CHEM10004 NOTES

L 1-2: Intro to Quantum Mechanics and Light

Quantum Mechanics

When we're talking about quantum mechanics in chemistry we're usually talking about describing electrons by looking at them as a wave. (Though this also involves looking at the properties of light).

Quantum Mechanics is used to describe bonds, protein functions, spectroscopy, orbital shapes, periodic table trends, and loads more. When you get down to the absolute fundamentals, all of chemistry is quantum mechanics.

This lecture introduces the concept of waves with particular reference to the nature of light.

Light's Wave-Particle Duality

Simply put, light is weird. Some of its behaviour is characteristic of a particle (a "photon"), while in other circumstances it is treated as a wave. As such, these notes will talk about light as a wave, then about light as a particle.

Light as a Wave

Light has several "wave-like" properties, but probably the most notable is that light has a frequency (ν - s^{-1}) and a wavelength (λ - m).

Frequency is number of oscillations per second, wavelength is distance per oscillation. You can multiply the two together to find the wave speed.

$$c = \nu \cdot \lambda$$

The wave nature of light also means that light waves can interfere with one another, either constructively or destructively, diffract, and create "Speckle Patterns" when reflected off a rough surface. However, some properties of light needs to be explained by a particle model.

The Particle Nature of Light

Light behaves like a particle in a number of circumstances. A photon is a discrete packet of light, with a specific energy, that can be calculated using this formula:

$$E = h \cdot \nu \quad \text{or} \quad E = \frac{h \cdot c}{\lambda}$$

- Where h is Planck's Constant, which is = $6.626 \times 10^{-34} Js$

You can use this to determine the number of photons emitted by a light source over a certain time period, provided you know its power and efficiency.

You can also use this to determine whether the energy from a mole of photons (An "Einstein" of photons) is greater than the molar bond formation energy of a certain bond. If it is, then the light can potentially cause a chemical reaction by shining on the chemical.

The Photoelectric Effect

We mentioned that photons have discrete quantities of energy, rather than just being a constant beam of energy. A consequence of this is that if the energy required to cause a chemical reaction is higher than the energy provided by a certain frequency of photon, then no matter how intense the light is, that chemical reaction will never proceed.

This is particularly relevant to the "**Photoelectric effect**", which is the chemical process by which light, when shined on a metal, gets absorbed, and causes the metal to eject electrons.

However, the energy required to eject an electron differs depending on the metal.

- This means that each metal has a minimum frequency of light: a "Threshold Frequency", ν_0.

How fast the electron is ejected (Its kinetic energy) depends on the frequency of the incident photon. As shown on the graph on the below, the energy will be zero for all frequencies below the threshold frequency, and increase linearly for all frequencies above the threshold frequency.

This gives rise to the formula:

$$E_k = \frac{1}{2}mv^2 = h\nu - E_{bind} = h\nu - h\nu_0$$

De Broglie Wavelengths

We have just shown that a wave can mathematically be considered to be a particle with momentum.

The physicist Louis De Broglie showed that the reverse is also true, and that any object with mass and velocity can be treated as a wave.

This can be demonstrated with a really simple rearrangement of the formulas we used with the Compton Effect:

$$\text{As } p = mv = mc, \quad m = \frac{h}{c\lambda} \implies p = \frac{h}{\lambda} \quad \text{and} \quad \lambda = \frac{h}{mv}$$

- Where units for $p = kgms^{-1}$, $v = ms^{-1}$, and $m = kg$

The wavelength we're calculating here is the "De Broglie Wavelength". The theory states that any object with mass and velocity will behave like a wave and have a De Broglie Wavelength, and this is true.

For example:

- A car (800 kg, 20m/s) has a De Broglie wavelength of 4.1 x 10^{-38} m.
  - This is not very wavelike.
- An electron (E_k = 1.6 x 10 J) has a De Broglie wavelength of 1.23 x 10^{-19} m.
  - This is wavelike.

This demonstrates that everything can act as a wave, and the lighter the object the more wavelike it is.

Whether or not light will interact with an object as a particle or a wave depends on that object's size.

If the wavelength is much smaller than the object (eg. gamma waves hitting a building) the light tends to act as a particle.

If the wavelength is much bigger than the object (eg. AM radio waves hitting a person) then it will act like a wave.

However, we know that there are colours which exist outside the visible light spectrum, so isn't it possible that hydrogen could absorb these wavelengths of light too?

Other physicists with more advanced equipment checked, and it turns out hydrogen does absorb other wavelengths. This means that n doesn't stop at 7 in the series, we just can't see the wavelength for n=8 because it's in the UV spectrum. However this series remains fixed between wavelengths of 656 nm (n=3) and 365 nm (n=∞), so there can't be any absorption lines outside this range according to this series.

But there ARE absorption and emission lines outside this spectrum, they're just invisible too. Other series were added to the Balmer Series over time by other physicists, but they all obey a similar formula to the first one.

They simply change the "2" into a different number, and start n at that number +1.

For example, there is the Lyman Series or the Paschen Series:

$$\frac{1}{\lambda} = hR_H(\frac{1}{1^2} - \frac{1}{n^2}) \quad where \quad n = 2,3,4,... \quad (Lyman \quad Series)$$

$$\frac{1}{\lambda} = hR_H(\frac{1}{3^2} - \frac{1}{n^2}) \quad where \quad n = 4,5,6,... \quad (Paschen \quad Series)$$

Johannes Rydberg eventually realised that these single-variable equations simply represented different versions of the same double-variable equation, which is now called the Rydberg Formula:

$$\Delta E = -hR_H(\frac{1}{n_f^2} - \frac{1}{n_i^2})$$

Where:

- n_f is the ‘final energy level’
- n_i is the ‘initial energy level’

However, the question still remains, what do these numbers represent?

L 7-8: Intro to Kinetics: Rate Laws.

This lecture introduced chemical kinetics, the second half of the physical chemistry section.

What is Chemical Kinetics?

Chemical Kinetics is very very similar to Thermodynamics, which we did last semester. However while thermodynamics was focused on whether a reaction would happen at all, kinetics is concerned with how FAST a reaction happens.

This goes above and beyond what thermodynamics could tell us; because while thermodynamics predicts stuff like diamond spontaneously turning into graphite, kinetics shows us that that process is so slow it can basically be considered to not happen at all.

The primary thing kinetics is interested in is the reaction rate

Reaction Rates

The rate of a reaction (How fast if happens) is calculated as

$$Rate = \frac{\Delta\ Concentration}{\Delta\ Time} \qquad Units = mol\ L^{-1}\ s^{-1}$$

(There are many other units used, as the concentrations and times you measure could be more convenient as another unit, like minutes or hours. However the SI unit is $mol\ L^{-1}\ s^{-1}$)

The rate can also be defined as the gradient of the concentration/time graph:

$$Rate = \frac{dc}{dt}$$

The actual concentration you measure can be any of the products or reactants. HOWEVER, these formulas (usually) don't take stoichiometry into account, so if you had the reaction:

$$H_2O \ \rightleftarrows \ 2H_2 + O_2$$

The concentration of hydrogen would change at twice the rate of oxygen.

This means that you may need to take stoichiometry into account when doing these calculations. The stoichiometrically adjusted formula is, for:

$$aA + bB \rightarrow cC + dD$$

The rate is:

$$Rate = \frac{-1}{a}\frac{d[A]}{dt} = \frac{-1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

The Rate Equation

Reaction rates are related to concentrations by the “Rate Equation”:

$$Rate = k[A]^a[B]^b[C]^c$$

Where:

- [A] is the concentration of the reactants (Not the products).
- A is NOT necessarily the stoichiometric coefficient, these are the ‘kinetic order coefficients’.
- k is the ‘rate constant’

Kinetic order coefficients can be any real number; and while they're usually positive integers, they can be negative, or even fractional.

If a reactant A has a kinetic order coefficient of a=1, we say that the reaction is "First Order Dependent" on A, if a=2, the reaction is "Second Order Dependent…”, and so on.

The kinetic order of the whole reaction is equal to the sum of the coefficients.

$$Order = a + b + c + \dots$$

For example, if the rate equation is:

$$Rate = k[A]$$

Then, we have a first order reaction.

If the equation is:

$$Rate = k[A]^2 \qquad or \qquad Rate = k[A][B]$$

We have a second order reaction.

If the reaction is just

$$Rate = k$$

We have a ‘zeroth order’ reaction (Which is possible).

The most common reactions you'll see are first and second order. Other orders are possible, just very rare.

Half Lives of 0th order reactions

Integrated Rate Law for 0th order: $[A]_t = [A]_0 - kt$

Half life equation for 0th order: $t_{\frac{1}{2}} = \frac{[A]_0}{2k}$

Half Lives of 1st order reactions

Since a first order reaction will follow the rule:

$$ln(\frac{[A]_0}{[A]_t}) = kt$$

And

$$\frac{[A]_0}{[A]} = 2 \qquad at \quad t_{1/2}$$

The half-life of a 1st order reaction can be calculated with the equation:

$$t_{1/2} = \frac{\ln(2)}{k}$$

So, half-life of a 1st order reaction does not depend on the concentration of reactants.

Half Lives of a 2nd order reactions

Second order reactions follow the rule:

$$\frac{1}{[B]} = 2kt + \frac{1}{[B]_0} \qquad \text{And} \qquad \frac{[B]_0}{[B]} = 2 \qquad at \quad t_{1/2}$$

So,

$$\frac{2}{[B]_0} = 2kt_{1/2} + \frac{1}{[B]_0}$$

Which rearranges to:

$$t_{1/2} = \frac{1}{2k[B]_0}$$

L 13-14: Organic Reactions and Acidity

Basically, a reaction can happen in one of two ways:

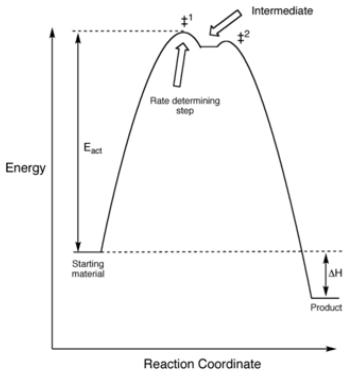
Firstly, there can be a collision between the reactants, and the products form instantaneously from the broken reactants. The bond breaking and formation occur simultaneously. This is called a "Concerted" or a “Synchronous” reaction.

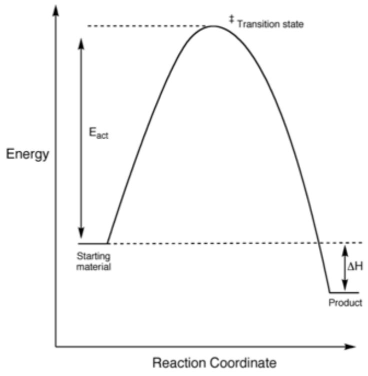
Secondly, there can be a collision between the reactants, and then an intermediate state is formed. That intermediate state then reacts again to form the products. This is called a "Stepwise" reaction.

$$A + B \ \ (Reactants) \rightarrow C \ \ (Intermediate \ \ State) \rightarrow D + E \ \ (Products)$$

There is a difference between the reaction energy pathways for synchronous and stepwise reactions.

While the synchronous reaction pathway is smooth (Shown on the right), the stepwise reaction pathway has two bumps, for the initial formation of the intermediate state, and the formation of the products (Shown on the left).





When a bond breaks between two atoms it can do so in one of two ways.

Firstly, the electrons in the bond can be shared between the two atoms, like this:

$$A - B \rightarrow A^{\bullet} + B^{\bullet}$$

This is called “Homolytic bond breaking" and it creates two radicals, which are very reactive

Alternatively, the more electronegative atom can take **both** of the electrons:

$$A^{\delta+} - B^{\delta-} \rightarrow A^{+} + B^{-}$$

This is called "Heterolytic bond breaking"

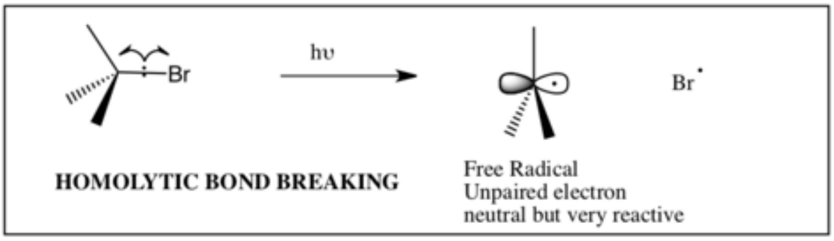
When describing processes like these, we're interested in the movement of electrons. This can either be the movement of a pair of electrons, or a single electron.

To show this on diagrams we use special arrows called "Mechanistic arrows".

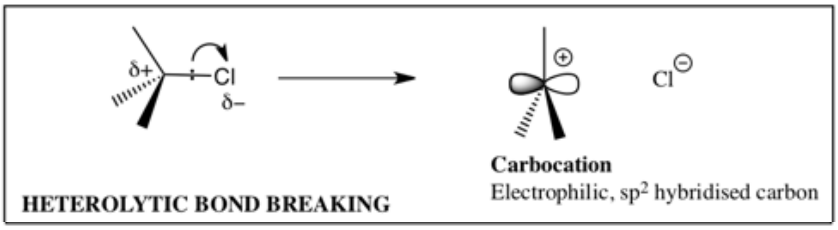
To indicate the movement of a pair of electrons, we use a full-headed arrow:

To indicate movement of a single electron, we use a single-headed arrow:

For example, we could use mechanistic arrows to indicate homolytic bond cleavage:



Or heterolytic bond cleavage



Just a side note on the CH_3^+ carbon compound we just created:

It's called a "Carbenium ion", and it's a member of the "Carbocation" group (Carbon based cations). It's a very unstable atom as it does not have a full octet. It is sp^2 hybridised, with an empty p-orbital. Because it has an empty orbital and an incomplete octet (It is "electron deficient"), carbenium is an electron-loving molecule. It is an "electrophile".

L 15-16: Nucleophilic Substitution

First Order Nucleophilic Substitution (S_N1): For step-wise reaction mechanism

The first, more simple way is a "First order reaction" (Also sometimes called a "Unimolecular" reaction).

It is called a "first order" reaction because if you measured the rate of reaction, it would be proportional to the product of ONE of the reactants (The one with the leaving group.)

$$Rate \propto [C-LG]$$

If you look at the reaction coordinate of this type of reaction, there are two 'humps' or energy barrier. The first one is the rate determining step, because the reaction rate is dependent on this step (forming the carbocation). Hence, the rate law is only 1st order reaction despite the reaction being a 2-step process.

There is a notation for classifying reactions, and for a first order nucleophilic substitution reaction it is:

S_N1

Where:

- "1" stands for "First order"
- "N" stands for "Nucleophilic",
- "S" stands for "Substitution reaction"

Second Order Nucleophilic Substitution (S_N2): For concerted reaction mechanism

The second order reaction is "Second order" because its rate is proportional to the concentration of both compounds: the nucleophile AND the carbon.

$$Rate \propto [C-LG][Nu:^{-}]$$

The reason for this (though it might seem counterintuitive) is that while a first order reaction involves two steps, and second order only needs one. To understand more about what's happening in an S_N2 reaction, consider the direction the nucleophile approaches from. We'll assume the leaving group is attached to a methyl carbon.

(It's also important to remember that the sp^3 orbital is not 100% one-sided, it has a small free area on the opposite side to the bond it's involved in.)

The Nernst Equation

We will now extend electrochemistry by determining the relationship between E° and the thermodynamics cell quantities such as ΔG° (Gibbs free energy) and K (the equilibrium constant).

In galvanic cells, chemical energy is converted into electrical energy, which can do work.

The electrical work is the product of the charge transferred multiplied by the potential difference (voltage):

$$\text{Electrical Work} = \text{Volts} \times \text{Q(charge in coulombs)} = \text{J}$$

The charge on 1 mole of electrons is given by **Faraday's constant** (*F*)

$$F = \frac{6.022 \times 10^{23} \ e^-}{mol} \times \frac{1.602 \times 10^{-19} \ C}{e^-} = 9.648 \times 10^4 \frac{C}{mol} = 9.648 \times 10^4 \frac{J}{V \cdot mol}$$

$$\text{Total charge} = (\text{number of moles of e}^-) \times F = zF$$

In this equation, z is the number of moles of electrons for the balanced oxidation-reduction reaction. The measured cell potential is the maximum potential the cell can produce and is related to the electrical work by:

$$W = -zF \cdot E_{cell}$$

The negative sign for the work indicates that the electrical work is done by the system (the galvanic cell) on the surroundings.

The free energy is defined as the energy that was available to do work. In particular, the change in free energy was defined in terms of the maximum work (W_{max}), which, for electrochemical systems, is W.

$$\Delta G = W_{max} = W$$

$$\Delta G = -zF \cdot E_{cell}$$

We can verify the signs are correct when we realise that z and *F* are positive constants and that galvanic cells, which have positive cell potentials, involve spontaneous reactions. Thus, spontaneous reactions, which have $\Delta G < 0$, must have $E_{\text{cell}} > 0$.

This provides a way to relate standard cell potentials to equilibrium constants, since

$$\Delta G^\circ = -RT \ln(K)$$

$$-zF \cdot E^\circ = -RT \ln(K) \implies E^\circ = \frac{RT}{zF} \ln(K)$$

Most of the time, the electrochemical reactions are run at standard temperature (298.15 K). Collecting terms at this temperature yields

$$E^{\circ} = \frac{(8.314\frac{J}{K \cdot mol})(298.15K)}{z(96{,}485\frac{J}{V \cdot mol})} \ln(K) = \frac{0.0257V}{z} \ln(K)$$

where z is the number of moles of electrons. For historical reasons, the logarithm in equations involving cell potentials is often expressed using base 10 logarithms (log):

$$E^{\circ} = \frac{0.0592\ V}{z} \log(K)$$

Thus, if ΔG°, K, or E° is known or can be calculated, the other two quantities can be readily determined.

Now that the connection has been made between the free energy and cell potentials, nonstandard concentrations follow. Recall that

$$\Delta G = \Delta G^{\circ} + RT\ \ln(Q)$$

where Q is the reaction quotient. Converting to cell potentials:

$$-zF \cdot E_{cell} = -zF \cdot E^{\circ}_{cell} + RT\ \ln(Q) \implies E_{cell} = E^{\circ}_{cell} - \frac{RT}{zF} \ln(Q)$$

This is the **Nernst equation**. At standard temperature (298.15 K), it is possible to write the above equations as:

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0592\ V}{z} \log(Q)$$

With the Nernst equation, it is possible to calculate the cell potential at nonstandard conditions.

The equation is INCREDIBLY useful. You can use this to build "Concentration Cells", calculate equilibrium constants, or work out concentrations of ions (Including H^+ ions in pH meters) and etc.