/[1]$ is unitless, so K is unitless as well. So in Gen Chem our K often had some funny units, but when we do it properly it has no units at all and is just a pure number!!

Just to complete this little exposition, let's look at other standard states:

For dissolved solutes the standard state is 1M concentration (as above)

For liquids or solids it is 1

For gasses it is the gas at 1 bar of pressure, and

1 bar is defined at 10^5 Pa \sim .987 atm

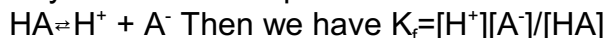
What are the take home lessons

1. The concentrations of solutes should be expressed in Molarity
2. The concentrations of gases should be expressed in atmospheres
3. The concentration of any pure solids or liquids may be omitted because the ratios for these numbers is 1
4. Since our solvent is almost a pure liquid, it may be omitted like that of other pure liquids.

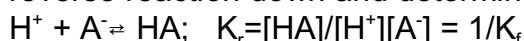
Manipulating Equilibrium Constants

(1) K for reverse reaction

Say we have the equilibrium

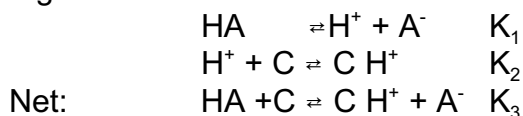


If we want the K of the reverse reaction, we simply take the reciprocal of the K. This is immediately obvious if you write the reverse reaction down and determine it's K



(2) K for multiple reactions

If you have two reactions with separate K's and you want to combine them into a single reaction, simply multiply the K's together

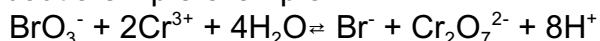


$$K_3 = \frac{[\text{HA}][\text{C}]}{[\text{CH}^+][\text{A}^-]} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \times \frac{[\text{CH}^+]}{[\text{H}^+][\text{C}]} = K_1 K_2$$

Le Châtelier's Principle

Who remember what Le Chat's's principle is? (If a system is disturbed from equilibrium the system will react in a way to try to restore the equilibrium)

How about a simple example:



$$K = \frac{[\text{Br}^-][\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^8}{([\text{BrO}_3^-][\text{Cr}^{3+}]^2)} = 1 \times 10^{11}$$

Looks like a complicated system. Say we are at equilibrium with $[\text{BrO}_3^-] = .043\text{M}$, $[\text{Cr}^{3+}] = .003\text{M}$, $[\text{Br}^-] = 1.0\text{M}$, $[\text{Cr}_2\text{O}_7^{2-}] = 0.1\text{M}$, and $[\text{H}^+] = 5.0\text{M}$

and we throw in enough dichromate to raise the concentration to 0.2 M , what happens to the system, will the reaction go in the forward or backward direction?

Well the way we disturbed the equilb is by adding a reactant. the way we return to equilb is to lower the concentration of the reactant, and the way we do this is by having the reaction go forward.

The reaction quotient

One handy calculation you should remember is the **Reaction Quotient(Q)**.

You should remember that is an equation that look like the equilibrium expression, expect that you plug in your initial concentration. If the resulting $Q > K$ the reaction - Too many products, **move toward reactants** moves **toward left**, if the resulting $Q < K$ - not enough products, the reaction **moves products. Moves to right**. For the above reaction **not** at equilibrium this look like

$$\begin{aligned} Q &= \frac{[\text{Br}^-][\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^8}{[\text{BrO}_3^-][\text{Cr}^{3+}]^2} \\ &= (1)(.2)(5)^8 / (.043)(.003)^2 \\ &= 2 \times 10^{11} > K \end{aligned}$$