NoBS Chemistry

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Author's Notes

NoBS

NoBS strives for succinct guides that use simple, smaller, relatable concepts to develop a full understanding of overarching concepts.

Dedication

Jeffrey Wang: "To all those that helped me in life: this is for you."

Sources

This guide borrows certain material from the following sources, which are indicated below and throughout the paper will be referenced by parentheses and their names:

- (Schwartz) Martin Schwartz, University of North Texas
- (Silberberg) Martin S. Silberberg, **Principles of General Chemistry, 3rd. Ed.**

Part I Atoms, molecules, and ions

Review your first semester of eighth grade science class.

Part II Stoichiometry

Woo mix stuff together in proportions to form new things in proportions Basically chemical equations

Part III Chemical reactions

There are three kinds: ionic, acid-base, and redox.

Part IV Gases

PV = nRT

Part V

Introductory thermochemistry

1 Hess's Law

Hess's Law? More like Hiss's Law.

Enthalpy is a state function. This means ΔH is independent of path.

Take 3 + 2. The answer is 5, right? Well, if I started out with 3, added 7, subtracted 6, and added 1 (3+7-6+1), the answer is also 5. While the middle paths are not the same, the beginning and the end result are the same. This is what a state function is.

Hess's Law takes advantage of the fact that enthalpy is a state function to calculate the enthalpies of reactions that we don't know. No matter how steps there are in a series of chemical reactions, the total enthalpy change is the sum of all the changes.

There are a few basic ground rules that come from enthalpy being a state function:

- 1. If reactants and products are reversed in a chemical equation, flip the sign of ΔH .
 - $CO_2(g) + 2H_2O(l) \longrightarrow CH_4(g) + 2O_2(g) \Delta H_1 = +890kJ$
 - $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \Delta H_2 = -890kJ$
- 2. If the amounts of reactants and products are changed by a certain ratio, then ΔH is changed in the same ratio.
 - $CO_2(g) + 2H_2O(l) \longrightarrow CH_4(g) + 2O_2(g) \Delta H_1 = +890kJ$
 - $2 \text{CO}_2(g) + 4 \text{H}_2\text{O}(l) \longrightarrow 2 \text{CH}_4(g) + 4 \text{O}_2(g) \Delta H_2 = +1780kJ$

We can combine these two rules. If the ΔH of $H_2(g) + Cl_2(g) \longrightarrow 2 \,HCl(g)$ is -185kJ, then what is the ΔH of $4 \,HCl(g) \longrightarrow 2 \,H_2(g) + 2 \,Cl_2(g)$?

We can identify two differences between these two reactions. First, it looks like the reaction was flipped. Second, it looks like the coefficients were multiplied by two. To account for these differences, we will (1) flip the sign of ΔH and (2) multiply ΔH by 2, which is the ratio that the coefficients were multiplied by. So the final ΔH is +370kJ.

Let's try a reaction such as $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$. We do not know the ΔH of this reaction because it cannot be measured. So, we will use Hess's Law to deduce the ΔH . (The following example was borrowed from Schwartz)

Given two reactions, we will "rearrange" and change the ratios to make it "fit" this reaction.

1.
$$CO_2(g) \longrightarrow C(s) + O_2(g) \Delta H_1 = +393.5kJ$$

2.
$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g) \Delta H_2 = -566.0kJ$$

Let's begin to find where the reactants are located in these two equations. Well, it looks like C(s) is found in the first equation on the products (right) side. In order to bring it to

the reactants side, we will reverse the equation and therefore flip the sign of ΔH .

(1')
$$C(s) + O_2(g) \longrightarrow CO_2(g) \Delta H_{1'} = -1 \cdot +393.5kJ = -393.5kJ.$$

Because $O_2(g)$ is found in both equations, let's not overcomplicate matters. Let's deal with CO(g). We need it in the product side, but it seems to only be found in the reactants side. That means we reverse the equation and flip the sign of ΔH . Furthermore, it seems this equation has double the amount of moles than needed, so we halve the sign of ΔH too.

(2')
$$CO_2(g) \longrightarrow CO(g) + \frac{1}{2}O_2(g) \Delta H_{2'} = -1 \cdot \frac{1}{2} \cdot -566.0kJ = +283.0kJ.$$

Adding equations (1') and (2') together, we get the original equation:

$$C(s) + O_2(g) + CO_2(g) \longrightarrow CO_2(g) + CO(g) + \frac{1}{2}O_2(g) \Delta H = -393.5kJ + 283.0kJ.$$

Just like in algebra, we're going to cancel out reagents that are on both sides of the equation.

$$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) \Delta H = -110.5kJ.$$

And that is the calculated ΔH for this reaction.

2 Enthalpy of formation

Another way to figure out the ΔH of something (in this case, compounds) is to use enthalpy of formation, also known as heat of formation. Summing the enthalpies of each individual element in a compound gives us that compound's enthalpy. We use the enthalpies of elements in their standard states, which is $25^{\circ}\mathrm{C}$ at 1 atm. You use the element's most preferable composition at standard state.

Instead of H, use H_2 . (All elements naturally occurring as diatomic should be used as diatomic for purposes of enthalpy of formation.)

If you want the enthalpy of H_2O , simply get the enthalpies for a hydrogen molecule (H_2) and half of an oxygen molecule $(\frac{1}{2}O_2)$. Note that 2H + O would be wrong because H and O are diatomic gaseous molecules at standard state.

The enthalpies of formation for each element will be given to you. No need to memorize them.

3 Bond energy/bond enthalpies

Each bond between atoms in a molecule has energy. When you break these bonds, you need to invest energy into it. When you form bonds, energy comes out.

Therefore, given a chemical reaction and how much energy each kind of bond has, you can calculate bond energies.

A single bond does not have the same amount of energy as a double bond. O-O, O=O, and O=O have very different bond enthalpies. You do not have to memorize bond enthalpies for each specific kind of bond, but you need to know how to do math with them.

bond enthalpy =
$$\Sigma$$
broken – Σ made

You can remember "broken minus made" by using the pseudo-mnemonic "bowel movement." (I didn't make this up, ok? It works though)

Part VI

Quantum theory and atomic structure

4 Waves

- A wave is an oscillation that results in a movement of energy. Light has characteristics of both waves and particles.
- Two characteristics of waves
 - wavelength (λ , length) distance between wave peaks
 - **frequency** (ν , per time) number of peaks that pass a point in one second HEY BTW " ν " IS NOT " ν " IT'S CALLED NU kthxbai jk get back to studying
- Frequency related inversely to wavelength:

$$\nu \propto \frac{1}{\lambda}$$

- Product of wavelength, frequency is **speed of light** (c, length per time)
 - Relationship: $\lambda \nu = c = 2.998 \times 10^8 m/s = 3.00 \times 10^8 m/s$
 - Remember from Algebra 1 that inverse relationships are defined by the relation xy = k? The "k" in this case is c_r , or the speed of light.
 - For any given wavelength, divide c by the wavelength to get the frequency.
 - Also, for any frequency, divide c by the frequency to get wavelength.
 - This c is seen in the famous equation $E=mc^2$.

5 Quantum theory

Energy

- Planck discovered energy comes in discrete "packets" called quanta. (Ergo, quantum theory.) So you can't break it apart. Just like how atoms are the smallest subdivision of matter, quanta are the smallest subdivision of energy.
- This is how we determine how much energy something truly has.
- Planck's constant = number of joules of energy a quantum (packet of energy) has = $h = 6.63 \times 10^{-34} J \cdot s$
- When electrons move down energy levels, they lose energy. This energy goes into
 photons, which are emitted from atoms. Photons have wave-like properties. Therefore, we can use that wave stuff to figure out the energy given by photons.

- Energy of each photon proportional to light frequency: $E_{photon} \propto \nu$
- $E_{photon} = h\nu = \frac{hc}{\lambda}$. (You can substitute ν for $\frac{c}{\lambda}$ because $\nu = \frac{c}{\lambda}$, per the waves section we just went over.)
- Multiply energy of a photon by Avogadro's number and hey look what you get, a mole of energy

Quantum numbers

- Use quantum numbers to determine what electron is in what orbital
- Four quantum numbers
- \bullet n principal quantum number
 - -n=1,2,3,...
 - Determines energy level and size of orbital (Lower energy level vs higher energy level. Higher energy levels means larger orbitals)
- *l* azimuthal quantum number
 - -l=0,1,2,...,n-1
 - Determines number and shape of orbitals
 - Better known as spdf
- m_l magnetic quantum number
 - $m_l = -l, ..., -1, 0, 1, ..., l$
 - Determines orientation of orbitals (Basically, only two electrons per orbital, so you have to make different "orientations" of the same orbital for each two electrons)
- m_s spin quantum number
 - $-m_s=-\frac{1}{2},\frac{1}{2}$
 - Determines "spin" of electron (because you get two electrons to an orbital, but they have to be going different ways, so this is how it's identified as going one way or another)
- Pauli Exclusion Principle no two electrons can share the same set of quantum numbers. (For example, this means they can have the same principal, azimuthal, and magnetic quantum numbers, but the couldn't have the same spin quantum number!)

Part VII

Electron configuration and periodicity

6 Electron configuration and orbital energy diagrams

Electron configurations

Electron configurations go like this:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, etc.

- s: 1, 2, 3, 4, 5, 6...
- p: 2, 3, 4, 5, 6...
- d: 3, 4, 5, 6...
- f: 4, 5, 6...

s: first two groups (columns) of the periodic table and He, groups 1 and 2. p: right-most six groups of the periodic table, excluding He, groups 13 through 18. d: middle "transition metals" area, group 3 through 12. f: Lanthanides and Actinides.

Count beginning with H (hydrogen) and continue right and down, following the natural ordering of atomic numbers until you reach your atom.

Condensed electron configuration is when you start from the nearest noble gas and simply do the electron configuration of the valence electrons. For example, the electron configuration of V is $1s^22s^22p^63s^23p^64s^23d^3$, but the condensed electron configuration is [Ar] $4s^23d^3$.

Orbital energy diagrams

Keep in mind the Pauli Exclusion Principle.

Since s has only one orbital (it only has one magnetic quantum number, 0), the two electrons fill up that orbital as it would be expected to. But for p, since there are three magnetic quantum numbers, -1; 0; and 1, addition of electrons should be spread out amongst the orbitals first. Since these three orbitals are all on the same energy level (let's pretend we're on 2p), then these three orbitals are called **degenerate orbitals**. Electrons will occupy degenerate orbitals that maximizes the number of unpaired electrons. This is called **Hund's Rule**. Think of a hostel's beds as degenerate orbitals of an energy level. Unless everybody is friends with benefits with each other (and electrons are not, because of Coulombic repulsion), the hostel guests will try to spread out as much as possible. If there are three beds and three people, all three will sleep separately. If a fourth comes in, there's no choice but for one of the beds to hold two people, and only then can an orbital be paired.

If all orbitals are paired, this is called **diamagnetic** and the atom/ion won't be magnetically attractive. But if some orbitals are unpaired, this is called **paramagnetic** and the

atom/ion will be magnetically attractive. The more orbitals unpaired, the more paramagnetic an atom/ion will be.

For ions, keep in mind that the number of electrons is NOT the same as the ion's atomic number. Be sure to incorporate that into your electron configurations. There is something special to keep in mind here: <u>transition metal cations'</u> nth s electrons will come off *before* the (n-1)th d electrons.

• Fe: [Ar] $4s^23d^6$.

• Fe^{2+} : [Ar] $3d^6$.

• Fe^{3+} : [Ar] $3d^5$.

7 Periodicity

Atomic radii

Note that this is not ionic radii but atomic radii. There are two kinds of atomic radii:

- van der Waals half of the atom's diameter
- **bonding radius** half of the diameter, where the diameter is defined as being the distance between the two nuclei of the covalent bond.

Trend: As you go right, atomic radii get smaller. As you go down, atomic radii get bigger.

This trend is only for the main group and not for transition metals or the lanthanides/actinides. Additionally, this trend is for both van der Waals and bonding radii.

Effective nuclear charge (Z-effect)

The effective nuclear charge (or Z-effect) is the number of protons minus the number of core electrons. The higher the effective nuclear charge is, the more nuclear charge the valence electrons see, and the more closely drawn they are to the center of the atom. This causes the atom to become smaller.

$$Z_{\text{effect}} = Z - S$$

$$Z_{\rm effect} \propto \frac{1}{\rm atomic\ radii's\ size}$$

Ionic radii

Radii of cations are always smaller than its neutral atom's radii. This is because the effective nuclear charge/Z-effect is bigger and causes smaller radii.

Radii of anions are always larger than its neutral atom's radii. This is because the effective nuclear charge/Z-effect is smaller and causes bigger radii.

Trend: As you go right, cations' radii start out small, then get smaller. At the "stairstep", anions become huge and get smaller while remaining bigger than the cations.

Ionization energy

This is the amount of energy needed to remove an electron from an atom. They will increase, but there is a massive jump at the $(\# \text{ of VE} + 1)^{\text{th}}$ ionization energy.

Factors affecting ionization energy of atoms:

- 1. effective nuclear charge higher Z_{eff} means more attraction to nucleus, which means it's harder to pry it off and increases the ionization energy.
- 2. distance from the nucleus the further away it is from the nucleus, the easier it is to pry it off and decreases the ionization energy.

Ionization energy is the exact opposite trend as atomic radii. However, ionization energy is directly related to the electronegativity.

$$IE \propto \frac{1}{\text{atomic radii}}$$

IE \propto electronegativity

Electron affinity

Opposite of ionization energy. This is how much energy is given off/used to bind an electron to an atom. Usually, energy is given off (negative), but not always.

Part VIII

Molecular shapes and covalent bonding

8 Ionic bonding

Where one or more atom(s) donate(s) electrons to (an)other atom(s) so that both/they all have perfect octets.

9 Covalent bonding

Lewis structures

A Lewis structure is used for demonstrating valence electrons. For example:

Ö

Covalent bonds share electrons so that each atom reaches eight valence electrons. The "shared" electrons count as valence electrons for both atoms. This sharing creates a covalent bond.

We will first count the number of valence electrons of each individual constituent atom of the compound. The sum is the number of valence electrons to be used across the Lewis diagram, represented by dots. Then, valence electrons will be shared, by creating a covalent bond, so that the constituent atoms of the compound that do not have an octet will have an octet.

Formal charge

In cases where multiple valid Lewis structures arise, the most equally-distributed version will prevail. We determine this through **formal charge**.

Formal charge is defined as:

FC = # of valence electrons -# of lone electrons (NOT PAIRS) -# of bonds

This is applied to every single constituent atom of a compound.

Formal charges should strive to be zero. This creates the most equally-distributed version of the compound and is therefore the correct version of the Lewis structure. On occasion, constituents may have a nonzero formal charge, but if there is no way to make every single constituent's formal charge zero, then such a Lewis structure is considered valid.

$$\ddot{O} - C \equiv O$$
:
FC = $(6-6-1)$, $(4-0-4)$, $(6-2-3)$
FC = -1, 0, 1

This Lewis structure for CO_2 is not valid because the formal charges are not all zero when it could be.

$$\ddot{O} = C = \ddot{O}$$

FC = $(6 - 4 - 2)$, $(4 - 0 - 4)$, $(6 - 4 - 2)$
FC = $0, 0, 0$

This above Lewis structure is now valid, because the FCs are all zero.

Bond order

Single bond means a bond order of one. Double bond, two. Triple bond, three. Simple. Until it isn't. See "Resonance" for more information.

Resonance

In SO_3^{2-} (sulfate), the extra electrons create resonance structures. Because one of the S-O bonds is a double bond and the other two are single bonds, any of the three S-O bonds can be the double bond, as long as the other two bonds are single. Because they are all S-O bonds and there are three distinct possibilities of SO_3^{2-} , we must draw three different structures.

However, in reality, the SO_3^{2-} bond lengths are the same, as proven through scientific methods. It turns out that instead of there being one double bond and two single bonds, there are three 1.33 bonds. Therefore, the bond order of SO_3^{2-} 's S-O bond is 1.33.

Remember to surround sulfate's Lewis structure with brackets and a superscript "2-" for its ionic charge.

Exceptions to the octet rule

Free radicals: these occur when there's an odd number of valence electrons. Why don't you usually see it? Because 1. giving you an odd number of electrons screws up your Lewis dot skills and 2. they're rare in nature. But when they exist, they are very unstable and highly reactive. It will force the atom to have seven valence electrons, even with bonds, instead of an octet.

Hydrogen and helium: Technically can't have an octet because they only have a possibility of two valence electrons.

Beryllium and boron: Beryllium only has four valence electrons, boron has six valence electrons. A mnemonic to remember this: Boron the Moron.

Expanded valence: The d orbital can also act as valence, and this causes more than eight valence electrons. This is seen in 3rd period or below. (It is impossible for second or first period elements to have expanded valences due to their lack of d orbitals.) As examples: BrF_5 , $TeBr_4$, ICl_4^- , PCl_5 , SF_6 .

Transition metal complexes: eighteen electron rule and ligands: Transition metals have 18 valence electrons. Ligands, such as CO, Cl, NH₃, and CN will donate a certain

amount of electrons. To figure out how many ligands attach to a transition metal (in the case of M(L)n), use this formula:

$$dn + v = 18$$

Where:

- d number of valence electrons each ligand contributes (d for donated)
- n number of ligands (n for number) you are solving for this
- v number of valence electrons the metal already has (v for valence)

For example, Cr(CO)n. d = 2, v = 6. 2n + 6 = 18. 2n = 12. n = 6.

Lewis structures of organic molecules

Guidelines:

- Hydrogen atoms have 1 bond
- Carbon atoms have 4 bonds
- Nitrogen atoms have 3 bonds and 1 e⁻ lone pair
- Oxygen atoms have 2 bonds and 2 e⁻ lone pairs
- Halogen atoms have 1 bond and 3 e⁻ lone pairs

Part M

Practice exercises

1 Acid-base equilibria

Problem 1.1 Amil adds 100mL of 1.75M $HC_2H_3O_2$ into his daily juice blend. Assuming he drinks this juice blend thrice a day and his stomach pH before drinking the juice is 2.3, what is the pH of his stomach after all three juices were swallowed? (Amil's stomach can hold 1L of liquid. He has 50mL of stomach acid. Assume he fills up his stomach completely and nothing flows into his duodenum between drinking each juice.)

Problem 1.2 DK adds 3.50M of NH_4Cl into his daily juice blend. Assuming he drinks this juice blend once a day and his stomach pH before drinking the juice is 2.1, what is the pH of his stomach after he swallows the juice? (DK drinks 100mL of ammonium chloride per cup, and his stomach can hold 1L of content. He has 50mL of stomach acid. Assume he fills up his stomach completely. Remember stomach acid is HCl.)