

## 0.1 Chemistry Lectures Grade 12 IB

### 0.1.1 Energetics

#### 0.1.1.1 What is Energy

To introduce the concept of energy, we will first introduce the idea of “work”.

In physics work is defined as:

$$W = \vec{F} \cdot \vec{d}$$

Where:

$W$  - work done by applying force on some object.

$\vec{F}$  - force you apply to an object (Newtons)

$\vec{d}$  - the distance the object travels (in the direction of applied force) while the force is applied (m)

Example of person pushing box.

Person pushes box w. force of 3 Newtons for 1 meter - Introduce units. Before box at rest, now box moving with some given speed.

The box “changed states” (rest to moving)

We therefore define change in energy as:

**Definition 1** *Change in energy  $\Delta E$  between two states, is the work required to go from one state to another.*

States (not gas or liquid) but state of being. But what are these states in chemistry?

Consider the following examples. Have:



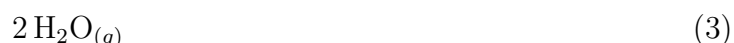
4 Hydrogen and 2 oxygen atoms (both in gaseous state (just floating around)).

The same atoms can also be in the following configuration:



Verify this is same number of atoms, however now they are bonded in some specific way (not the same configuration as above).

Everyone is also familiar with the following configuration



Notice that we can also have the water as a liquid (and that is quite different from water as a gas)



These are examples, of different states the same molecules in (1) can be in.

What is the change in energy going from one state to another?

From our definition, work required to “push” the atoms together to get these bonds (force of pushing the atoms multiplied by the distance they are pushed).

\*Note that energy change scales linearly with how many molecules are pushed together.

Also have the idea of energy difference per mol (if react 1 mol of this, what would the change in energy be there be).

### 0.1.1.2 Hess’ Law

Suppose given some configurations  $A, B, C$  of the same atoms, we want to find the energy difference between states  $A$  and  $B$ . We don’t know the energy difference between  $A$  and  $B$ , but we DO know the energy difference between  $A$  and  $C$  and  $B$  and  $C$ .

You could set up a complicated and expensive experiment to measure it directly.

This however turns out to be unnecessary because Hess’ Law holds

**Hess’ Law:** *Sum of changes in energy of going from configuration  $A$  to  $C$  and  $C$  to  $B$ , is equal to the change in energy of going from  $A$  to  $B$ .* (Diagrams commute)

Problems of computing changes in energy simply come down to finding a path through states where the changes in energy are already known.

### 0.1.1.3 Enthalpy

From now on, instead of calling it energy change/difference, refer to it as “Enthalpy” of a given reaction and denote it with  $\Delta H$ .

(Note that enthalpy / energy change only associated with the reaction, not the state itself).

Go back to initial question of finding Enthalpy going from configuration of Molecules  $A$  to  $B$ .

Need to find suitable reactions for which enthalpy is known!

Let’s list these reactions

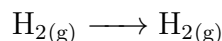
Type of Reaction (its associated enthalpy)	Description	Example
Bond dissociation	Take reactants and break all of their bonds (left with just atoms)	$\text{H}_2\text{O}_{(\text{g})} \longrightarrow 2\text{H}_{(\text{g})} + \text{O}_{(\text{g})}$
Formation $\Delta H_f$	Given a target product, assemble it from its constituent elements in their standard form at STP (E.G. If has hydrogen in it, $\text{H}_{2(\text{g})}$ is a reactant, as at room temp and pressure hydrogen is always in $\text{H}_{2(\text{g})}$ )	$\text{H}_{2(\text{g})} + \text{O}_{2(\text{g})} \longrightarrow \text{H}_2\text{O}_{(\text{l})}$
Combustion	Reactants react w. oxygen, producing $\text{CO}_2$ with water	$\text{CH}_{4(\text{g})} + 2\text{O}_{2(\text{g})} \longrightarrow 2\text{H}_2\text{O}_{(\text{g})} + \text{CO}_{2(\text{g})}$
Vaporization	Reactant turns from liquid to gas	$\text{H}_2\text{O}_{(\text{l})} \longrightarrow \text{H}_2\text{O}_{(\text{g})}$
Lattice	Reactant is ionic solid. To make product, break reactant into individual ions in gaseous form	$\text{NaCl}_{(\text{s})} \longrightarrow \text{Na}_{(\text{g})}^{+} + \text{Cl}_{(\text{g})}^{-}$
Electron Affinity (name of enthalpy)	Reactant gains an electron	$\text{Cl}_{(\text{g})} + \text{e}^{-} \longrightarrow \text{Cl}_{(\text{g})}^{-}$
Ionization	Remove an electron from reactant in gaseous state	$\text{Na}_{(\text{g})} \longrightarrow \text{Na}_{(\text{g})}^{+} + \text{e}^{-}$
Sublimation	Reactant goes from gas straight to solid	$\text{H}_2\text{O}_{(\text{g})} \longrightarrow \text{H}_2\text{O}_{(\text{s})}$
Fusion	Reactant goes from solid to liquid	$\text{H}_2\text{O}_{(\text{s})} \longrightarrow \text{H}_2\text{O}_{(\text{l})}$
Hydration	Water is attached to a reactant	$\text{Li}_{(\text{aq})}^{+} + 4\text{H}_2\text{O}_{(\text{l})} \longrightarrow \text{Li}^{+}(\text{H}_2\text{O})_{4(\text{aq})}$

Table 1: Note that the enthalpies associated to these reactions are called [type of reaction] Enthalpy E.G. Combustion Enthalpy, Lattice Enthalpy etc. Exception: Electron Affinity is the name of the enthalpy rather than the reaction. There are tables for these enthalpies in your data booklet (enthalpy of formation found in “Selected Compounds - Thermodynamic data”).

Let's consider some examples, where compute enthalpies of some given reaction, by finding a way to get from reactants to products using steps in Table 1.

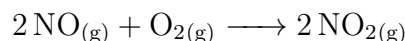
1) What is the enthalpy of formation of  $\text{H}_{2(\text{g})}$ ?

Well what reaction is the enthalpy of formation associated with?



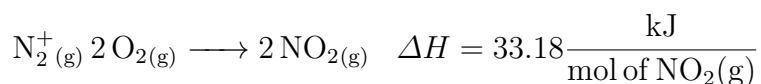
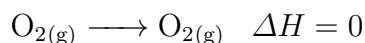
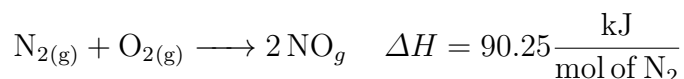
Did anything happen? No!  $\Rightarrow \Delta H = 0$

2) Compute enthalpy of following reaction



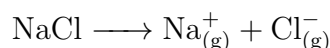
Propose another "indirect" path to get from reactants to products. \*Balancing is key (2 mols, so multiply by 2).

Have steps:



$$\Delta H = -2 \cdot 90.25 + 2 \cdot 33.18 = -114.1 \frac{\text{kJ}}{\text{mol O}_2}$$

3) Find enthalpy of



Break into elements, then molecules (change states if needed), then ionize then bring back.

#### 0.1.1.4 Calorimetry

Great. But how would we measure an enthalpy experimentally (to fill up our tables?)

Enthalpy often is related to a release in heat. So we should try and measure that.

Introduce endothermic & exothermic and what will be "felt" by the surrounding environment in each case. Introduce temperature:

**Definition 2** *Temperature of an object is the measure of the average kinetic energy of a particle in an object.*

Note that:

$$E_k = \frac{1}{2}mv^2 \quad (5)$$

Where:

$E_k$  - kinetic energy of object

$m$  - mass of object

$v$  - speed of object

\*Temperature is not exactly equal to the kinetic energy, but it is proportional to it (this fact will be useful later).

From physics, get this formula gives exactly work required to do to speed something of mass  $m$  up from rest to speed  $v$  (so do have an absolute 0). \*Make remark that this is still not “absolute” energy.

But how is change in temperature of an object really correlated with change in energy? Turns out on the macro scale, do not worry about average over molecules etc and the following relation works:

$$\Delta Q = mc(T_f - T_i) \quad (6)$$

Where:

$\Delta Q$  - change of energy in object

$m$  - mass of object

$c$  - constant representing how much energy is required to heat up 1 kg of this type of object by 1 degree

$T_i$  and  $T_f$  - initial and final temperatures

Show that this choice of  $T_i$  first is good for endothermic exothermic things etc.

So idea is. To figure out change in enthalpy, we measure change in temperature of the reactants/products. This can sometimes be quite difficult (gasses etc. are weird). So we have a trick!

Place reaction inside water and observe the change in temperature of water. Claim:  $\Delta Q_{reaction} = -\Delta Q_{environment}$

Using this, we design a coffee cup style calorimeter.

Calorimeter has following assumptions

- All heat absorbed by water
- No heat is absorbed by the calorimeter
- No heat transfer to the outside
- Concentration of reactants much smaller compared to water
- I think there is a fifth one, I forget

Introduce method for correcting for all of these going wrong using graphs.  
Introduce 3 kinds of systems

- Open
  - Exchanges mass and energy with surroundings
- Closed
  - Exchanges energy, not mass with surroundings
- Isolated
  - Exchanges neither energy nor mass with surroundings

Gibbs free energy as non-expansive work done by system (energy not used to expand stuff).

Motivate energy diagrams for reactions. Say, hey we have initial energy and final energy.

Maxwell- Boltzman Distribution Diagram (area under curve from  $a$  to  $b$  gives probability that a given particle is traveling with speed between  $a$  and  $b$ ). Stress that only for gasses, but still useful when thinking about energy.

$$f(v) = \frac{4}{\sqrt{\pi}} \left( \frac{m}{2k_b T} \right)^{\frac{3}{2}} v^2 e^{\frac{-mv^2}{2k_b T}} \quad (7)$$

Where:

$f(v)$  - Boltzman distribution function for an ideal gas with particles of mass  $m$  at temperature  $T$

$v$  - individual speed of particle

$k_b$  - Boltzman constant (some number)

Use it to explain “middle” of energy diagram for limiting rate of reactions.

## 0.1.2 Chemical Kinetics

### 0.1.2.1 Math Detour

You got two baskets. You are picking balls out of the first one, and then the second one. How many possible pairs can you pick.

Now consider  $n$  baskets (do the underline stuff).

### 0.1.2.2 Transition from Energetics to Chem. Kinetics

Before this moment, we looked at chemical reactions as a way from getting from one state of arrangements of atoms to another. We characterized the transition itself with a “change in energy”, and mostly looked at a “before” and “after” states of the reaction. We did not really what is going on during the reaction.

Let’s come up with a description of a chemical reaction to build a mathematical model.

### 0.1.2.3 What happens during a chemical reaction

Need to motivate postulates:

Think of a reaction as molecules colliding. Recall that a reaction is either breaking bonds, or making new ones. So two things need to either fly into each other so that one of them breaks or they stick together.

1) Things react by colliding.

Start off by thinking of them as little balls flying around. Imagine that to break something / force two things to stick together need to have enough force.  $\Rightarrow$  Fly in strong enough, need enough momentum  $\Rightarrow$  need enough kinetic energy (as the two are related).

2) Even if two things collide, need sufficient energy for reaction to take place (Activation Energy link).

Now think of what could affect particle's energy - Temperature (cause literally by definition)

Now recall vesper exists. Particles can look weird and different.  $\Rightarrow$  might need to hit that specific bond so it gets knocked off  $\Rightarrow$  the required geometry for each reaction plays a part.

Now think about collisions themselves:

If particles are spread apart (or there are not that many of them), then reaction doesn't go as fast (cause more difficult for things to collide into each other).

$\Rightarrow$  concentration of our things also affect the rate of reaction.

Now think of some practical ideas. In industry etc. it is very often useful to understand/predict how fast a chemical reaction can / will take  $\Rightarrow$  can we find an equation, for how fast a chemical reaction will be moving along given some initial conditions (and can we then use that to predict, how much product will be made after  $t$  time).

We can rephrase the question above as:

#### ***What is the rate of a reaction?***

First recall what the rate of reaction is: how much product/reactant is produced per second (like speed). Note that if you had a function of how much reactant you have at a time, it is the derivative of that function.

From above, we know that the rate of a reaction depends on temperature, on the reaction's geometry, its activation energy as well as what collides in the reaction.

Our equation we will come up with, for the rate of a reaction, must therefore "answer" all of these questions. The first 3 are quite difficult, so start with the last one.

Let's see how exactly, the stuff that "collides" in a reaction actually affects its rate.

Keep exploring this question with an example. Suppose have the following reaction:



Let's try and come up with an equation for how many particles successfully react per second (rate

of reaction), for this reaction. Start off by using the fact above of what is reacting.

$m$  particles of  $A$  collide, and  $n$  particles of  $B$  collide and all stick together.

An approach we could take, is list all of the possible reactions that COULD happen, and take the percentage of the ones that DO happen.

Similar to the taking balls out of baskets, imagine have two baskets with particles  $A$  and particles  $B$ .

First pick out of basket w.  $A$  (has  $[A]$  prticles) and basket w.  $B$  (has  $[B]$ ) particles. Get:

$$[A]([A] - 1) \dots ([A] - m + 1) \cdot [B]([B] - 1) \dots ([B] - n + 1) \approx [A]^m [B]^n \quad (9)$$

Now thinking about the number of particles in the entire reaction, may not be too useful. We can rephrase the question in terms of concentration. This is good for 2 reasons:

You can have lots of particles, but they are all clumped up in a single area (so that would mess things up).

You can have mixtures with different numbers of particles, but same concentrations. In this case if we express everything into concentrations, we can then easily convert to number of particles (and don't ever have to account for the volume in which they are in), but if we dealt with just the number of particles then we would somehow have to account for how they are spaced out (in some different way).

Formulating everything in terms of concentration is still the same as # of particles, but now just looking at number of particles in a single litre.

So return to idea: is list all of the possible reactions that COULD happen, and take the percentage of the ones that DO happen. Simply relabeling our equation above for  $[A]$  to mean concentration of  $A$  and  $[B]$  for  $B$  respectively, get the same as equation (9).

This gives us the total number of ways the particles can collide. Now we could come up w. something fancy to give us the percentage of collisions that do take place and are successful (but its complicated). So for now just slap a constant  $k$  representing that percentage that we will claim to get experimentally (quite poor physics but excellent chemistry).

$$r = k[A]^m[B]^n \quad (10)$$

Mention units of  $k$  and how it has to account for all of the kewl factors from above.

Define the order of the reaction and stuffs.

#### 0.1.2.4 “Edge Cases”

- Solids - surface area
- Gasses - pressure



### 0.1.2.5 So what is this mysterious k factor

Have arrhenius eqn:

$$k = A \cdot e^{-\frac{E_a}{RT}} \quad (11)$$

Where:

$E_a$  - activation energy of reaction

$R$  - universal gas constant

$T$  - temperature (IN KELVIN!!!)

$A$  - Arrhenius constant (responsible for geometry or something o-rather)

Makes sense because something something Maxwell-Boltzman distribution, looks kinda similar, git gud.

Now rate law looks like:

$$r = Ae^{-\frac{E_a}{RT}} [A]^m [B]^n \quad (12)$$

### 0.1.2.6 Concentration after time t

We now got kewl eqn for rate. So now let's solve for concentration after time  $t$  for simple examples and see what it looks like (and how to test for it).

$$r = k[A]$$

$$r = k[A]^2$$

$$r = k[A]^0$$

Talk about how graphs look like.

### 0.1.2.7 Reaction Mechanisms

Throw 10 erasers and have them all hit each other at once. Unlikely  $\Rightarrow$  reactions happen in steps.

How do we compute rate law for this? (Answer when get to equilibrium).

### 0.1.2.8 Problems

Solve some a sample problem where given concentrations (initial and final) (or rate), figure out what kind of rate law it is.

Draw a graph and see how it would change if temperature changed etc.

### 0.1.2.9 Misc

Energy diagrams for multi-step reactions