

# Foundatin Chemistry

## Contents

<b>1</b>	<b>Structure and Bonding</b>	<b>09/10/17</b>	<b>3</b>
<b>2</b>	<b>Structure of the atom</b>	<b>10/10/17</b>	<b>6</b>
<b>3</b>	<b>Physical/ Inorganic Titration</b>	<b>16/10/17</b>	<b>7</b>
<b>4</b>	<b>Molecular Forces</b>	<b>23/10/17</b>	<b>8</b>
<b>5</b>	<b>Chemical Reactions: Equations and formulae</b>	<b>30/10/17</b>	<b>10</b>
<b>6</b>	<b>Redox reactions and the Electrode potential</b>		<b>12</b>
6.1	Competition for Electrons . . . . .		12
6.2	Half Cells and Cell Voltages . . . . .		12
6.3	Standard Hydrogen Half Cell . . . . .		13
6.4	Cell Potentials . . . . .		14
6.5	Why We Care . . . . .		15

## Introduction

All lectures will take place within the Great Hall and all practicles shall take place in lab C18. This can be accesed from the left hand corridor of Engineering Central. All notes are available on the Blackboard.

## Recommended Reading

- Chemistry : molecules, matter, and change / Peter Atkins, Loretta Jones

## Testing

There will be tests on Blackboard throughout the year which will make up 10% of the final mark. There will also be two practicals, each worth 7.5%, and a final end-of-year test worth 75%

# 1 Structure and Bonding

09/10/17

**Atomic number (Z)** - The number of protons in an atom's nucleus

**Atomic mass ( $A_r$ )** - The number of protons and neutrons within an atomic nucleus

**Isotopes** - The same element (so the same Z) but with a different  $A_r$ , meaning more neutrons within the nucleus

**Volatile** - Evaporate at normal (room) temperatures and pressures

**Semiconductor** - A material with an electrical conductivity less than a conductor, such as copper, but greater than an insulator, such as glass. Their resistance decreases as temperature increases, which is the opposite of how metals behave.

The  $A_r$  displayed on some Table of Elements is a decimal as the  $A_r$  is the average of all isotopes of that element. For example, 99% of naturally occurring carbon is  $^{12}\text{C}$  and 1% is  $^{13}\text{C}$ , meaning that:

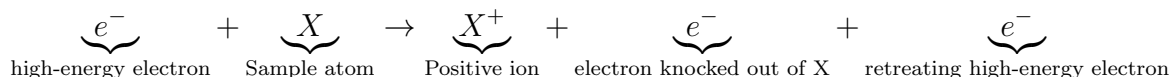
$$\begin{aligned}A_r(\text{C}) &= \frac{99}{100}(12) + \frac{1}{100}(13) \\ &= 12.011\end{aligned}$$

## Mass Spectrometer

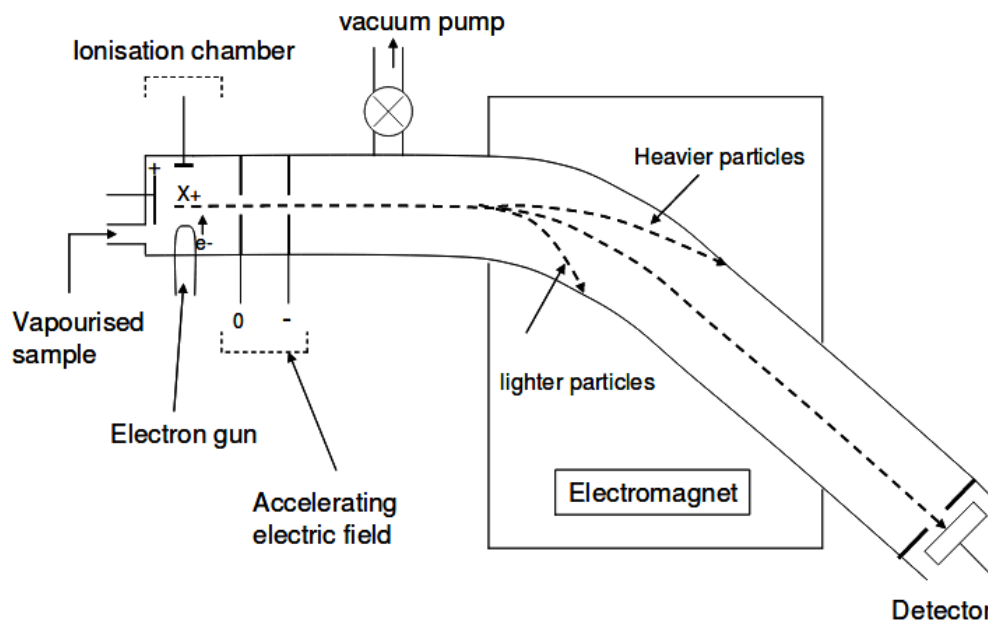
A mass spectrometer is used to measure the atomic mass of an element. This is a five step process.

1. The sample is vapourised
2. The vapour is bombarded by an electron beam, ionising it positively
3. The ions are accelerated by an electric field. The strength of this field is known
4. The ions are deflected by a magnetic field. The strength of this field is known
5. Ions are detected by a plate

Volatile samples are injected into the ionization chamber, while involatile samples are first vapourised with pre-heating. The mass spectrometer is held under vacuum. In the ionisation chamber when the electrons collide with the vapourised atoms the electron stream can knock electrons out of the outer shell.



The positive then pass through holes in two charged plates, accelerating the ion forwards. These ions pass through the magnetic field generated by the electromagnet and are deflected dependant on their mass. Constant electric and magnetic fields are applied so only ions of a particular mass are deflected to the ion detector. Lighter ions are deflected the most while heavier ions are deflected more. Therefore gradually increasing the magnetic or electric field allows ions of different masses to hit the detector. Masses can be calculated from the known fields, but the instrument is normally calibrated with a known mass. The relative peak heights give the relative abundance of different ions present.



Molecules have more complex spectrometry graphs than atoms as they can be made of different isotopes of the same atom. For example  $\text{Cl}_2$  can be  $^{35}\text{Cl}-^{35}\text{Cl}$ ,  $^{35}\text{Cl}-^{37}\text{Cl}$ , or  $^{37}\text{Cl}-^{37}\text{Cl}$ .

## Patterns in the periodic table

The simplest classification in the periodic table is to split it into metals, metalloids, and non-metals.

**Metals** - Metals are typically lustrous solids which conduct electricity and have high melting points. They have a gigantic metallic structure and often act as reducing agents in reactions.

**Non-Metals** - Non-metals are typically solids, liquids or gasses, that have a discrete molecular structure and do not conduct electricity. They generally have low melting points.

**Metalloids** - These have characteristics between metals and non metals, being reasonably strong solids with a giant molecular structure. They are neither conductors nor insulators and have very high melting points. These materials are semiconductors.

## Groups

There is still a lot of variation within these groups so more refined groups are needed in order to make predictions about how elements will react. The elements are broken up into columns, called groups, and these are defined by the number of electrons in an elements outer shell. The number of electrons in the outer shell controls the chemical properties and the bonding to other atoms, meaning that all elements within a group react similarly. For example, when reacting with water all group 1 metals form a metal hydroxide and hydrogen gas.

Elements also belong to a certain period, which is the row in the periodic table that they are in. As the period increases reactions tend to become much more violent. For example, in group 1 Lithium, a period 2 element, gently reacts with water, while caesium, also group 1 but period 6, explodes violently.

Another pattern shown by the periods is the trend from metal to non-metal, although there are also trends in the elements chemical properties. For example, in forming oxides.

Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>2</sub>	ClO	Formula of the oxide
0.5	1	1.5	2	2.5	2	1	Number of oxygens per atom in oxides

## **2 Structure of the atom**

**10/10/17**

Most of the material in this section was covered in Fundamentals of Materials lectures 1 and 2.

The ionisation energy is the amount of energy required to displace a valence electron from an atom or ion. Using a graph of the Number of ionisations (x-axis) against the  $\log(\text{ionisation energy})$  (y-axis) we can tell how many shells an atom has and also how many atoms are in each of these shells. We can use known high energy x-rays to find ionisation energy.

### **3 Physical/ Inorganic Titration 16/10/17**

**O** xidisation

**I** s

**L** oss (of electrons)

**R** eduction

**I** s

**G** ain (of electrons)

The pattern of ionisation energy of each atom repeats each period, although tends lower as you go further down the periodic table.

## 4 Molecular Forces

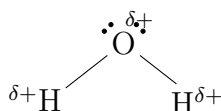
23/10/17

Intermolecular attractions are attractions between one molecule and a neighbouring molecule. Don't confuse these with intramolecular forces which hold a molecule together, such as covalent bonds. Covalent bonds are very strong while intermolecular forces are weak.

### Dipoles

Electronegativity is a measure of how strongly an atom attracts bonded electrons within a molecule. In general metals have a low value while non-metals have a higher value, so a stronger desire to gain electrons.

A high difference in electronegativity causes the atom with the higher value to pull bound electrons towards it. This causes that atom to gain a slight negative charge, while the atoms that the electrons are being pulled away from have a slight positive charge. For example:



### Hydrogen Bonding

Hydrogen bonding is a type of bonding that occurs in substances where the molecules are made up of hydrogen bonded to a highly electronegative element. This causes a dipole, as we see above in water, and the positively charged hydrogen from one molecule attracts the negatively charged element, in water's case oxygen, from another molecule. This binds the molecules together with a relatively weak force.

### Van der Waals forces

Van der Waals forces are weak, short range forces between molecules that are caused by molecules becoming temporary dipoles. These temporary dipoles exist because, at any given instant, the electron cloud will not be perfectly symmetrical. As we move along the groups and down the periods of the periodic table these forces become stronger.

These forces are weaker in small, simple molecules like  $\text{CH}_4$ , but in large molecules with many contact points they are substantial, such as in polymers like polythene.



This causes a problem for ideal gas laws, as they assume that gas molecules do not exert force on each other. However, at standard pressures and temperatures these forces are not significant and so can be ignored.

Graphite is carbon allotrope, meaning there are different forms of the same element in the same state (eg graphite, diamond). Within layers there are strong covalent bonds, while between layers there are weak Van der Waals forces. This allows the layers to slide over each other, acting as a solid lubricant.

## **Giant Molecular Materials**

Metallouids form giant structures in their compounds, undergoing covalent bonding to give full outer shells. These bonds are incredibly strong, meaning they have:

- High melting points
- Hard and rigid
- Some semiconductive properties
- Insoluble in all types of solvents

## 5 Chemical Reactions: Equations and formulae

30/10/17

Molecular Mass of a molecule is the sum of the atomic weights. For example,  $\text{CaCO}_3 = 40 + 12 + (3 * 16) = 100 \text{ gmol}^{-1}$

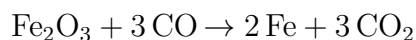
$$\text{Number of Moles}(n) = \frac{\text{Mass}(kg)}{\text{Molecular/ Atomic Weight } (mw/aw)}$$

So, in 4Kg of limestone ( $\text{CaCO}_3$ ) there are  $\frac{4000}{100} = 40$  moles.

$$\text{Concentration} = \frac{\text{Number of Moles}(n)}{\text{Volume } (dm^3)}$$

Note that  $dm^3$  is equivalent to a litre so concentration is often given with the units ( $\text{mol L}^{-1}$ ).

Calculate the mass of a product from a known mass of reactant: Fe extraction from its ore by CO, How much iron if we start with 10Kg of ore?



$$\begin{aligned} \text{Molar Ratio} &= \frac{2 \text{ mols Fe}}{1 \text{ mol Fe}_2\text{O}_3} \\ n(\text{Fe}_2\text{O}_3) &= \frac{\text{mass}}{mw} \\ &= \frac{10000}{160} \\ &= 62.5 \text{ mols of Fe} \end{aligned} \quad \begin{aligned} mw(\text{Fe}_2\text{O}_3) &= 160 \\ \text{Using molar ratio } n(\text{Fe}) &= 62.5 * \frac{2}{1} \\ &= 125 \text{ mol Fe} \end{aligned}$$

$$n(\text{Fe}) = \frac{\text{mass}}{aw} \text{ so:}$$

$$\text{mass} = n(\text{Fe}) * Am(\text{Fe}) = 125 * 56 = 7000g = 7Kg$$

### Types of reactions

#### Redox Reactions

A full equation made from two half reactions, an oxidation reaction and a reduction reaction.

**Acid base reaction**

A reaction between an acid and a base. An acid is a compound that contains hydrogen and reacts with water to form hydronium ions. Strong acids are completely ionised in solutions, while other acids do not completely ionise.

An alkali or base is a substance which produces hydroxide ions in solution. Strong bases ionise completely in solution, while weak bases do not. Metal oxides can also be bases, such as  $\text{CaO}$  which reacts vigorously with water. Some metal bases are Amphoteric, and react with both acids and bases.

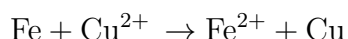
**Precipitation reaction**

A reaction between two aqueous substances that form a solid precipitate.

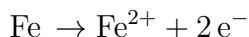
## 6 Redox reactions and the Electrode potential

### 6.1 Competition for Electrons

If you place a iron rod into a copper sulphate solution the copper plates the iron while the iron dissolves.



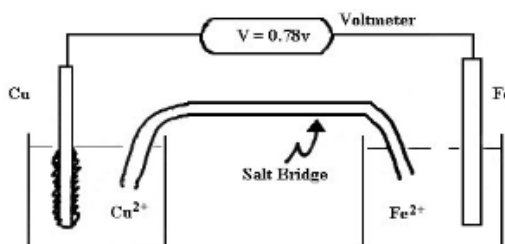
This reaction involves two half reactions, the oxidation of iron and the reduction of copper.



Iron is a stronger reducing agent than copper while copper ions are stronger oxidising agents than iron ions. This is why this reaction occurs in this way.

### 6.2 Half Cells and Cell Voltages

By physically separating these two half reactions and representing them in separate pots we now have what is known as two half cells. In each half cell we have a sample of the metal, acting as an electrode, dipped into a solution of its ions.



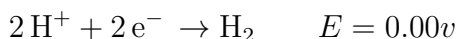
The two metal electrodes are connected using a wire and volt meter while the two solutions are connected by an ionic conductor salt bridge. Once connected, the iron begins to dissolve as it oxidises and electrons flow from the iron to the copper, where they then reduce the copper ions. The electrode that is undergoing oxidation, in this case iron, is known as the anode while the electrode that's undergoing reduction, in this case copper, is known as the cathode. As electrons are flowing between the two electrodes there must be a potential difference between them, which is known as the electrode

potentials. This electrode potential is a direct measure of the ability of a metal, or material, to be oxidised or reduced. In this case the electrode potential ( $E$ ) is 0.78v.

### 6.3 Standard Hydrogen Half Cell

If different half cells are used then a wide range of potentials are possible. This isn't helpful for comparing the relative strength of reactants, but is the main principle behind modern batteries.

In order to compare different reactants a standard is needed, hence the use of the standard hydrogen half cell. In this half cell the half reaction is the reduction of hydrogen ions to hydrogen gas.



The standard hydrogen half cell is a plated platinum electrode which is in contact with 1 mol per dm<sup>3</sup> acid solution and hydrogen gas at 1atm pressure at a temperature of 298K, which is room temperature. All other cells can then be measured with respect to this cell, keeping the concentration of the solution and the temperature constant.

In the table below the standard electrode potentials for many systems are shown, each expressed as reduction reactions. If you wish to use these potentials but the material is being oxidised the sign for the  $E$  needs to be change (eg positive to negative).





Consider potassium ions as oxidising agents



This tells us that is it extremely difficult to convert potassium ions to potassium metal as potassium ions are very poor oxidising agents. If we reverse the reaction we also reverse the sign of the electrode potential

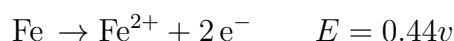
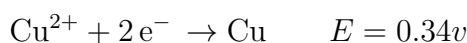
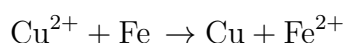


This tells us that potassium metal is an extremely strong reducing agent and will give up an electron quicker than a catholic girl. This means that potassium metal is a very poor choice for structural applications as it will react violently with many substances.

TABLE 18.1		Standard Reduction Potentials at 25°C	
	Reduction Half-Reaction	$E^\circ$ (V)	
<p>Stronger oxidizing agent</p> 	$F_2(g) + 2 e^- \longrightarrow 2 F^-(aq)$	2.87	<p>Weaker reducing agent</p> 
	$H_2O_2(aq) + 2 H^+(aq) + 2 e^- \longrightarrow 2 H_2O(l)$	1.78	
	$MnO_4^-(aq) + 8 H^+(aq) + 5 e^- \longrightarrow Mn^{2+}(aq) + 4 H_2O(l)$	1.51	
	$Cl_2(g) + 2 e^- \longrightarrow 2 Cl^-(aq)$	1.36	
	$Cr_2O_7^{2-}(aq) + 14 H^+(aq) + 6 e^- \longrightarrow 2 Cr^{3+}(aq) + 7 H_2O(l)$	1.33	
	$O_2(g) + 4 H^+(aq) + 4 e^- \longrightarrow 2 H_2O(l)$	1.23	
	$Br_2(l) + 2 e^- \longrightarrow 2 Br^-(aq)$	1.09	
	$Ag^+(aq) + e^- \longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	0.77	
	$O_2(g) + 2 H^+(aq) + 2 e^- \longrightarrow H_2O_2(aq)$	0.70	
	$I_2(s) + 2 e^- \longrightarrow 2 I^-(aq)$	0.54	
	$O_2(g) + 2 H_2O(l) + 4 e^- \longrightarrow 4 OH^-(aq)$	0.40	
	$Cu^{2+}(aq) + 2 e^- \longrightarrow Cu(s)$	0.34	
	$Sn^{4+}(aq) + 2 e^- \longrightarrow Sn^{2+}(aq)$	0.15	
	$2 H^+(aq) + 2 e^- \longrightarrow H_2(g)$	0	
	$Pb^{2+}(aq) + 2 e^- \longrightarrow Pb(s)$	-0.13	
	$Ni^{2+}(aq) + 2 e^- \longrightarrow Ni(s)$	-0.26	
<p>Weaker oxidizing agent</p> 	$Cd^{2+}(aq) + 2 e^- \longrightarrow Cd(s)$	-0.40	<p>Stronger reducing agent</p> 
	$Fe^{2+}(aq) + 2 e^- \longrightarrow Fe(s)$	-0.45	
	$Zn^{2+}(aq) + 2 e^- \longrightarrow Zn(s)$	-0.76	
	$2 H_2O(l) + 2 e^- \longrightarrow H_2(g) + 2 OH^-(aq)$	-0.83	
	$Al^{3+}(aq) + 3 e^- \longrightarrow Al(s)$	-1.66	
	$Mg^{2+}(aq) + 2 e^- \longrightarrow Mg(s)$	-2.37	
	$Na^+(aq) + e^- \longrightarrow Na(s)$	-2.71	
	$Li^+(aq) + e^- \longrightarrow Li(s)$	-3.04	

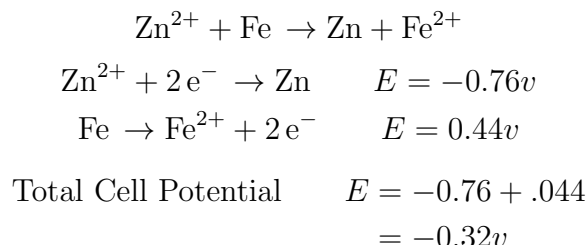
## 6.4 Cell Potentials

Consider again the cell made from the copper electrode and the iron electrode dipped into molar ion solutions. If we look at the table then we can see the stronger oxidising agent has reacted with the stronger reducing agent to form a weaker reducing agent and a weaker oxidising agent. A positive cell potential means the reaction will occur, while a negative potential means the reaction is very unlikely to occur.



$$\begin{aligned} \text{Total Cell Potential} \quad E &= 0.34 + .044 \\ &= 0.78v \end{aligned}$$

Consider if we replaced the copper cell with a zinc cell



This means that the reaction would actually occur in reverse, with the zinc dissolving and the iron forming. When working out cell potentials do not multiply half cells by the stoichiometry, as it only effects the current flowing, not the potential difference.

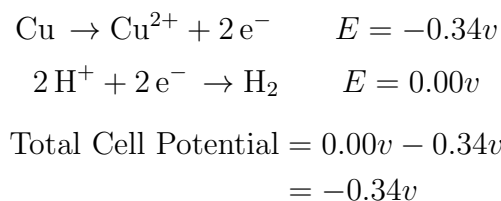
## 6.5 Why We Care

### Predicting the success of a reaction

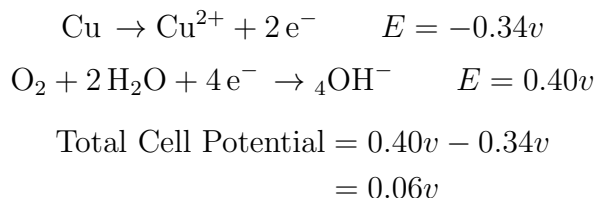
As shown above we can use electrode potential to predict whether a chemical reaction will occur. This is helpful, although it gives no indication of the speed of the reaction.

### Corrosion Reactions

The anode reaction for a metal is  $\text{M} \rightarrow \text{M}^{n+} + n\text{e}^-$  and the cathode reaction for an acidic solution is  $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ , while under normal pH the cathode reaction is  $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$ . We can use these to predict whether a metal will corrode either in acid or in normal pH levels by finding the Total Cell Potential of the reaction. For example, for copper in acidic solution



So copper will not corrode in acid. In a normal pH



So copper will corrode in a normal pH solution.

## Corrosion Protection

One of the main ways of protection metals from the damaging effects of corrosion is by galvanising. In this method a more electropositive metal is used in a more electropositive will corrode in preference to the other metal which will act as the cathode. Zinc is often applied as a coating or a sacrificial anode to protect iron from corrosion.

## Plating

Some metals will plate naturally onto iron (copper, silver etc) and this can be used as a method of metal recovery as well as plating. Zinc is often plated onto iron, although this will not plate directly from solution since the electrode potential for the reaction is negative. There are two ways to force this reaction; the first is to dip the iron into molten zinc (hot dipped galvanising) and the second is to make the iron very negatively charged. This will attract zinc ions in solution to the iron cathode if the potential of the metal is more negative than zincs reduction potential. This plating mechanism is used in the manufacture of high quality automotive steels.

## Extraction

Different metals have different ease of extraction. For example, gold is found as a pure metal, copper is easy to extract by heating its sulphide ore, iron requires the use of chemical reducing agen and aluminium can only economically be extracted by electrolysis. This is reflected in the electrode potentials for the different metals

