

Chemistry Revisions

Inter- and Intramolecular Forces

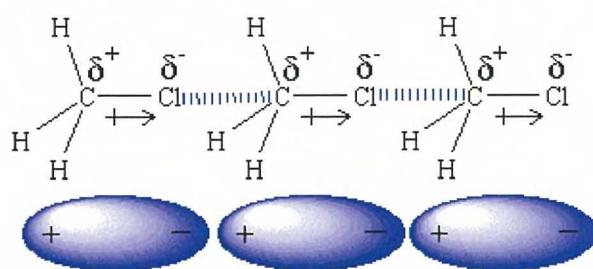
Intermolecular Attraction/Repulsion

The way in which molecules interact will dictate the physical characteristics of a compound (Solid/Liquid/Gas). When two molecules are brought into close proximity, they either attract or repel each other. In general, for simple gases, the forces are attractive until the gas molecules approach so close that they infringe upon each others' atomic radius. When this occurs, the relatively weak attractive forces instantly become large repulsive forces and the two gas molecules are rapidly repelled.

In contrast to gases, the situation for multi-atomic organic compounds is complex and there are many parameters to consider (dipole moments, functional groups). However, three main types of attractive forces play a major role in dictating the physical characteristics of a compound and thus in part its chemical reactivity.

Dipole-Dipole Forces

Most molecules have permanent dipole moments as a result of their polar bonds. These inherently polar molecules will therefore orient themselves in the most stable arrangement (+ve:-ve:+ve:-ve) so as to minimise charge repulsions. The above arrangement results in a net attractive force and thus this strong attractive force must be overcome in order to melt/vapourise/dissolve the polar compound.



Hydrogen Bonding

A hydrogen bond is not a covalent bond but a particularly strong transient dipole-dipole interaction. A hydrogen atom can participate in hydrogen bonding if it is linked covalently to an electronegative atom such as oxygen, nitrogen or fluorine. Hydrogen bonding is a strong intermolecular interaction, requiring ~5kcal mol⁻¹ to break (c.f. ~100kcal mol⁻¹ required to break a C-H or N-H covalent bond). Hydrogen bonding is replete in nature (i.e. DNA base pairing) and has a large effect upon the physical properties of organic compounds.

http://users.ox.ac.uk/~mwalter/web_05/year1/structure_bonding/forces.htm

Bonding : Intramolecular Forces of Attraction

1902-1916 - G.N. Lewis

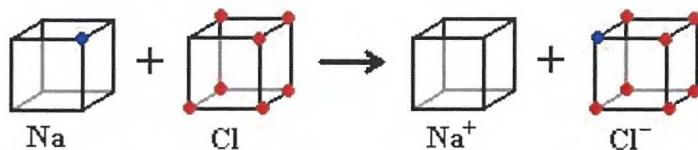
Described atoms with a cube model, explaining that the electron in an atom were arranged in positions at the corners of a cube. This model was based upon the following assumptions:



1. The number of electrons in an atom's outermost cube is equal to the number of electrons lost when an atom forms a positive ion.
2. Each successive neutral atom on the periodic table (as the atomic number increases) has one more electron in its outermost cube.
3. To fill the corners of the cube, it takes eight electrons, or an **octet**.
4. When a cube has filled its octet, it becomes the center about which another cube can be built.

Lewis explained simple ionic compounds by assuming that atoms with less than four electrons in their outermost cube transferred those electrons to another atom which needed to gain that many electrons to fill its octet. Both atoms, then, would end up with an outer cube that was either completely filled or completely empty.

e.g. Na loses one electron to Cl to form Na^+ and Cl^- .



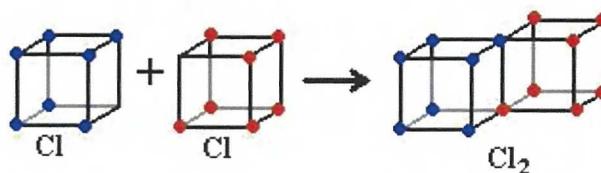
It was later understood why Lewis's "octet" theory was valid. It requires eight electrons to fill the s (1) and p (3) orbitals in one shell which are the outermost orbitals in a shell. The outermost shell of an atom came to be known as the **valence shell**, and the electrons which reside in the valence shell are now known as **valence electrons**.

- **Valence electrons** - The electrons on an atom that are not present in the previous atom with a filled-shell [electron configuration](#), ignoring filled d and f orbitals. (See [electron configuration notes](#))

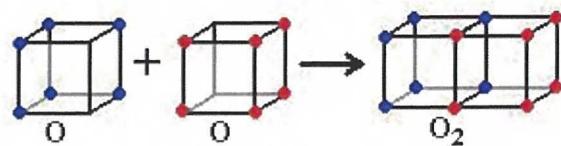
e.g. Bromine has the electron configuration: $[\text{Ar}] \ 4\text{s}^2 3\text{d}^{10} 4\text{p}^5$. If we add up the electrons in the s and p orbitals only, we find that bromine has 7 valence electrons.

Lewis later found that atoms could fill their outermost cubes by sharing one or more pairs of electrons.

e.g. One Cl atom can share one of its outermost electrons with another Cl atom to form the diatomic molecule Cl_2 .

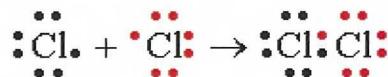


e.g. One O atom can share two of its outermost electrons with another O atom to form the diatomic molecule O_2 .

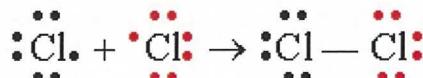


Since atoms always seemed to share pairs of electrons when they formed bonds, Lewis changed his cube model with the eight electrons in the corners to a model with pairs of electrons. These models are known as Lewis Structures (or Lewis Dot Structures). See notes on [Lewis Structures](#).

e.g. The bonding of two Cl atoms for form Cl_2 would now be written as:



These Lewis Structures models are still in use today. The only major difference between Lewis's system, and the system in use today is that the covalent bonds between the atoms today are represented by a line instead of two dots. Double bonds are represented by a double line and triple bonds are represented by triple lines.

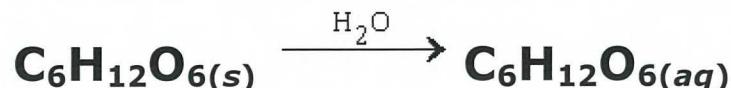


Intramolecular Forces of Attraction - The forces of attraction that exist between bonds **within** a molecule.

- **Ionic bond** - A bond between two ions which are formed from the **TRANSFER** or electrons from one (which forms a positive ion) to another (which forms a negative ion). The bond is held together by the force of attraction from the opposite charges of the ions formed.
 - Ionic compounds dissociate into their ions when they dissolve in water. This makes them **GOOD CONDUCTORS** of electricity in aqueous solution.



- **Covalent bond** - A bond between two atoms formed by the **SHARING** of electrons.
 - Covalent compounds cannot dissociate when they dissolve in water. This makes them **POOR CONDUCTORS** of electricity in aqueous solution.



Electronegativity and Polarity

- **Electronegativity** - The tendency of an atom to draw electrons in a bond toward itself.
- There are two periodic trends concerning electronegativity.
 1. **As you move down a group, electronegativity decreases.**

2. As you move across a period, electronegativity increases.

H 2.2 0																H e *	
Li 0.9 8	Be 1.5 7									B 2.0 4	C 2.5 5	N 3.0 4	O 3.4 4	F 3.9 8	N e *		
N a 0.9 3	M a g 1.3 1									Al 1.6 1	Si 1.9 0	P 2.1 9	S 2.5 8	Cl 3.1 6	Ar *		
K 0.8 2	C a 1.0 0	Sc 1.3 6	Ti 1.5 4	V 1.6 3	Cr 1.6 6	M n 1.5 5	Fe 1.8 3	Co 1.8 8	Ni 1.9 1	C u 1.9 0	Z n 1.6 5	G a 1.8 1	G e 2.0 1	As 2.1 8	S e 2.5 5	Br 2.9 6	Kr *
R b 0.8 2	Sr 1.9 5	Y 1.2 2	Zr 1.3 3	Nb 1.6	Mo 2.1 6	Tc 1.9	Ru 2.2	Rh 2.2 8	Pd 2.2 0	A g 1.9 3	C d 1.6 9	In 1.7 8	S n 1.9 6	S b 2.0 5	Te 2.1	I 2.6 6	Xe *
Cs 0.7 9	B a 0.8 9	La 1.1	Hf 1.3	Ta 1.3	W 2.3 6	Re 1.9	Os 2.2	Ir 2.2 0	Pt 2.2 8	A u 2.5 4	H g 2.0 0	Tl 2.0 4	Pb 2.3 3	Bi 2.0 2	Po 2.0	At 2.2	Rn *
Fr 0.7	R a 0.9	Ac 1.1	Un q	Un p	Un h	Un s	Un o	Un e									

Bonds can be classified according to the difference in electronegativities of the atoms (ΔEN).
 Bonds are:

- **ionic if $\Delta EN > 1.8$.**
- **polar covalent if $1.8 \geq \Delta EN \geq 0.4$**
- **nonpolar covalent if $\Delta EN < 0.4$**

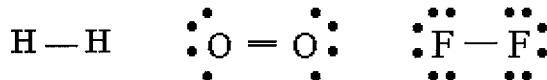
The larger the difference in the electronegativities of the atoms in a bond, the stronger the strength of the bond. As the bond becomes stronger, melting and boiling points generally increase as well.

When comparing bonds with the same atoms but with different oxidation states, we have to consider another factor besides the difference in the electronegativities of the atoms since this will be the same if the atoms are the same. As the oxidation number on an atom increase, its ability to draw electrons in a bond toward itself increases as well. For example, the electronegativity of an Mn atom in Mn_2O_7 (oxidation number of +7) is much greater than the electronegativity of an Mn atom in MnO (oxidation number of +2).

Polar Versus Nonpolar Bonds

Nonpolar covalent - Covalent bond in which the electrons are shared equally.

e.g. The diatomic elements (BrINClHOF) are all examples of nonpolar covalent bonds.



Two general relationships between single, double and triple bonds

1. **BOND STRENGTH** increases from single to double to triple

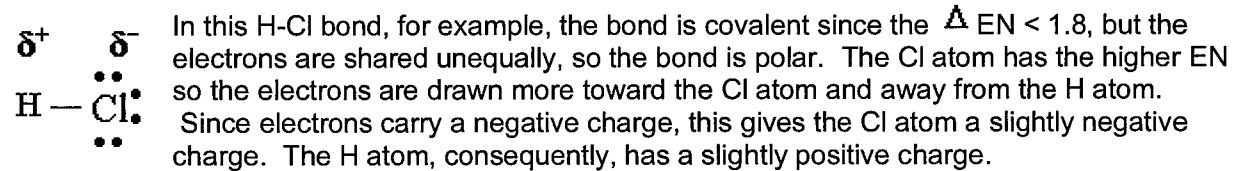
SINGLE < DOUBLE < TRIPLE

2. **BOND LENGTH** decreases from single to double to triple

SINGLE > DOUBLE > TRIPLE

Polar covalent - Covalent bond in which the electrons are NOT shared equally. The charged ends are called **dipoles** and are represented by the symbol δ .

- The end of the bond with the larger electronegativity is the slightly charged negative end.
- The end of the bond with the smaller electronegativity is the slightly charged positive end.

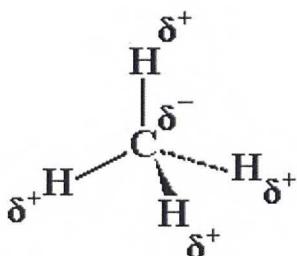


Polar Versus Nonpolar Molecules

Molecules that contain polar covalent bonds may or may not be polar molecules. The polarity of a molecule is determined by measuring the **dipole moment** which is represented by the symbol μ . This depends on two factors:

1. The degree of the overall separation of charge between the atoms in the bond
2. The distance between the positive and negative poles

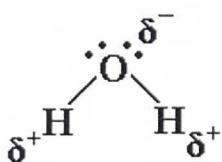
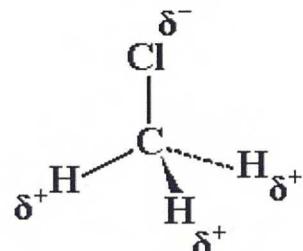
If there are equal polar bonds that balance each other around the central atom, then the overall molecule will be **NONPOLAR** with no dipole moment, even though the bonds within the molecule may be polar.



In this molecule, CH₄, the C atom has a higher EN than the surrounding H atoms. This makes the individual C-H bonds polar with a slightly negative charge on the C atom and a slightly positive charge on the H atoms. However, the polarities on these bonds balance each other out around the central C atom. The overall dipole moment of the molecule is therefore 0 and the molecule is nonpolar.

If there are unequal polar bonds around the central atom, then the overall molecule will be POLAR with an a dipole moment.

In the this molecule, CH₃Cl, all of the bonds around the central C atom are not equal. The the Cl atom has a higher EN than the central C atom, so the electrons are more drawn toward the Cl atom. The H atoms have a lower EN than the central C atom and cannot balance out the large EN of the Cl atom. Therefore, the overall molecule has a dipole moment with a slightly negative charge on the Cl end and a slightly positive charge on the H ends, making the molecule polar.



In this molecule, H₂O, the two O-H bonds are polar but are equal to each other. However, the central O atom has a higher EN than the H atoms so the electrons are drawn toward the O atom. The O atom also has two pairs of nonbonding electrons, and combined the nonbonding electrons and the electrons drawn toward the O from the O-H bonds result in an overall dipole moment. Therefore, this molecule is polar.

<http://library.thinkquest.org/C006669/data/Chem/bonding/intra.html>

Lewis Dot Structure - A symbolic description of the distribution of valence electrons in a molecule. Dots are used to represent individual electrons and lines are used to represent covalent bonds.

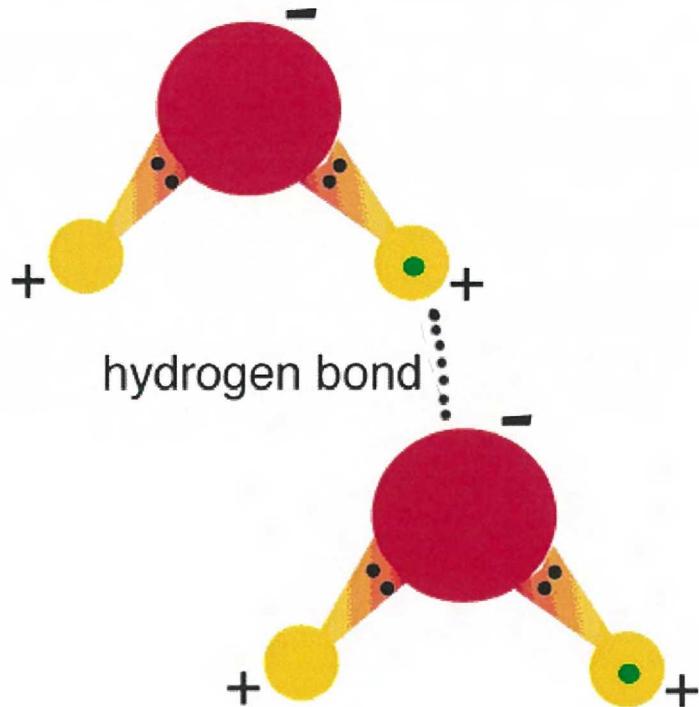
Drawing Lewis Dot Structures

1. Add up the total number of valence electrons in the molecule by totalling the valence electrons on each atom in the molecule or polyatomic ion.
 - o If you are drawing a Lewis Structure for a polyatomic ion:
 1. **Negative Ion:** Add the number of electrons equal to the negative charge on the ion.
 2. **Positive Ion:** Subtract the number of electrons equal to the positive charge on the ion.
2. Draw the skeleton structure of the molecule or polyatomic ion in which the covalent bonds between the atoms are drawn as single lines. Each bond equals two valence electrons. If the molecule has more than two atoms, the atom with the lowest electronegativity is generally the central atom and is written in the middle.
3. Distribute valence electrons around the outer atoms as nonbonding electrons to until each atom has a complete outer shell (i.e. 8 electrons except for H which has only 2 valence electrons).
4. Add the remaining valence electrons to the central atom.

- **BONDING ELECTRONS + NONBONDING ELECTRONS = TOTAL VALENCE ELECTRONS**
5. Check the central atom.
- If the central atom has eight electrons surrounding it, the Lewis Structure is complete.
 - If the central atom has less than eight electrons, remove a nonbonding electron pair from one of the outer atoms and form a double bond between that atom and the central atom. If needed, continue to remove nonbonding electron pairs from the outer atoms until the central atom has a complete octet.
 - If the central atom has more than eight electrons, then this means that the central atom has expanded its valence shell to hold more than eight electrons. This is allowed for atoms with valence shells in the third energy level or higher (i.e. in or beyond the third period of the periodic table).

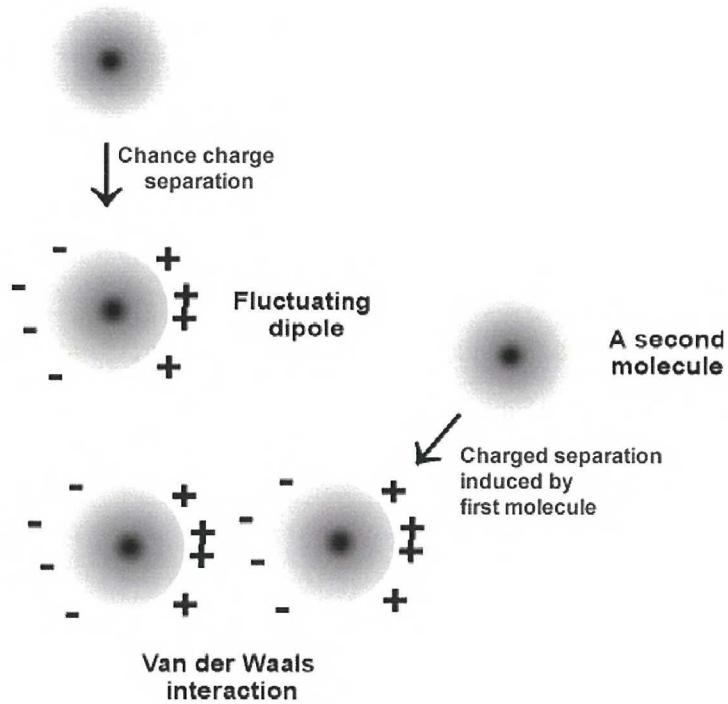
<http://library.thinkquest.org/C006669/data/Chem/bonding/intra.html>

- **Intermolecular Bond**



1) Hydrogen bond

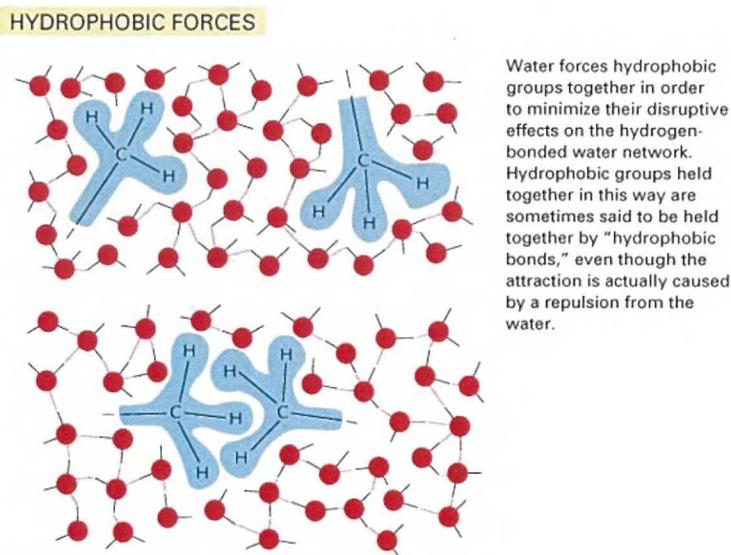
- electrostatic attraction between an electronegative atom (O / N) atom that is covalently bonded to 2nd electronegative atom
- + a hydrogen
- increase electronegativity of atom bonded to hydrogen = increase bond strength
- can be either intermolecular o intramolecular



2) Van der Waals

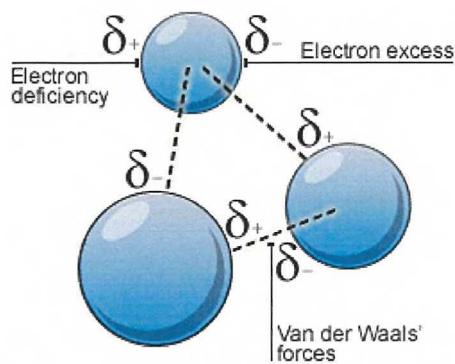
-short-range forces / between molecules or parts of molecules / where atoms attract when they are at certain distance / and repel when the atoms approach (tendency to maintain distance)

-more significant when (increase pressure / decrease temperature)

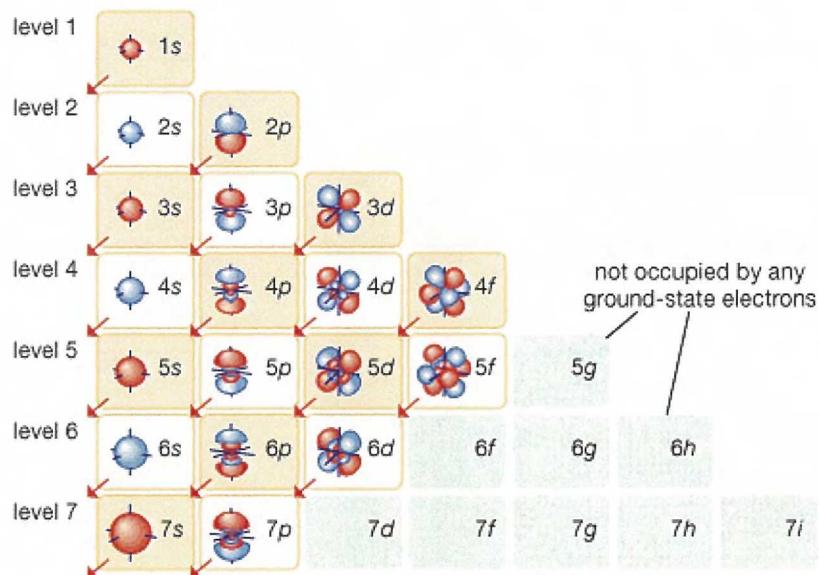


3) Hydrophobic Attraction / Interaction (Molecule – Ion Interaction)

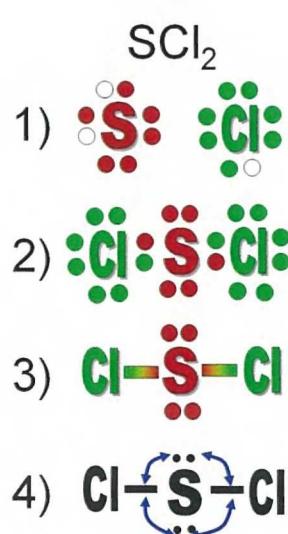
-Interaction / between non-polar side chain molecule / and other non-polar side chain molecule / which tend to aggregate minimizing surface area exposed to water (to avoid water molecules) / allowing these molecules to associate with each other in aqueous environment



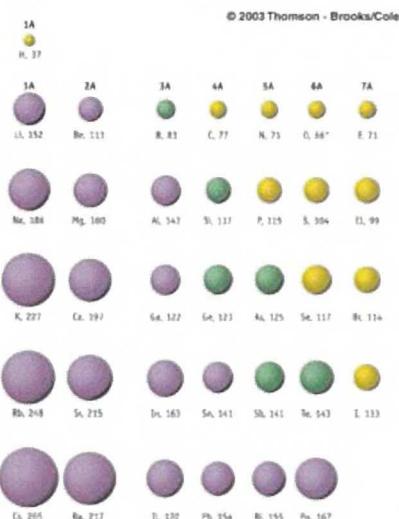
http://www.bbc.co.uk/scotland/learning/bitesize/higher/chemistry/energy/bsp_rev3.shtml



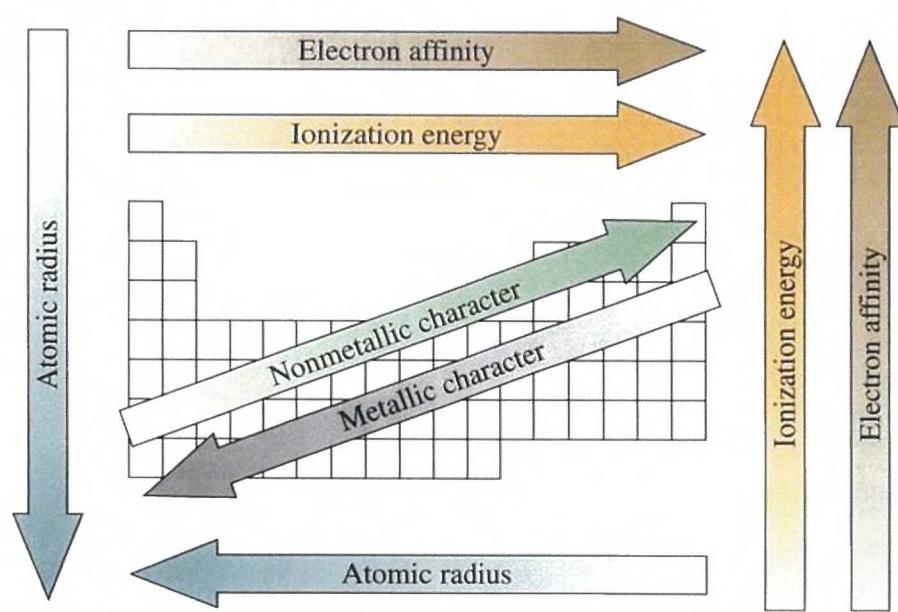
<http://www.infolizer.com/?title=Electron+shell>



<http://www.chemistryland.com/CHM151W/08-Bonds/VSEPR/VSEPR.html>



http://sphs.spusd.net/apps/classes/show_assignment.jsp?classREC_ID=261506&start=0&pff=1&showAll=true&show=1000



<http://www.ireference.ca/search/Periodic%20trends/>

Acid-Base Titrations

The Titration Experiment

Titration is a general class of experiment where a known property of one solution is used to infer an unknown property of another solution. In acid-base chemistry, we often use titration to determine the pH of a certain solution.

A setup for the titration of an acid with a base is shown in :

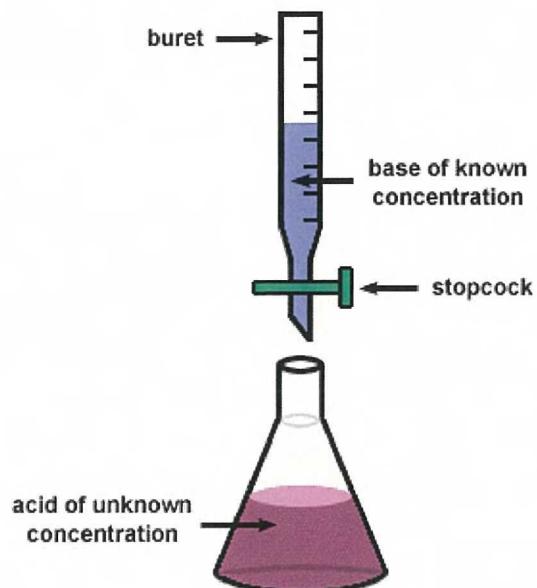


Figure %: A titration setup

We use this instrumentation to calculate the amount of unknown acid in the receiving flask by measuring the amount of base, or titrant, it takes to neutralize the acid. There are two major ways to know when the solution has been neutralized. The first uses a pH meter in the receiving flask adding base slowly until the pH reads exactly 7. The second method uses an indicator. An indicator is an acid or base whose conjugate acid or conjugate base has a color different from that of the original compound. The color changes when the solution contains a 1:1 mixture of the differently colored forms of the indicator. As you know from the [Henderson-Hasselbalch equation](#), the pH equals the pK_a of the indicator at the endpoint of the indicator. Since we know the pH of the solution and the volume of titrant added, we can then deduce how much base was needed to neutralize the unknown sample.

Titration Curves

A titration curve is drawn by plotting data attained during a titration, titrant volume on the x-axis and pH on the y-axis. The titration curve serves to profile the unknown solution. In the shape of the curve lies much chemistry and an interesting summary of what we have learned so far about acids and bases.

The titration of a strong acid with a strong base produces the following titration curve:

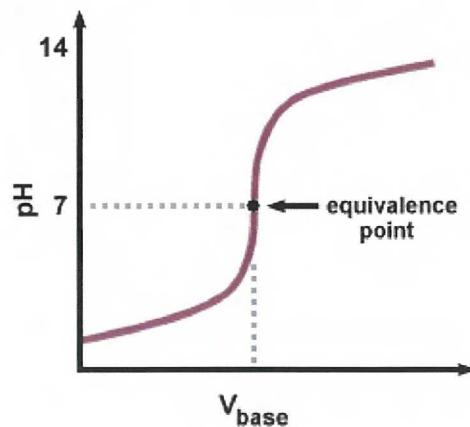


Figure %: Titration curve of a strong base titrating a strong acid

Note the sharp transition region near the equivalence point on the . Also remember that the equivalence point for a strong acid-strong base titration curve is exactly 7 because the salt produced does not undergo any hydrolysis reactions.

However, if a strong base is used to titrate a weak acid, the pH at the equivalence point will not be 7. There is a lag in reaching the equivalence point, as some of the weak acid is converted to its conjugate base. You should recognize the pair of a weak acid and its conjugate base as a buffer. In , we see the resultant lag that precedes the equivalence point, called the buffering region. In the buffering region, it takes a large amount of NaOH to produce a small change in the pH of the receiving solution.

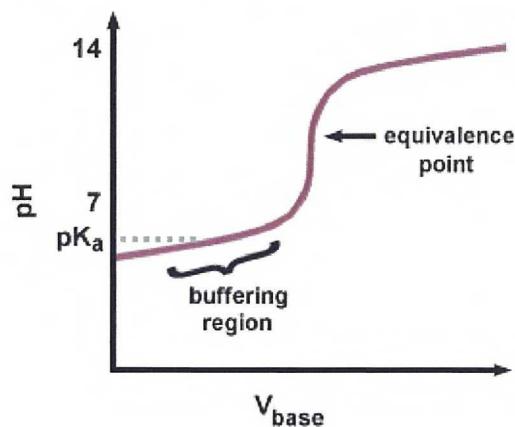


Figure %: Titration curve of a strong base titrating a weak acid

Because the conjugate base is basic, the pH will be greater than 7 at the equivalence point. You will need to calculate the pH using the Henderson-Hasselbalch equation, and inputting the pK_b and concentration of the conjugate base of the weak acid.

The titration of a base with an acid produces a flipped-over version of the titration curve of an acid with a base. pH is decreased upon addition of the acid.

Note that the pH of a solution at the equivalence point has nothing to do with the volume of titrant necessary to reach the equivalence point; it is a property inherent to the composition of the solution. The pH at the equivalence point is calculated in the same manner used to calculate the pH of weak base solutions in Calculating pH's.

When polyprotic acids are titrated with strong bases, there are multiple equivalence points. The titration curve of a polyprotic acid shows an equivalence point for each protonation:

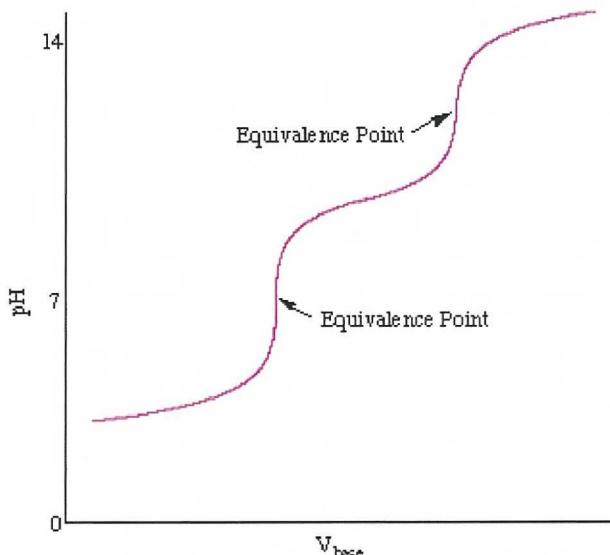


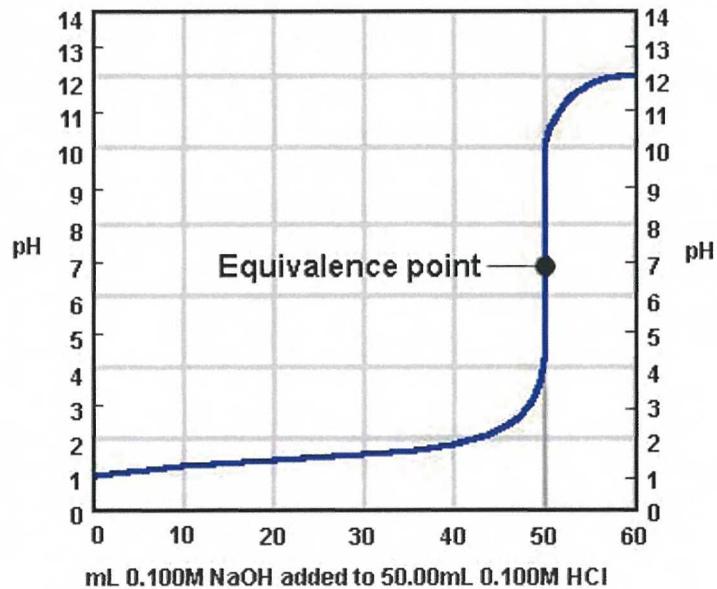
Figure %: Titration curve of a strong base titrating a polyprotic acid

The titration curve shown above is for a diprotic acid such as H_2SO_4 and is not unlike two stacked . For a diprotic acid, there are two buffering regions and two equivalence points. This proves the earlier assertion that polyprotic acids lose their protons in a stepwise manner.

<http://www.sparknotes.com/chemistry/acidsbases/titrations/section1.html>

Strong Acid-Strong Base Titrations

Here is an example of a titration curve, produced when a strong base is added to a strong acid. This curve shows how pH varies as 0.100 M NaOH is added to 50.0 mL of 0.100 M HCl.



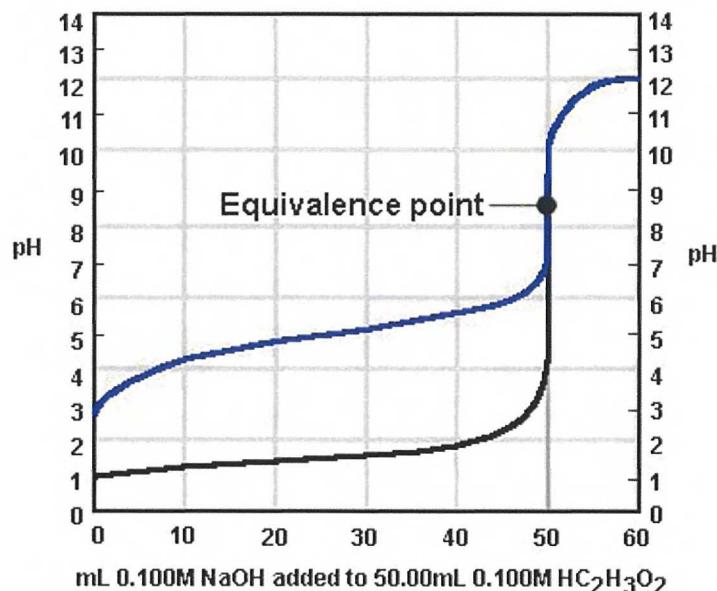
The **equivalence point** of the titration is the point at which exactly enough titrant has been added to react with all of the substance being titrated with no titrant left over. In other words, at the equivalence point, the number of moles of titrant added so far corresponds exactly to the number of moles of substance being titrated according to the reaction stoichiometry. (In an acid-base titration, there is a 1:1 acid:base stoichiometry, so the equivalence point is the

point where the moles of titrant added equals the moles of substance initially in the solution being titrated.)

Notice that the pH increases slowly at first, then rapidly as it nears the equivalence point.
Why?

Titrations Involving a Weak Acid or Weak Base

Titration curve of a weak acid being titrated by a strong base:



Here, 0.100 M NaOH is being added to 50.0 mL of 0.100 M acetic acid.

There are three major differences between this curve (in blue) and the one we saw before (in black):

1. The weak-acid solution has a higher initial pH.
2. The pH rises more rapidly at the start, but less rapidly near the equivalence point.
3. The pH at the equivalence point does not equal 7.00.

POINT OF EMPHASIS : The equivalence point for a weak acid-strong base titration has a pH > 7.00.

For a strong acid-weak base or weak acid-strong base titration, the pH will change rapidly at the very beginning and then have a gradual slope until near the equivalence point. The gradual slope results from a buffer solution being produced by the addition of the strong acid or base, which resists rapid change in pH until the added acid or base exceeds the buffer's capacity and the rapid pH change occurs near the equivalence point.

<http://www.chem.ubc.ca/courseware/pH/section14/index.html>

Problem :

List the major species at points A, B, C, and D on the following titration curve of the titration of ammonia with HCl.

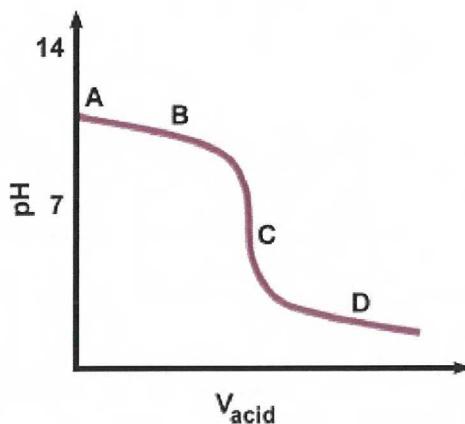


Figure %: Titration of ammonia with hydrochloric acid

Solution for Problem 1 >>

Problem :

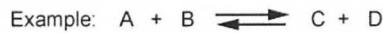
Why is it acceptable to use an indicator whose pK_a is not exactly the pH at the equivalence point?

<http://www.sparknotes.com/chemistry/acidsbases/titrations/problems.html>

LeChatelier's Principle: If a system at equilibrium is disturbed, it will respond by reacting in the direction that offsets the disturbance.

Disturbance

Effect: System shifts left or right, or not at all



$$A + B \rightleftharpoons C + D \quad K = \frac{[C][D]}{[A][B]}$$

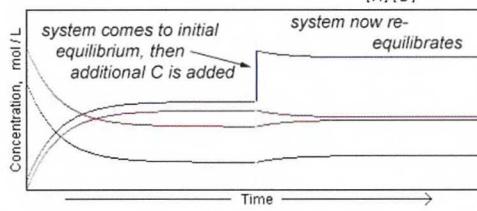
Concentration:

More reactant added

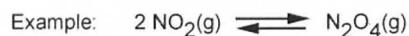
Reactant removed

Product added

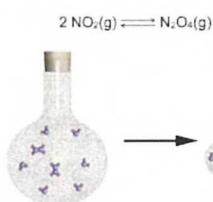
Product added



Volume: (only matters for gas-phase reactions)



Volume is decreased

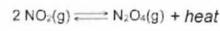


Volume is increased

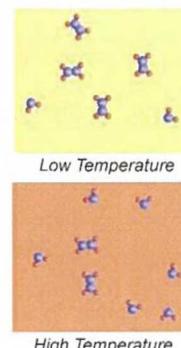
Temperature (in this case only, the value of K changes)

Exothermic Example: reactants \rightleftharpoons products + heat

Temperature is increased



Temperature is decreased

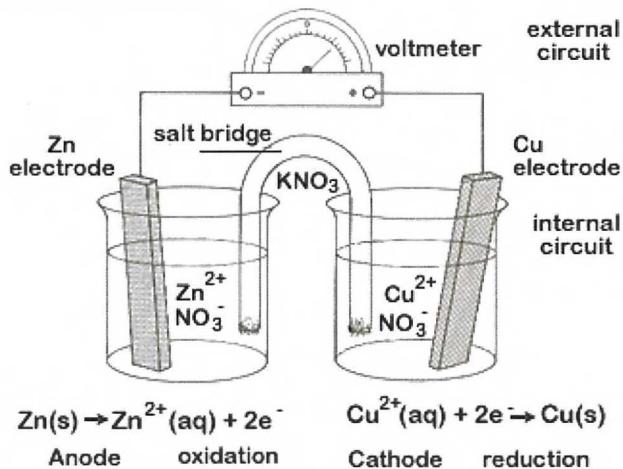


Endothermic Example: reactants + heat \rightleftharpoons products

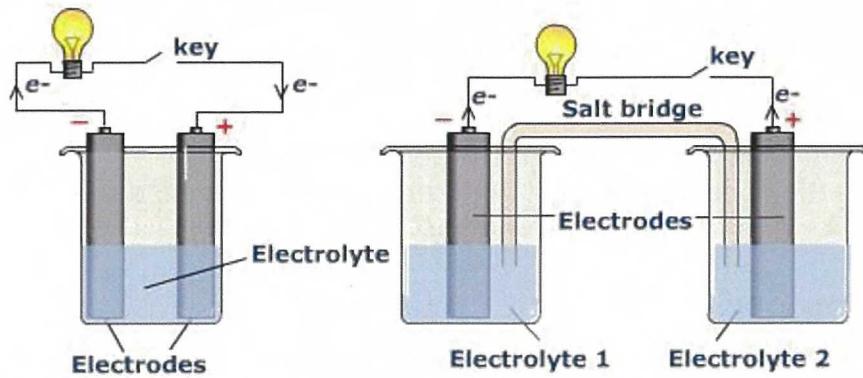
Temperature is increased

Temperature is decreased

<http://employees.oneonta.edu/viningwj/Chem112/index.html>



http://www.saskschools.ca/curr_content/chem30_05/6_redox/redox2_2.htm



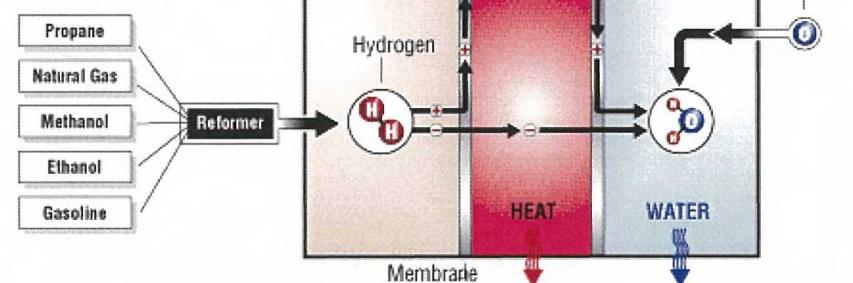
(a) Using one electrolyte

(b) Using two electrolytes

<http://www.tutorvista.com/topic/zinc-copper-galvanic-cell>

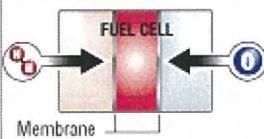
How fuel cells work

Fuel cells can use one of several approaches to generate electricity. An increasingly popular method, particularly for applications such as cars, is the proton-exchange membrane. Here's how it works:



1 Hydrogen is extracted from methanol, ethanol, propane, gasoline or natural gas in a unit called a reformer, then filtered to remove carbon dioxide, which can damage the fuel cell itself.

2 Inside the fuel cell are two plates, separated by a platinum-coated polymer (membrane). Hydrogen flows in one side, oxygen the other.



- 3** Hydrogen atoms give up electrons, producing current.
- 4** Hydrogen protons flow through the membrane, recombining with the electrons and oxygen to produce water and give off waste heat.

MACAULAY CAMPBELL / P-I

<http://www.seattlepi.com/business/fuel03.shtml>

How does a mixture of a weak acid and its conjugate base help buffer a solution against pH changes?

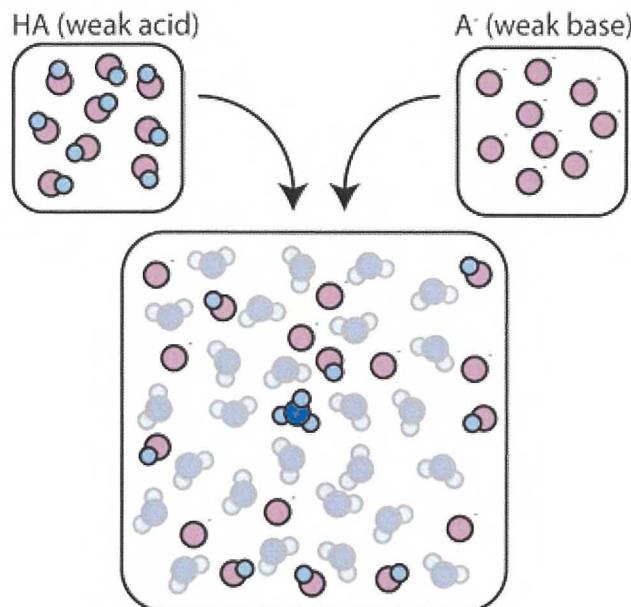
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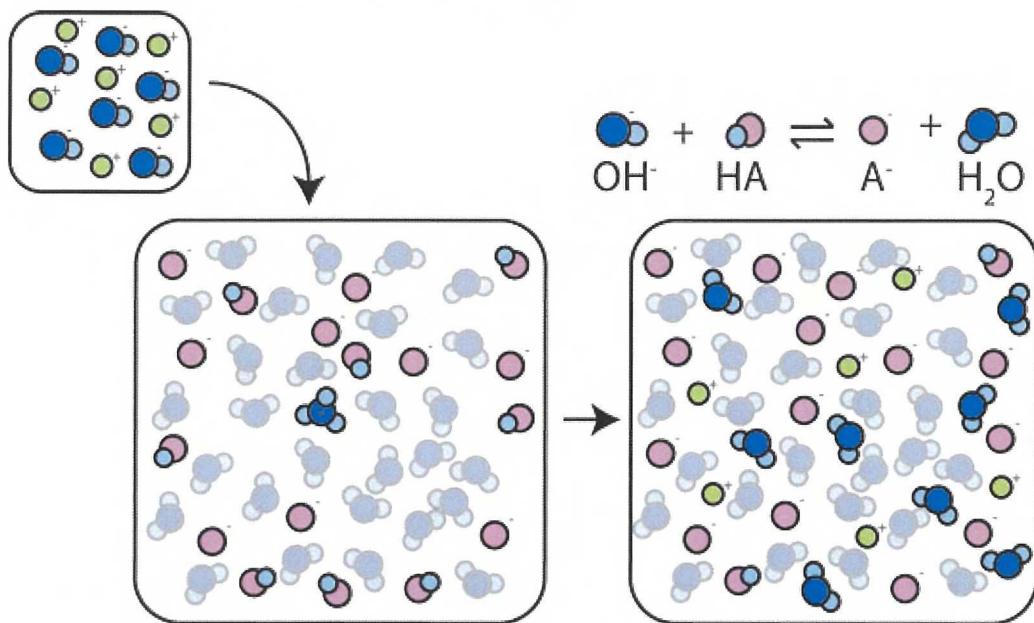
If we mix a weak acid (HA) with its conjugate base (A⁻), both the acid and base components remain present in the solution. This is because they do not undergo any reactions that significantly alter their concentrations. The acid and conjugate base may react with one another, $\text{HA} + \text{A}^- \rightarrow \text{A}^- + \text{HA}$, but when they do so, they simply trade places and the concentrations [HA] and [A⁻] do not change. In addition, HA and A⁻ only rarely react with water. By definition, a weak acid is one that only rarely dissociates in

water (that is, only rarely will the acid lose its proton H⁺ to water). Likewise, since the conjugate base A⁻ is a weak base, it rarely steals a proton H⁺ from water.

So, the weak acid and weak base remain in the solution with high concentrations since they only rarely react with the water. However, they are very likely to react with any added strong base or strong acid.

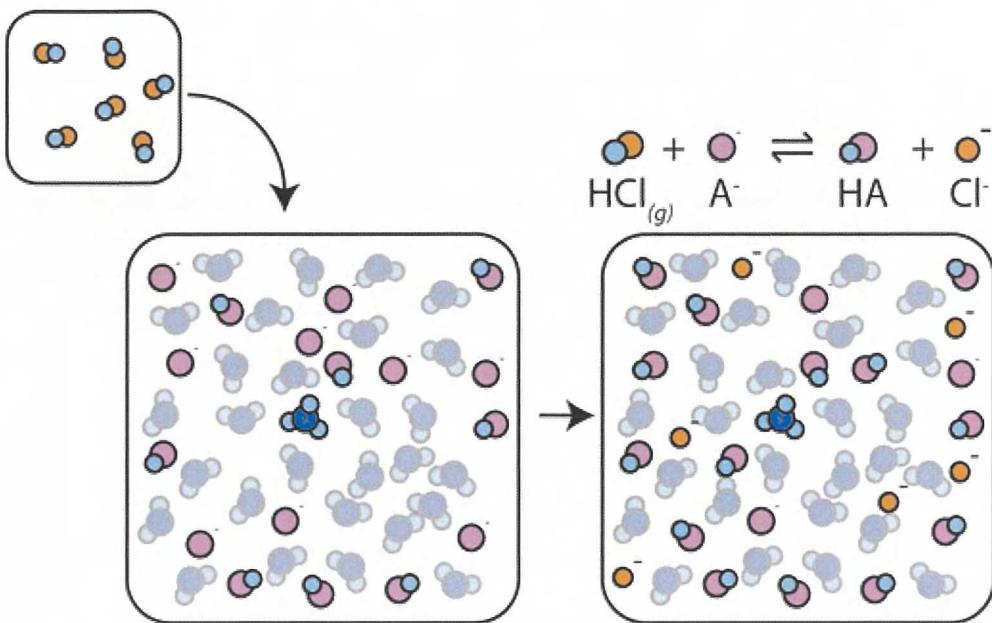


If a strong base is added to a buffer, the weak acid will give up its H⁺ in order to transform the base (OH⁻) into water (H₂O) and the conjugate base: HA + OH⁻ → A⁻ + H₂O. Since the added OH⁻ is consumed by this reaction, the pH will change only slightly.



If a strong acid is added to a buffer, the weak base will react with the H⁺ from the strong acid to form the weak acid HA: H⁺ + A⁻ → HA. The H⁺ gets

absorbed by the A^- instead of reacting with water to form H_3O^+ (H^+), so the pH changes only slightly.



See the next page for a tutor that leads you through the calculations involved in making a buffer.

<http://www.chemcollective.org/buffers/buffers3.php>

The organization of Matter - Atoms

- All matter is composed of atoms
- All atoms have a central nucleus surrounded by electrons
 - Nucleus comprised on protons (+) and neutrons (0)
 - Electrons zip around nucleus and are negative (-)
- The nucleus
 - The **Atomic Number** is the number of protons in the nucleus
 - Changes in the number of protons changes the element
 - Changes in the number of neutrons does not change the element - it creates an **isotope**
 - Example: C¹² and C¹⁴ - C¹² has 6 protons and 6 neutrons, C¹⁴ has 6 protons and 8 neutrons. Both of these carbon atoms will have the same chemistry. The only difference is that C¹² is stable while C¹⁴ is radioactive.
- Electrons
 - Electrons have virtually no mass (compared to protons and neutrons)
 - They float around the atom in distinct shell-like arrangements called **orbitals**
 - The first electron "shell" contains 2 electrons
 - The second electron "shell" contains 8 electrons
 - The third electron "shell" contains 8 electrons
 - There are many more electron shells, but we will not be addressing them
 - These shells are illustrated in the below graphic of the periodic table. Notice how the first row contains two elements, Hydrogen and Helium, corresponding to the two electrons in each shell. The next row contains eight electrons, corresponding to the eight electrons in the next electron shell.

Periodic Table of the Elements

1 H	IIA												0 He				
3 Li	4 Be											2 Ne					
11 Na	12 Mg	III B	IY B	V B	VIB	VII B	VII			IB	IB	III A	IYA	VA	VIA	VIIA	
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	+Ac	104 Rf	105 Ha	106 106	107 107	108 108	109 109	110 110	111 111	112 112						

Naming conventions of new elements

* Lanthanide Series

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
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+ Actinide Series

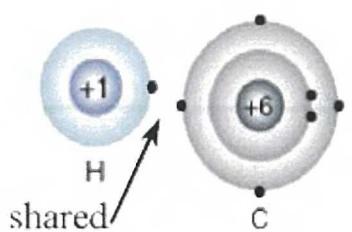
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr
-------	-------	------	-------	-------	-------	-------	-------	-------	-------	--------	--------	--------	--------

- In a typical atom, the **number of protons = number of electrons**. When this is not so, it creates an ion

The organization of Matter - Chemical Bonds

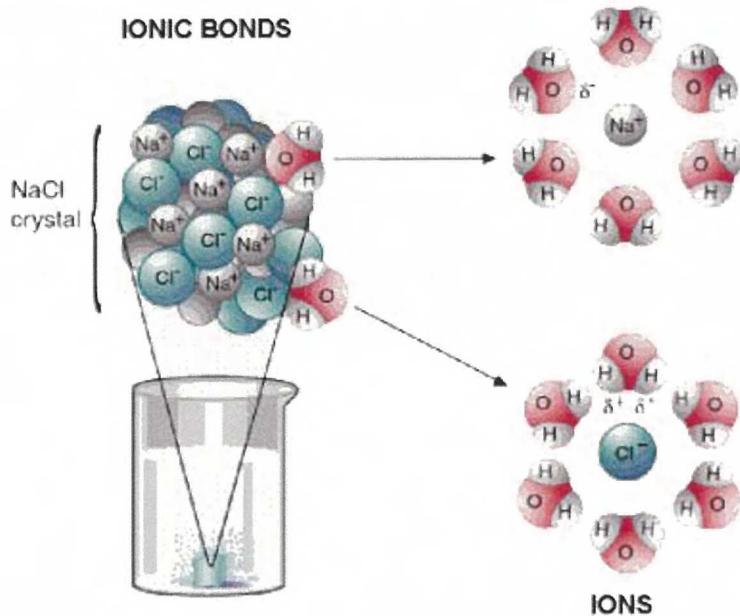
Molecular bonds depend upon the arrangement of electrons. There are two types of molecular bonds that we will be looking at, **covalent bonds** and **ionic bonds**

Covalent Bonds



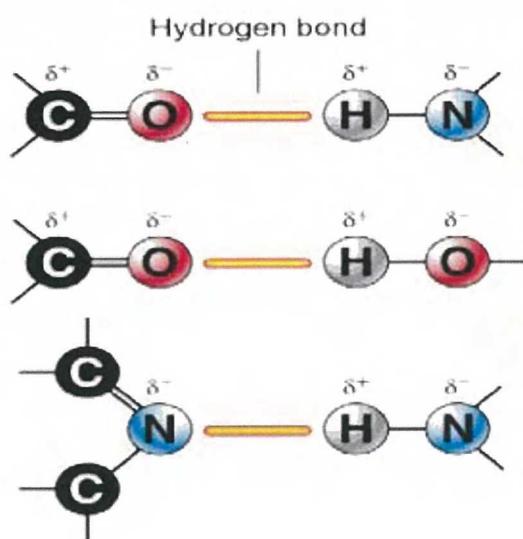
- Atoms are most stable when they have a full electron shell.
- In order to accomplish this, they must share electrons

Ionic Bonds



- Some atoms have a very strong or very weak attraction to electrons
- The atoms with a very strong attraction to electrons can "steal" an electron from the atom with a very weak attraction to electrons
- Compounds formed in this way are called **salts**.

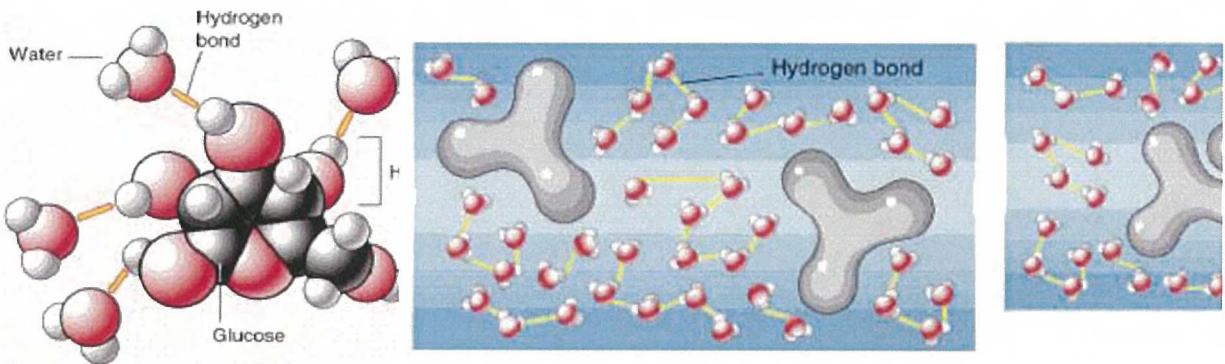
Hydrogen Bonds



- Often when atoms share electrons in a covalent bond, the sharing is not equal. The electrons tend to aggregate nearer to one atom than to the other atom.
- This creates what is known as a **dipole**. In a molecule with a dipole, one end has a higher concentration of electrons than the other end. The end with more electrons has a partial negative charge while the other end has a partial positive charge. Water, as will be discussed below, has a strong dipole.
- A **hydrogen bond** is formed when the negative end of one molecule becomes oriented to and semi-attached to the positive end of another. Hydrogen bonds are fairly weak, but many of them in series, as seen in DNA, can be quite strong.
- Molecules with a dipole are known as **polar** or **hydrophilic** molecules, those without a dipole are known as **non-polar** or **hydrophobic** molecules.

Hydrophilic Interactions

Hydrophobic Interactions



Water

Some properties of water

- **Ubiquity** - Water is plentiful - about 75% of earth is covered with it. Water makes up anywhere from 70 to 90+% of the body weight of living things. At most temperatures on the surface of the earth water is a liquid. In this state water is an excellent solvent and because there is so much of it available on the earth's surface water is home (oceans, lakes and rivers) to much of life. The [water cycle](#) is one of the most important biogeochemical processes. You may also want to review some [general facts](#) about water.
 - Structure of water. H_2O as a liquid
- Water is a **polar molecule** and can bond both to itself and to other water molecules by weak attractions called [hydrogen bonds](#). Each water molecule can bond with as many as 4 others (See Figure 1).

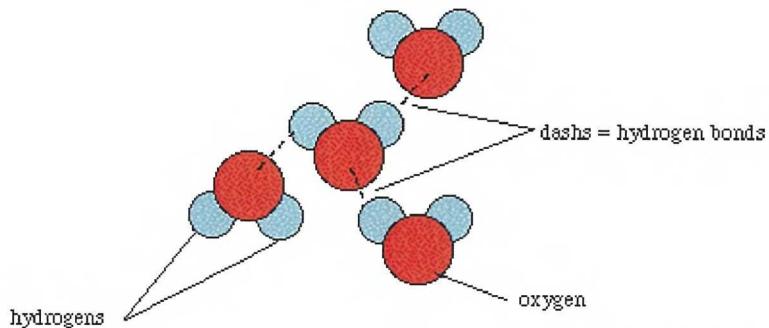


Figure 1 - Note that only three of the possible four hydrogen bonds are shown.

- **Hydrogen bonds** make water an excellent solvent. The hydration shells of water molecules which form around both positive and negative ions as they dissolve, keep these ions in solution by eliminating their ionic attraction. See Figure 2 below.

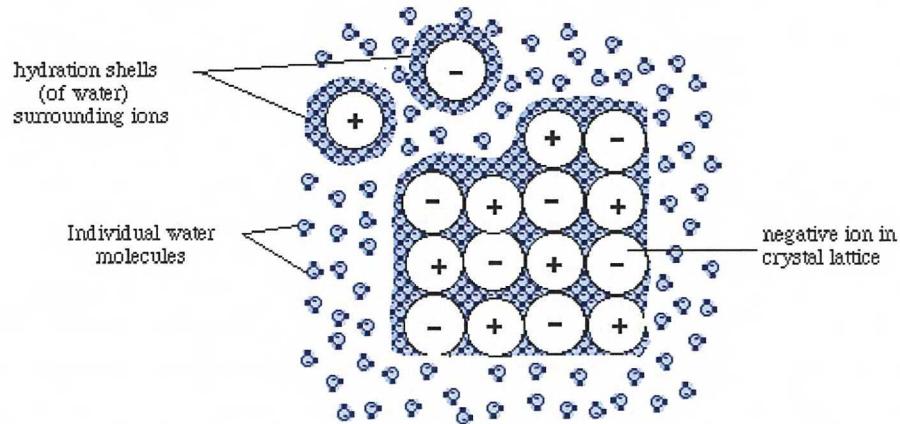


Figure 2 - Water dissolving NaCl (table salt)

- Hydrogen bonding is responsible for the **unusual thermal properties** of water including:
 - Water's high specific heat capacity. Specific heat is defined as the amount of heat energy needed to raise the temperature of one gram of a substance 1°C. Since it takes much more energy than normal to break all the hydrogen bonds in liquid water, water resists rapid temperature fluctuations, adding stability to earth's environments where liquid water is plentiful.
 - Water has a very high heat of vaporization. The heat of vaporization is defined as the energy needed to change the phase of a liquid to a gas. Again, because of the number and relative strength of water's hydrogen bonds, it takes a great deal of energy to break a molecule free of its liquid partners. Heat of vaporization causes a cooling effect because as the warmer molecules evaporate from your skin they take the heat energy with them, leaving you cooler.
 - Water also has a high heat of fusion. This is the amount of heat necessary to melt (or freeze) 1.00 mole of a substance at its melting point

- Capillary action involves two properties of water, cohesion and adhesion.
- In cohesion water's hydrogen bonds make liquid water self-sticky. This stickiness makes water bead up more on a surface than other substances. See Figure 3.



Figure 3 - Surface Tension causes water to bead

- Water is also highly adhesive. This property of water gives it the ability to literally climb the wall of any container it is in. The top of the water column assumes a u-shape called a meniscus. See Figure 4.

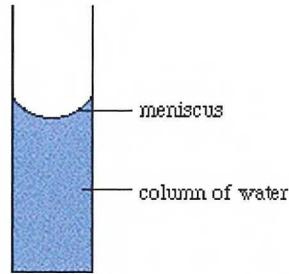


Figure 4 - Adhesion creates a meniscus in a pipette

- When the container happens to be the woody walls of xylem in a plant, both adhesion and cohesion of water molecules produce a force called capillary action. As water evaporates (Transpiration) from the air sacs within the spongy layer of a plant leaf, the meniscuses in these air spaces become more concave increasing the tension on the water columns in the xylem. Along with capillary action this force, described below, helps move water (against the force of gravity) from the root up to the leaves of a mighty tree. (See TACT forces in Wallace)
- **Surface Tension**, the force produced by the difference in hydrogen bonding at water's surface versus its interior, is able to create the illusion that a body of water has a skin. Insects are light enough that they can literally walk on water. Without the natural surfactant (soapy material) produced in our lungs water's high surface tension could actually collapse them, cutting off our air supply. Learn about complications resulting from the lack of surfactants in premature babies at the Merck Manual site (look for "Respiratory Distress Syndrome").
- **Structure of Ice.** Ice (solid water) has a regular bonding arrangement between the molecules of water which actually increases the distance between molecules in certain directions. The result is that ice is not as dense as liquid water at 4°C. Therefore ice FLOATS. This is beneficial to bottom dwellers in lakes, rivers and oceans. You figure out why.
 - Water acts as both an **acid** and a **base**
 - Acid release H⁺
 - Base accepts H⁺
 - We define the pH of a solution as the negative logarithm of the hydrogen ion concentration.
 - at pH 7.0, a solution is neutral
 - at lower pH (1-6), a solution is acidic
 - at higher pH (8-14), a solution is basic

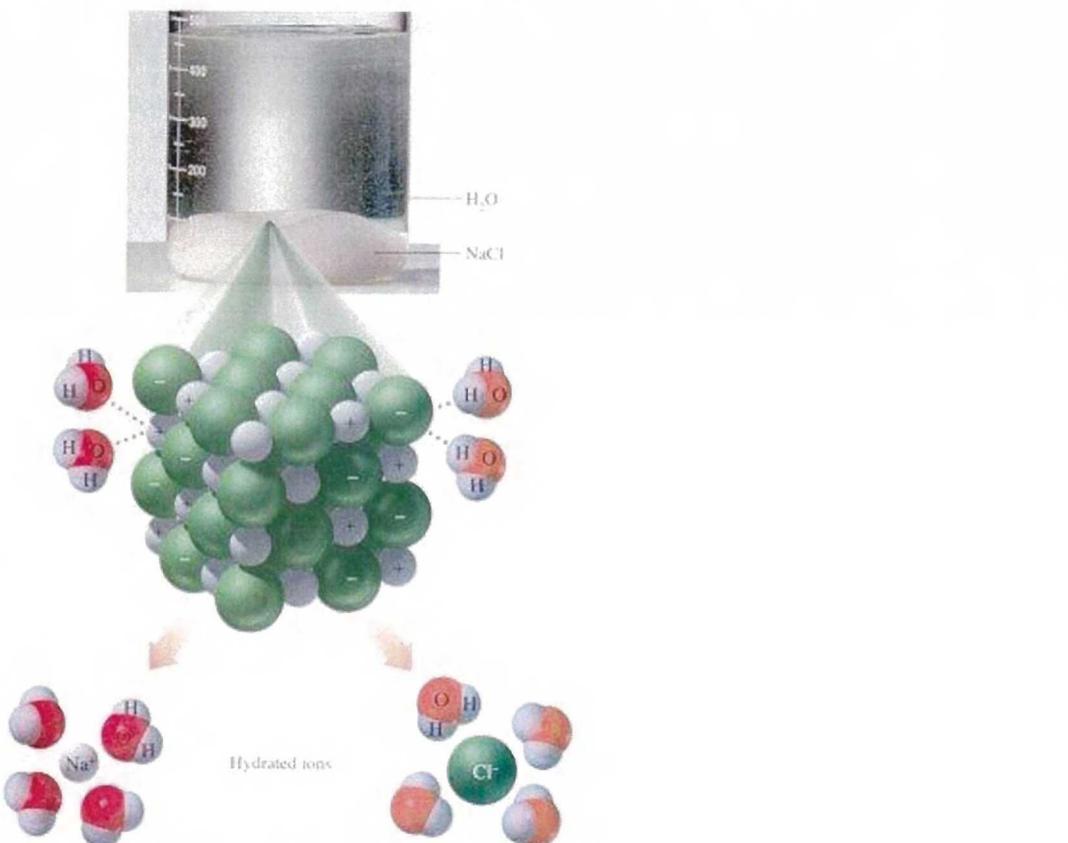
More fun facts about water

- Campbell's Guide to Water
 - SemNet: Properties of Water
 - USGS Water Science for Schools
 - Detergent Chemistry Properties of Water - Kiwi Web
-

Acids and Bases

- Water can ionize (dissociate into charged particles)
 - $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$
- In pure H_2O (distilled water):
 - $[\text{H}^+] = [\text{OH}^-]$
- Dissolved solutes can change relative $[\text{H}^+]$ and $[\text{OH}^-]$
 - **Acids** increase $[\text{H}^+]$ by donating H^+
 - $\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$
 - **Bases** decrease $[\text{H}^+]$ in solution by accepting H^+
 - $\text{NaOH} \rightleftharpoons \text{Na}^+ + \text{OH}^-$
 - Remember $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$
 - OH^- combines with H^+ thereby lowering the $[\text{H}^+]$
 - NH_3 (ammonia) dissolved in water
 - $\text{NH}_3 + \text{H}^+ \rightleftharpoons \text{NH}_4^+$
- pH is a measure of the relative concentration of H^+ in solution
 - $\text{pH} = -\log[\text{H}^+]$ where $[\text{H}^+]$ means the molar concentration of hydronium ions, $M = \text{moles/liter}$
 - Each change in pH is a 10 fold increase or decrease
 - when pH is less than 7, the solution is acidic
 - when pH is greater than 7, the solution is basic

<http://www.uic.edu/classes/bios/bios100/lecturesf04am/lect02.htm>



<http://universe-review.ca/F12-molecule.htm>
(great site for a myriad of topics)

Hydrolysis

(F)

From \$1

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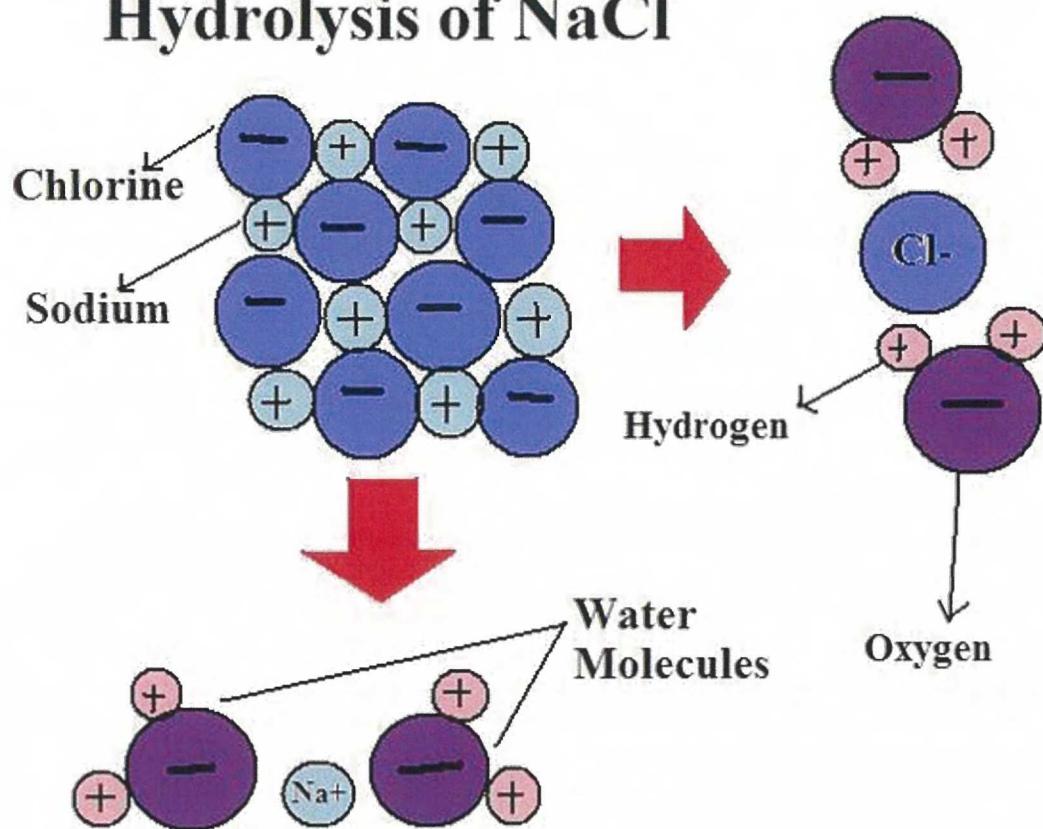
Hydrolysis is a reaction involving the breaking of a bond in a molecule using water. The reaction mainly occurs between an ion and water molecules; often times, it may lead to a change in the [pH](#) of a solution. In chemistry, there are three main types of hydrolysis: acid hydrolysis, base hydrolysis, and salt hydrolysis.

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Introduction

H_2O can act as an acid or a base based on the Bronsted-Lowry theory. If it acts as a Bronsted-Lowry acid, the water molecule would donate a proton (H^+), or in other words a hydronium ion (H_3O^+), if it acts as a Bronsted-Lowry base, it would accept a proton (H^+).

Hydrolysis of NaCl



Acid Hydrolysis

An acid hydrolysis reaction is very much the same as an acid dissociation reaction.



In the above reaction, the proton H^+ from CH_3COOH (acetic acid) is donated to water, producing H_3O^+ and a CH_3COO^- . The bonds between H^+ and CH_3COO^- are broken by the addition of water molecules. A reaction with CH_3COOH , a weak acid, is similar to an acid-dissociation reaction, and water forms a conjugate base and a hydronium ion. When a weak acid is hydrolyzed, a hydronium ion is produced.

Basic Hydrolysis

A base hydrolysis reaction will also resemble the reaction for base dissociation. A common weak base that dissociates in water is ammonia:



- In the hydrolysis of ammonia, the ammonia molecule accepts a proton from the water (because water acts as a Bronsted-Lowry acid), producing a hydroxide anion (OH^-). Similar to a basic dissociation reaction, ammonia forms ammonium and a hydroxide from the addition of a water molecule.

Salt Hydrolysis

Salts will dissociate completely in water forming ions.



- In the above reaction, the salt NH_4Br dissociates into two ions: NH_4^+ and Br^- . Br^- is an anion that cannot be hydrolyzed, thus the cation NH_4^+ goes through hydrolysis.

There are four possible ways of forming salts:

- Combining a strong base and strong acid
- Combining a strong acid and weak base
- Combining a strong base and weak acid
- Combining a weak base and weak acid

- If the salt is formed from a strong base and strong acid, then the salt is neutral, indicating that the bonds in the salt solution will not break apart (indicating no hydrolysis occurred) and is basic.
- If the salt is formed from a strong acid and weak base, the bonds in the salt solution will break apart and becomes acidic.
- If the salt is formed from a strong base and weak acid, the salt solution is basic and hydrolyzes.
- If the salt is formed from a weak base and weak acid, will hydrolyze but the acidity or basicity depends on the equilibrium constants of K_a and K_b . If the K_a value is greater than the K_b value, the resulting solution will be acidic and vice versa.

Examples & Practice



a. Identify which of these is the conjugate base and which is the weak acid.

b. Does the weak acid hydrolyze?

2)

a. Write out the chemical equation for the hydrolysis HF.

b. Is water acting as a Bronsted-Lowry acid or Bronsted-Lowry base?

3)

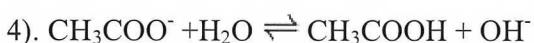
a. Write out the equation for the dissociation of the salt NH_4Br .

b. Write out the hydrolysis of the cation that is produced from the dissociation of the ammonium bromide.

c. From what kinds of acids and bases is ammonium bromide (NH_4Br) made from? Strong acid/strong base? Strong acid/weak base? Strong base/weak acid? Weak base/weak acid?

d. State whether salt hydrolyzes.

e. State whether solution is acidic or basic.



What is the pH of 0.30 M of sodium acetate?

(Hint: First find K_b value)

Given: K_a of $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$

5)

- Does sodium acetate (from previous problem) hydrolyze?
- Is solution acidic or basic?

Solutions to Example Problems

1)

- The conjugate base is the HCO_3^- . The weak acid is the H_2CO_3 .
- Yes it hydrolyzes.

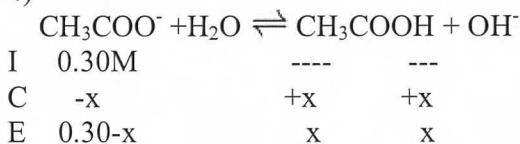
2)

- $\text{HF} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^-$
- Water is acting as a Bronsted-Lowry base because it is accepting a proton (H^+) from the HF.

3)

- $\text{NH}_4\text{Br} \rightarrow \text{NH}_4^+ + \text{Br}^-$
- Br^- does not hydrolyze; it is an ion.
 $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NH}_3^-$ <--- Hydrolysis of NH_4^+
- HBr is a strong acid. Ammonia is a weak base. So NH_4Br is made of a strong acid and weak base.
- Yes it hydrolyzes.
- Acidic

4)



$$K_b = \frac{K_w}{K_a \text{ of } \text{CH}_3\text{COOH}}$$

$$= \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}$$

$$K_b = 5.6 \times 10^{-10}$$

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

$$5.6 \times 10^{-10} = \frac{x^2}{0.30-x} \quad \text{--> Assume } x \ll 0.30$$

$$x^2 = 1.68 \times 10^{-10}$$

$$\begin{aligned} x &= 1.30 \times 10^{-5} = [\text{OH}^-] \\ \text{pOH} &= -\log(1.30 \times 10^{-5}) = 4.89 \\ \text{pH} &= 14.00 - 4.89 = 9.11 \end{aligned}$$

5)

- Yes it hydrolyzes
- Basic solution

Use of Hydrolysis in the "Real World"

In nature, living organisms are only able to live by processing fuel to make energy. The energy that is converted from food, is stored into ATP molecules (Adenosine Triphosphate). Life requires many processes in order to sustain itself such as cellular respiration, respiration, muscle contraction, distribution of hormones, transmittance of neuro-transmitters in the brain, etc. All of these important processes require an input of energy. To distribute this energy, the energy from the ATP molecules must be released. To release the energy stored in the bonds of ATP molecules, hydrolysis must occur to break a phosphate group off of an ATP molecule, thus releasing energy from the bonds. ATP now becomes ADP (Adenosine Diphosphate) from losing a phosphate group through hydrolysis.

References

- Petrucci, et al. General Chemistry Principles and Modern Applications. 9th ed. New Jersey: Prentice Hall, 2007. 686-690.
- Freeman, Scott. Biological Sciences. 4th ed. San Francisco: Pearson Prentice Hall, 2011.

Outside Links

- Hydrolysis: <http://en.wikipedia.org/wiki/Hydrolysis>
- Hydrolysis of
Ions: <http://spinner.cofc.edu/genchemlab/hydrolysis.htm?referrer=webcluster&I>
- Salt
Hydrolysis: <http://www.chemistry.nmsu.edu/studntres/chem112.spring.1997/Hydrolysis.htm>
- Acid-Base Reaction: http://en.wikipedia.org/wiki/Acid–base_reaction
- Salt Hydrolysis: http://ibchem.com/IB/ibnotes/full/aab_htm/18.4.htm

Contributors

- Patrina Kim (UCD)
- Gretchen Hehir

http://chemwiki.ucdavis.edu/Physical_Chemistry/Acids_and_Bases/Solubility/Hydrolysis%3A_With_Respect_to_Acids,_Bases,_and_Salt_Solutions

Section 13.8 Amines and amides

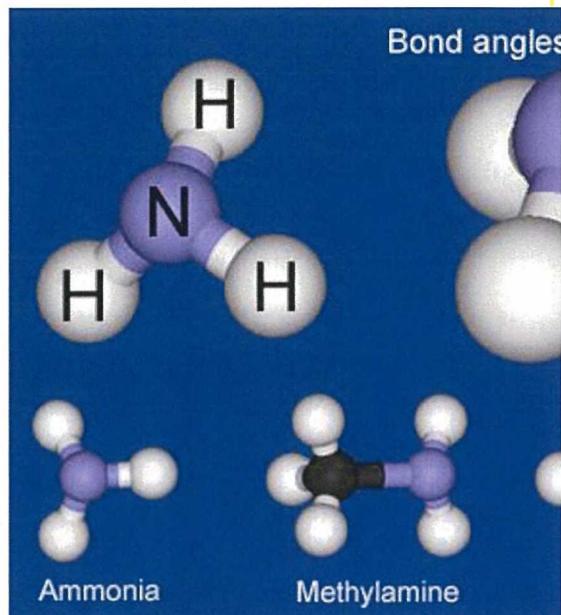
Slightly relevant fact: amines and amides get their name from am- in ammonia

Highly irrelevant fact: ammonia gets its name from *sal ammoniac*, an outdated word for ammonium chloride NH_4Cl . The name came from *sal ammoniacus*, Latin for 'salt of Ammon'. The word *ammoniacus* came into the Latin vocabulary from Greek, in the form of the Greek word *ammōniakos* (ἀμμωνιακός), meaning 'of Ammon'.

Shockingly pointless fact: What's Ammon and why is ammonium chloride named after it, you ask? The salt found by the Greeks near the temple of Jupiter Ammon at Siwa in Egypt was in fact ammonium chloride. As far as the Greeks were concerned this was just some random salt – they didn't know it contained nitrogen or hydrogen or chlorine. They just named it *ammōniakos* after the temple.

What are amines and how are they named?

- Amines are the organic versions of ammonia
- An alkyl group takes the places of one, two or three of the hydrogens
- They are called primary, secondary and tertiary amines, respectively
- Smaller (lower) primary amines are called things like methylamine ($\text{CH}_3\text{-NH}_2$) and ethylamine ($\text{CH}_3\text{-CH}_2\text{-NH}_2$).
- Simple secondary and tertiary amines are also easy to name. Dimethylamine is $\text{CH}_3\text{-NH-CH}_3$ and trimethylamine is $\text{CH}_3\text{-N(CH}_3\text{)}\text{-CH}_3$
- Bigger amines have names beginning with amino. For example, $\text{CH}_3\text{-CH(NH)}\text{-CH}_2\text{-CH}_2\text{-CH}_3$ is called 2-aminopentane.
- Amines with low RMM are gases or volatile liquids
- Volatile amines have strong smells like ammonia
- Ethylamine and trimethylamine smell like decaying fish
- 1,4-diaminobutane and 1,5-diaminopentane are called putrescine and cadaverine because they are given off when flesh rots



Properties of amines

- Amines are similar to ammonia but the alkyl groups modify their properties
- Most of their behaviour can be explained by the lone pair of electrons on the N

The lone pair of electrons explains why amines and ammonia are:

- very soluble in water
- a base
- a Ligand
- a nucleophile

Solubility of amines

- Amines form hydrogen bonds with water
- Small amines are soluble in water
- Larger amines are less soluble because their long alkyl groups disrupt the hydrogen bonding in water

Amines as bases

- The lone pair on the N can take part in dative covalent bonding
- An amine can donate a pair of electrons to an H^+
- By generously donating two electrons, the amine is an H^+ acceptor and acts as a base
- The amine in question becomes an alkylammonium ion, with one extra hydrogen than normal and a +1 positive charge

- If the amine has nicked a proton from water, an OH⁻ is left over, causing the solution to be alkaline
- Solutions of amines are alkaline
- Amines react with acids (usually the oxonium ion H₃O⁺) to form alkylammonium ions. Since the lone pair is playing the dative covalent bonding game, it can't interact with everything else so much. Therefore, alkylammonium ions lose their smell
- The result is, adding acids to amines takes away their smell

Amines as ligands

- The lone pair on the N can take part in dative covalent bonding
- An amine can donate a pair of electrons to an H⁺

There should be a paragraph on **amines as nucleophiles** but I haven't written it yet. It's on page 332 of Chemical Ideas.

There should also be sections on

What are amides?

Hydrolysis of amides and

Condensation polymers involving the NH₂ group

but I couldn't be bothered to write them when I made this page.

Hopefully I'll update it sometime. Watch this space. It's all on p332-334 of Chemical Storylines. At least I've given you the answers to the questions so you can pretend you did them for homework.

Problems for 13.8

- 1** Name the amines with the following structures.

a		Ethylamine
b		Dimethylamine
c		2-aminopropane
d		Ethyldimethylamine
e		Cyclohexylamine

- 2** Draw structures for the following amines.

a	Propylamine	
b	Phenylamine	
c	Diethylmethylamine	
d	Butylethylmethylamine	
e	3-aminopentane	
f	2,4-diaminopentane	

3 Draw structures for the products formed when 2-aminopropane reacts with:

a Hydrochloric acid

4 Write equations for the reactions of the following pairs of substances:

b Ethanoyl chloride

c Chloroethane

5 a Which of the reactions of amine described in Section 13.8 could not be undergone by a tertiary amine such as trimethylamine? Briefly explain your answer.

Tertiary amines cannot react with acyl chlorides to form amides because the amines are not bonded to any hydrogen atoms. Acyl chlorides can replace a hydrogen atom bonded to a nitrogen atom, liberating HCl, but they cannot replace an alkyl group.

b Explain, in terms of intermolecular forces and with the aid of a diagram, why butylamine is soluble in water.

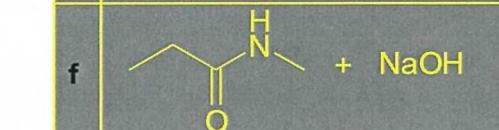
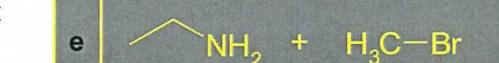
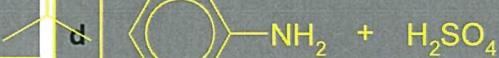
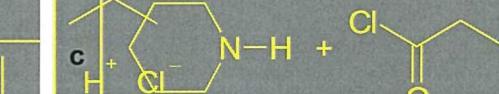
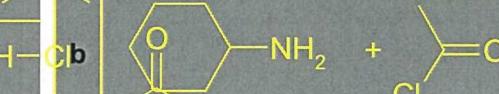
The carbon chain in a butylamine molecule is terminated by an amine group, which has dipoles. The nitrogen atom has a partial negative charge due to its electronegativity being much higher than the hydrogen atoms it is bonded to.

Butylamine can dissolve in water by forming hydrogen bonds with water. Oxygen atoms in water hydrogen-bond to hydrogen atoms on the amine group. The nitrogen atom in the amine group hydrogen-bonds to hydrogen atoms in water molecules.

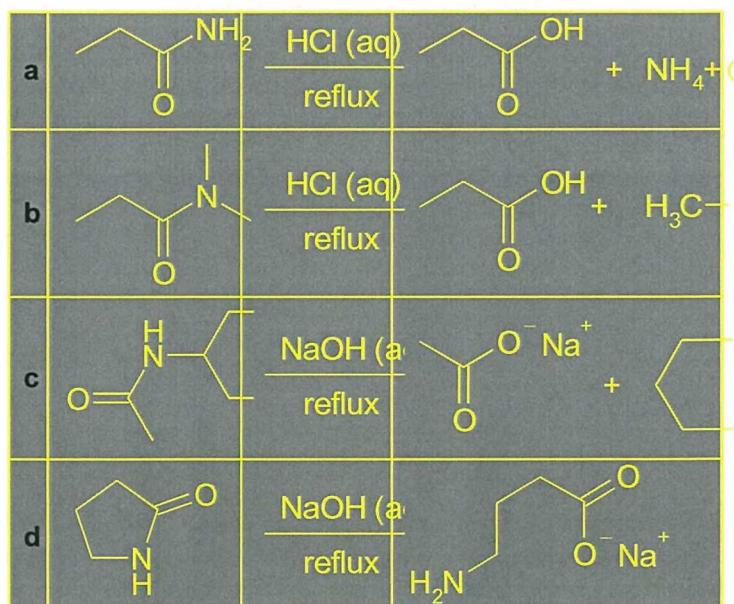
a Hydrochloric acid

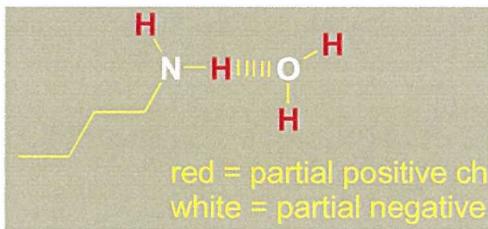
b Ethanoyl chloride

c Chloroethane

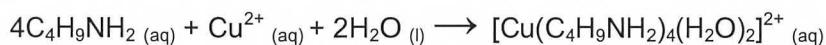


6 Complete the following reaction schemes by inserting the structures of the missing reactants or products, or by writing the reaction conditions on the arrow.





b Explain, with an equation, why a deep blue colour is formed when butylamine is added to copper(II) sulphate solution.

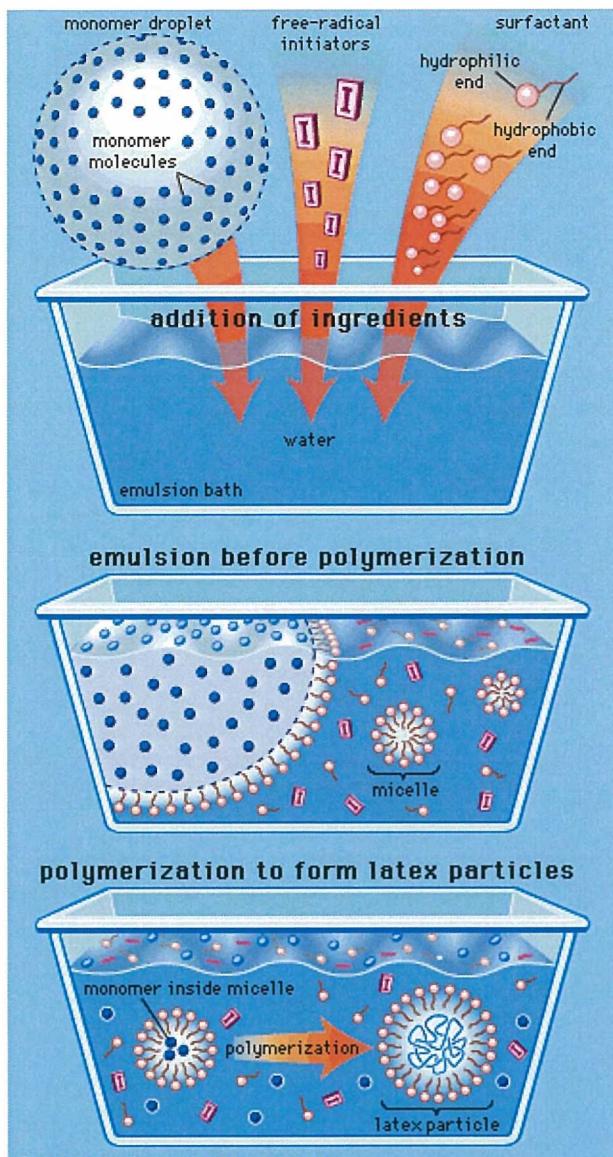


Copper sulphate solution is a source of aqueous copper(II) ions. Four butylamine molecules will each form a dative covalent bond to a single copper(II) ion using the electrons in the lone pairs on their nitrogen atoms. In doing so, butylamine molecules are acting as ligands.

The complex formed is a deep blue colour because the butylamine ligands create new energy levels for the copper atoms electrons in d-orbitals. These electrons can be excited to the new energy levels by photons of light.

When the excited electrons return to a lower energy level, they emit photons of light. These photons have the same energy as the difference in energy between the two electronic energy levels. The photon energy dictates its wavelength and therefore its colour, in this case deep blue.

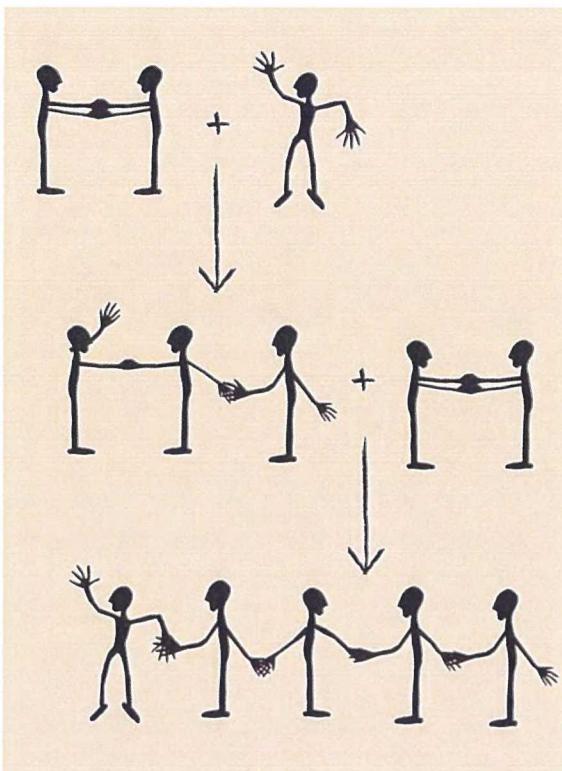
<http://www.ben.mills.btinternet.co.uk/chemistry/section-13.8.htm>



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<http://www.liv.ac.uk/researchintelligence/issue32/latex.htm>

Polymerisation



<http://www.scienceinschool.org/2009/issue13/drama>

Temperature and equilibrium

Temperature and the equilibrium position

The equilibrium will shift to oppose any change imposed on it. What will happen to the equilibrium as the temperature is increased or decreased? What will be observed?

summary

$[Co(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CoCl_4]^{2-} + 6H_2O$

+ΔH
-ΔH

drag the test tube to the hot water bath or the ice bath

summary

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http://www.boardworkseducation.com/ap-chemistry_131/product-showcase

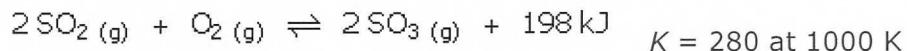
Le Châtelier's principle states that a system at equilibrium will respond to counteract the effect of a disturbance such as a change in concentration, pressure, and/or temperature. Disturbances that are not counteracted are the addition of a catalyst, an increase in the surface area of a solid species, and a change in pressure when opposite sides of a system possess the same number of gas moles.

Although it has been stated on several occasions to this point, equilibrium constants (K values) are temperature dependent; that is, they only apply to systems at specified temperatures. A change in temperature changes the value of K ; however, no other disturbance has this affect on a K value.

Lets consider some disturbances on a system at equilibrium in terms of Le Châtelier's principle and the equilibrium constant.

A Change in Concentration

What should happen to the concentrations of the species in this system if more oxygen gas is added?



According to Le Châtelier's principle, increasing the concentration of a species is counteracted by favouring the reaction that consumes that species; in this case, the forward reaction.

In the new equilibrium, the $[\text{SO}_3]$ will be higher and $[\text{SO}_2]$ will be lower. The $[\text{O}_2]$ will also be higher, but lower than the sum of the original plus the added O_2 . The equilibrium position shifts to the right.

A look at the equilibrium constant expression should help you to understand the response by the system:

$$K = 280 = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]}$$

By increasing $[\text{O}_2]$, the value of the denominator increases, and as a result, the quotient (the value of the expression) is less than 280.

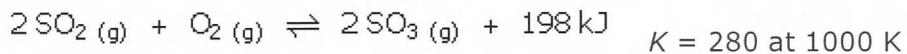
In order for the value of this quotient to increase back to 280, the $[\text{SO}_3]$ must increase and the $[\text{SO}_2]$ must decrease to offset the increase in $[\text{O}_2]$.

Can you predict the effect of adding SO_3 ?

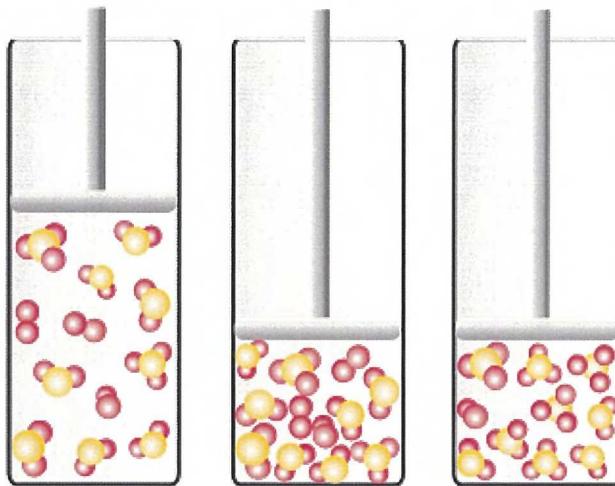
Important Note: It is worthwhile pointing out here that adding a solid or a liquid to a system that contains gases or aqueous species does not change the position of the equilibrium. Amounts of solids and liquids in these systems are not expressed as concentrations. These species are not included in the equilibrium constant expression. Adding or removing them does not affect the value of the quotient, so the concentrations of the other species do not adjust to maintain K .

A Change in Pressure by Changing Volume

What should happen to concentrations of species in this system



if the volume of the container is reduced to half of the original volume?



According to Le Châtelier's principle, this system should counteract the pressure increase by favouring the side with fewer gas moles.

In this system, the left side has three gas moles compared to two gas moles on the right.

Since two moles of SO_3 occupy less space than three moles of reactants, the increased pressure can be relieved if SO_2 and O_2 combine to make more SO_3 .

In other words, in the new equilibrium the amounts of SO_2 and O_2 should be lower and the amount of SO_3 should be higher. You conclude that the position of the equilibrium shifts to the right.

The position of a gas system equilibrium only changes when the number of gas moles is not equal on both sides.

You should also notice that the changes have been expressed in terms of the amounts of these species as opposed to their concentrations! Concentration in this course is equated with molar concentration or mol/L - it is a function of both the number of moles of a substance and the volume it occupies.

Have another look at middle part of the diagram above. Do you see that by reducing the volume, all three molar concentrations are actually higher? (number of moles divided by a smaller volume = higher concentration!)

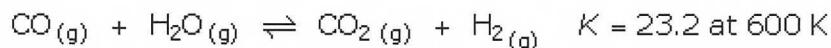
When dealing with volume changes of gases, it is best to make predictions in terms of changes in number of moles, not molar concentration.

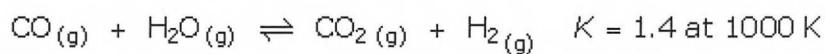
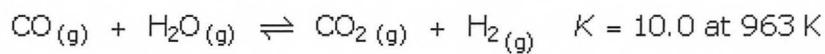
Note however, that the value of K does not change.

K values are unchanged when pressure is altered by increasing or reducing the volume of a system.

A Change in Temperature

Consider these equations for a system at three different temperatures:

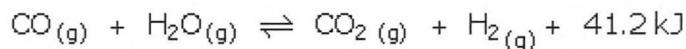




Do you see a trend?

How can the trend be explained?

Perhaps a modification of the equilibrium equation might help.



An increase in the temperature of a system, say from 600 K to 1000 K can be thought of as the addition of heat. Conversely cooling a system down involves the removal of heat.

According to Le Châtelier's principle, adding heat to a system is counteracted by absorption of the heat. In other words, it favours the endothermic reaction - the reaction that absorbs the added heat - and the position of the equilibrium shifts away from the location of the energy term. In the above example, the equilibrium position shifts to the left.

In terms of actual concentrations, it should be easy to see why K values are functions of temperatures.

By carrying out the reaction at a higher temperature, the equilibrium concentrations of CO_2 and H_2 will be lower and those of CO and H_2O will be higher. This in turn makes the numerator of the equilibrium constant expression smaller and the denominator larger. The value of K is smaller as a result.

You can predict the effect of a temperature increase on a K value by looking for the energy term:

Table 1: Effects of changing temperature on K values.

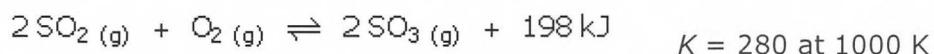
Class of Reaction	Increase in Temperature	Decrease in Temperature
forward endothermic	K increases	K decreases
forward exothermic	K decreases	K increases

Le Châtelier's Principle allows you to make qualitative predictions about shifts in the position of an equilibrium

Equilibrium constants allow you to determine whether a system is at equilibrium and the direction of a shift if a system is not at equilibrium.

Sample Exercise 1

Based on this equation:



Biff and Molly decide to add 0.068 mol of SO_2 , 0.38 mol of O_2 , and 0.098 mol of SO_3 to a 1.00 L flask at 1000 K.

Is the system established by Biff and Molly at equilibrium? If not, then how will the concentrations of the three species have changed to establish the equilibrium?

Plan a Strategy

1. Write the equilibrium constant expression for the system.
2. Calculate the concentration of each species and substitute them into the equilibrium constant expression.
3. Compare the quotient value to the accepted K value.
 - o If the values are the same, the system is at equilibrium.
 - o If the quotient value is lower, then the amount of SO_3 will have to increase and the amounts of SO_2 and O_2 will have to decrease.
 - o If the quotient value is higher than K , then the amount of SO_3 will have to decrease and the amounts of SO_2 and O_2 will have to increase.

Step 1: Write the equilibrium constant expression.

$$K = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$$

Step 2: Calculate the concentrations and substitute.

Since the container is a 1.00 L container, concentration equals the mole amount.

$$K = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = \frac{[0.098]^2}{[0.068]^2[0.034]} = 61$$

Step 3: Evaluate the quotient and communicate the answer.

Since the value calculated by substituting Biff and Molly's data produces a quotient that is lower than the accepted value of 280, the system is not at equilibrium. The position of the system they established has to shift to the right. The concentration of SO_3 must increase while those of SO_2 and O_2 must decrease.

http://www.cdli.ca/courses/chem3202/unit01_org03_il03/b_activity.html