Fundamentals of Materials (EG-080)

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Introduction

Lecturer Dr Shirin Alexander, available in room 204 ESRI building. Office hours are Friday 1-3pm, although she needs to be emailed before you turn up.

0.1 Recommended Reading

- Chemistry: molecules, matter, and change / Peter Atkins, Loretta Jones.
- General Chemistry E2 *Free*Aie by BELLAMA
- Engineering materials 1: an introduction to properties, applications and design / Michael F. Ashby and David R. H. Jones.
- Materials science and engineering : an introduction / William D. Callister, Jr.

0.2 Testing

There will be three Blackboard tests, worth a total of 25%, each test being worth 8%, 9%, and 8% respectively. There will also be a final exam in January worth 75%

03/10/2017

1 Atoms and Elements

Matter - Has volume and mass

Substance - A pure form of matter, containing only a single type. For example, pure water

Element - A substance composed of a single kind of atom

Isotope - An atom with the same atomic number but a different molecular weight

Homogenous Mixture - A solution that will naturally seperated if left

Heterogeneous Mixtures - A mixture of substances that require a physical technique to seperate

1.1 Atomic Configuration

Proton Mass (Positive) = 1.67×10^{-24} Neutron Mass (Neutral) = 1.67×10^{-24} Electrons (Negative) = 9.11×10^{-28}

 $^{A}_{Z}X$

Where:

- **Z** Is the atomic number, the number of protons
- **A** Is the atomic weight, the total number of protons and neutrons
- **X** Is the atomic symol

Quantum numers for an atoms electrons can be used to calculate properties of the electrons, such as their energy

- n Principal quantum number (or Shell number) represents the energy of the electron. The greater n, the higher the shells energy level and the weaker it's bound to the nucleus
- 1 Orbital angular quantum number. This specifies the shape of the orbital
- \mathbf{m}_l Magnetic quantum number. This specifies the indivdual orbital of a particular shape and is also associated with the orbital direction

The number of electrons that an occupy a single shell is $2n^2$

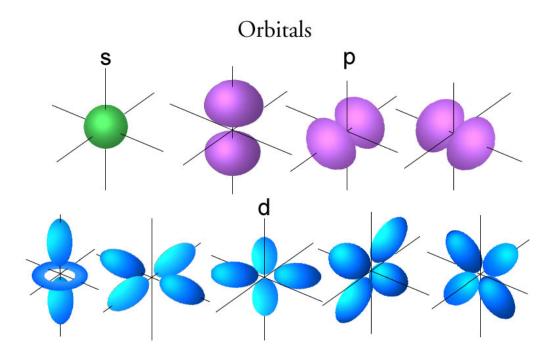


Figure 1: The different possibilities for s, p, and d orbitals

1.2 Implications of Quantum Physics

- Electrons can only occupy discrete orbitals
- Orbitals have different energies, shapes and directions
- There are only a maximum of 2 electrons per orbital (spinning opposite ways)
- Electrons will fill empty shells first before doubling up
- Orbitals are clouds of probablility, not true orbits
- Orbitals can be represented using a number for the energy level and a letter for the shape. For example 1s, 2p, 3d

Electrons in electron shells can be represented using written notation. For example, $Mg = 1S^22S^22p^63S^2$. This can be written shorthand by using the previous nobel gas to represent complete shells. For example, $Mg = [Ne]3S^2$

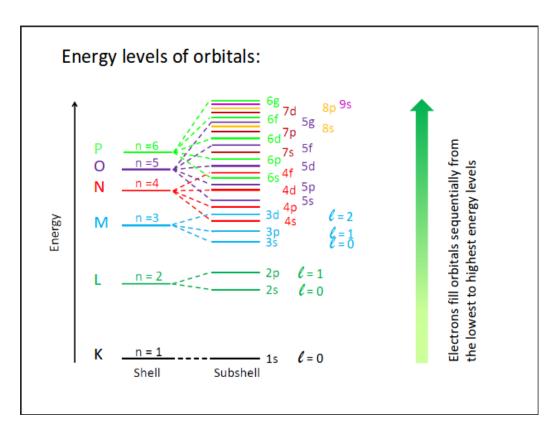


Figure 2:

How to fill orbitals?

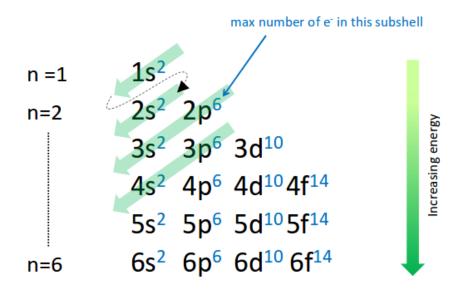


Figure 3:

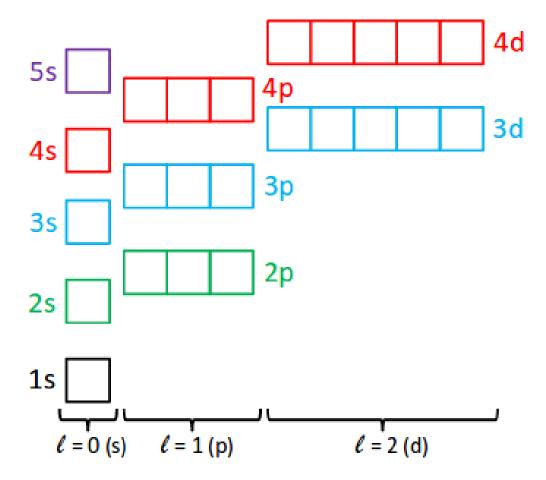


Figure 4: This diagram can be used to show how electrons fill shells. Within each row electrons will always g to an empty box before filling a box completely. These boxes represent the different options withing each shell layer (reference Figure 1)

23	24	25	26	27	28	29
V	Cr	Mn	Fe	Co	Ni	Cu
50.94	52.00	54.94	55.85	58.93	58.71	63.54
3d ³ 4s ²	3d ³ 4s ¹	^{3d³4s²}	3d ⁶ 4s ²	3d ⁷ 4s ²	3d*4s²	3d ¹⁰ 4s ¹
41	42	43	44	45	46	47
Nb	Mo	Tc	Ru	Rh	Pd	Ag
92.91	95.94	98.91	101.07	102.91	106.4	107.87
4d ⁴ 5s ¹	4d ⁵ 5s ¹	4d ⁵ 5s ²	4d ⁷ 5s ¹	4d*5s1	4d ¹⁰	4d ¹⁰ 5s ¹
73	74	75	76	77	78	79
Ta	W	Re	Os	Ir	Pt	Au
180.95	183.85	186.2	190.2	192.2	195.09	196.97
4f ¹⁴ 5d ³ 6s ²	4f ¹⁴ 5d ⁴ 6s ³	4f ¹⁴ 5d ⁵ 6s ²	4f ¹⁴ 5d ⁶ 6s ²	4f ¹⁴ 5d ⁷ 6s ²	4f ¹⁴ 5d ⁹ 6s ¹	4f ¹⁴ 5d ¹⁰ 6s ¹

Figure 5: These are the exceptions to these rules. They may ask about the highlighted ones

2 Atomic Bonding

The Valence Electrons (VE) of an atom are the electrons in the outer shell of an atom, so are the ones involved in forming bonds to adjacent atoms. Lewis symbols and be used to show the valence electrons in an atom. For example, ••.

Atoms aim to gain stability by gaining or losing electrons with an aim to gain the same electronic configuration of the closest (in terms of atomic number) noble gas. The interaction of atoms through chemical bonding leads to an overall decrease in the energy. The energy is stored as potential energy.

Ionic and covalent are terms used to describe two extremes of chemical bonds. In most substances the bonds lie between purely covalent or covalent. When describing bonds between non-metals covalent bonding is a good metal, while when the bond is between metals and non-metals ionic bonding is a good model.

2.1 Ionic Bonding

Ionic bonding occurs when one atom looses at least one electron from its valence band to another atom to gain stability. Atoms that undergo ionic bonding become positively/ negatively charged.

Salt, NaCl

$$\begin{array}{ll} \mathrm{Na} = 1s^2, 2s^2, 2p^6, 3s^1 & \mathrm{Na} \boldsymbol{\cdot} \\ \mathrm{Cl} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^5 & \boldsymbol{\cdot \ddot{C}l} \boldsymbol{\cdot} \end{array}$$

For Na and Cl the third shell holds the valence electrons. Na loses one electron while Cl gains it, producing Na⁺:Cl̄:

Ionic solids tend to stack together in regular crystalline structures as the charged electrons in the molecule atract to the other charged atoms in other molecules. This strong electrostatic attraction between oppositely charged ions in ionic solids accounts of their typical properties such as high melting and boiling points, as well as brittleness.

When an ionic solid is hit the positive ions that normally line up with negative ions now line up with positive ions, forcing the lattice apart. This is why ionic solids are brittle.

In the lattice strong coulomb forces ionically bond each Na⁺ ion to six neighbouring Cl⁻, meaning it takes a lot of energy to break all of these bonds. This accounts for the high melting and boiling points.

The ionisation energy of an atom increases as its position in the periodic table moves down and to the right. This is based on the distance of the nucleus to the valence shell.

2.2 Covalent Bonding

Covalent bonding occurs when pairs of valence electrons are shared between two atoms. This means that neither atom gains or loses any charge. Nonmetal elements tend to interact via covalent bonding (instead of ionic) because their ionisation energy is too high.

Covalent bonds are very strong; it takes a large amount of energy to seperate atoms bonded in this way. For example, diamond is 100% covalent bonds, while graphite is only partially covalent.

Hydrogen

$$H = 1s^2$$
 $H \cdot \cdot H$

Hydrogen wants to be as stable as the closest noble gas, Helium. The sum of attractive electrostatic forces (nucleus \leftrightarrow electrons) and repulsive electrostatic forces (electron \leftrightarrow electron, nucleus \leftrightarrow nucleus) it overall attractive therefore bonding occurs.

$$H \cdot \cdot H \rightarrow H : H \rightarrow H \longrightarrow H$$

Here the two hydrogen atoms share their bond, resulting in a single covalent bond being formed.

Water

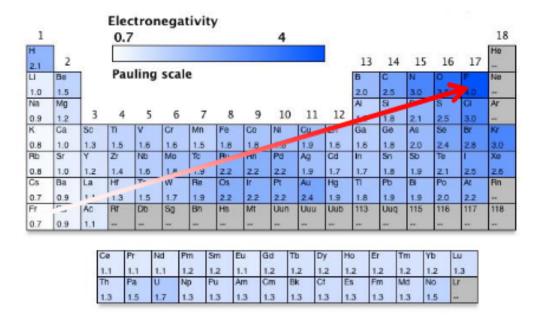
H =
$$1s^2$$
 H· O = $1s^2, 2s^2, 2p^4$; $\dot{\bigcirc}$:

H·· $\dot{\bigcirc}$ ··H → H: $\ddot{\bigcirc}$: H ≡ H — $\ddot{\bigcirc}$ — H

The presence of the doublet of negative electrons the two hydrogens are squeezed together as the two doublets repel from each other. This force results in water having a bond angle of 104.5°. The oxygen atom pulls on the shared electrons in each hydrogen, meaning one side of the molecule is positively charged and the other side is negatively charged. This means it is a polar molecule.

In liquid water these partial charges cause weak electrostatic attraction between molecules, called hydrogen bonds, that keep the molecules together.

2.3 Electronegativity



Electronegativity defines the power of an atom in a bond to draw electrons from the other atom. We can use the difference in electronegativity between two elements to predict the most appropriate bonding model for a chemical bond between them. In general, if the electronegativity difference, \mathbf{x} , between the two elements is:

$$x \geq 1.7 \to \text{Ionic Bond}$$

$$x < 0.5 \to \text{Covalent Bond}$$

$$0.5 \leq x < 1.7 \to \text{Polar Covalent Bond}$$

17/10/17

3 Metallic Bonding

Delocalisation - When an electron is freed from its orbital

Malleable - Can be pressed to form sheets

Ductile - Can be stretched to form wires

Metallic bonding can be explained according to the Drude model, which is a simplistic model. It was developed to explain the transport of electrons in metals, although does not explain all of their electronic properties.

The drude model assumes a 'sea of free, vibrating, electrons' which are rebounding off of heavier, relatively immobile ions. Valence electrons are free to drift through the entire metal as they are not bound to any single atom, while the nonvalence electrons and the atomic nuclei form the ion cores. When metallic atoms come close the valence electrons become delocalised as orbitals overlap and lose energy. This loweres the overall energy and holds the atoms together, forming the sea of free electrons, or "Drude Glue".

3.1 Metallic properties within the Drude model

Partially explains melting points

The overall energy is lowered significantly when the atoms are close together so a lot of energy needs to be added to seperate them. The electrons are homogeneously shared, meaing there is a strong bonding between metal atoms. This gives metals their solid structure.

The more outer electrons an atom has the more "Drude Glue" there is between atoms, meaning there is a higher melting points, although this is only true to a certain extent. Some examples:

- Sodium $(1s^2, 2s^2, 2p^6, 3s^1)$: 98° C
- Magnesium ([Ne] $3s^2$): 650° C
- Aluminium ([Ne] 3s², 3p¹): 660°C

There are exeptions to this, such as mercury ([Xe] 4f¹⁴, 5d¹⁰, 6s²) which has very weak atomic interaction, so very little Drude Glue.

Explains conductivity

The outer electrons are free to move so can carry electric charge (current). Also, the more valence electrons there are the higher the conductivity. Valence electrons also carry heat through vibrations, so metals are good thermal conductors.

Explains shininess

When a photon of light hits a metal surface, knocks an electron up to one of the many empty orbitals of a higher energy. This electron is unstable so drops back down, re-emitting the energy as a photon identical to the first. This is called reflection.

Explains malleabitily

Metallic bonding is non-directional, so atoms can move along slip planes by a small a amount. As long as the atoms stay close together the metallic bonds stay in place, meaning metals can be deformed.

19/10/17

4 Introduction To Metals

Smelting - A process where metals are extracted from an ore by using a combination of heat and a reducing agent.

Monoatomic - A stable molecule composed of a single atom (such as nobel gases)

4.1 Crystalline vs Amorphous

- Atoms in a crystalline material are in a repeating/ orderly array over large atomic distances.
- All metals (and many ceramics) form crystalline structures
- Amorphous materials are characterised by no/very little ordering of their atoms. Their layout is random

Crystalline materials have a small energy difference between the conduction band and the valence band, while amorphous materials have a large energy difference. This is why amorphous materials are insulators, while crystaline materials are conductors or semiconductors.

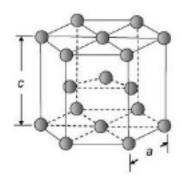
4.2 How atoms in a metal stack

There are three main ways in which atoms stack -

- Hexagonal close packing (hcp)
- Cubic close/ face-centered cubic packing (ccp/fcc)
- Body-centered cubic packing (bcc)

This stacking controls the ductility, electronic and magnetic properties of metals.

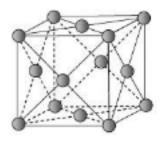
- Coordination Number The number of near neighbours, at equal distance, to a central atom in a crystal
- Packing Density The fraction of space filled by the atoms (assuming the atoms are perfect spheres)
- **Unit Cell -** The smallest hypothetical unit that when stacked together repeatedly with no gaps will produce an entire crystal



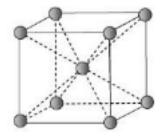
Hexagonal Close Packing (HCP)

- Each atom is surrounded by 6 others in each layer
- Coordination number of 12
- $\bullet~74~\%$ packing density
- 3 slip systems
- Examples Magnesium, Zinc

Cubic Close Packing (CCP)



- Each atom is surrounded by 6 others in each layer
- Coordination number of 12
- 74 % packing density
- 12 slip systems (4 slip planes, 3 directions)
- Examples Aluminium, Copper, Gold



Body Centred Cubic (BCC)

- More open structure
- Coordination number of 8
- 68 % packing density
- 48 slip systems (but planes are not closely packed, so more force is required)
- Examples Iron, Sodium, Potassium

4.3 Slip in metals

Metals deform in planes, with one plane of atoms sliding over another plane. Atoms want to stay as close to eachother as possible, meaning slip is easiest on closely packed planes in closely packed directions.

A slip system describes the set of symmetrically identical slip planes and the associated family of slip directions for which dislocation motion can easily occur and lead to plastic deformation.

HCP

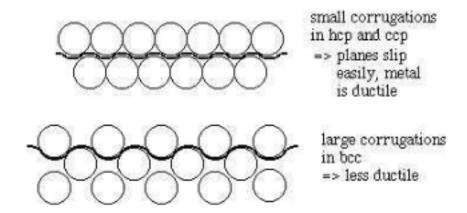
HCP has only one close packed plane, with three directions, so three slip systems. This means it is limited to slipping only if force is applied in certain directions. In most cases, it is quite brittle.

CCP/FCC

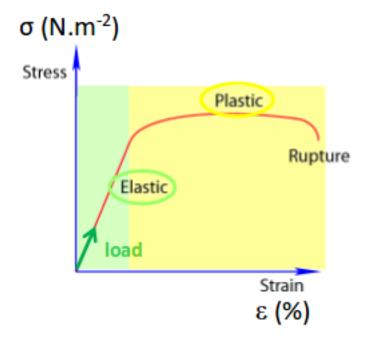
CCP has four close packed planes, each with three close packed directions, so 12 slip planes. It can slip in many arrangements, meaning it is ductile.

BCC

BCC has the most slip systems (up to 48) but the planes are not tightly packed, meaning a higher force or higher temperature is needed.



4.4 Plastic vs Elastic Deformation



Elastic deformation is one is which stress and strain are directly proportional. The deformation is also reversible. The equation for elastic deformation is

$$\sigma = E\epsilon$$

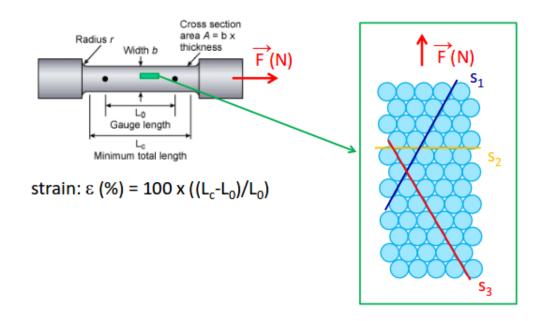
Where:

 $\sigma = Stress$

E =Young's modulus

 $\epsilon = \operatorname{Strain}$

Plastic deformation is one in which stress and strain are no longer proportional. This deformation is not reversible.

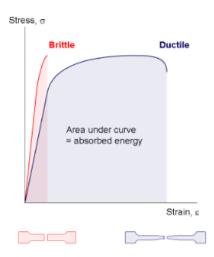


4.5 Ductile vs Brittle

Ductility - A measure of the extent of plastic deformation a material can sustain before fracture; a ductile metal can be stretched into a wire without breaking

Malleability - The ability of a solid to deform under pressure

Brittle - A material is brittle is it fractures at less than $\sim 5\%$ strain



Brittle metals have very clean breaks when they fracture, while malleable metals will deform and tear before they break.

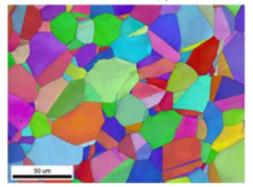
Metals can change from ductile to brittle, for example below $912^{\circ}\mathrm{C}$ Iron and steel transform from CCP to BCC, from ductile to brittle.

5 Properties of metals

5.1 Metallic Grains

As a metal starts to solidify crystals start growing in many different directions. These crystals merge, giving the metal a grain structure. Every grain has its own crystalline orientation.

Figure 6: Orientation map of an Inconel 600 superalloy sample (Ni-based corrosion resistant alloy)



EBSD is magic! (Electron Back-Scattered Diffraction analyses) Each colour corresponds to a specific grain orientation. How pretty!

Slip is difficult across a grain boundary. Smaller grains means more boundaries, reducing slip so forming a harder/ stronger metal. Small grains can be obtained by fast cooling, use of a chemical agent (such as a very strong acid), or through phhysical treatment, like ultrasounds.

Reducing slip in a metal makes the metal harder, normally stronger, but sometimes more brittle. There are two ways to make it harder for atoms to slip, these are:

- Alloying
- Decreasing the grain size

Alloying

Alloy - An alloy is a metallic sub-

stance which is composed of two or more elements with a metallic structure.

A mix of differently sized atoms makes it harder for atoms to slip over each other, the the more alloying the harder it is for atoms to slip. For example:

Mild steel -0.15% Carbon Malleable and ductile (tubes, round bars etc.)

Cast iron - 4% Carbon Much harder and brittle Used for rolled structural sections Used in foundaries to make complex objects

Interstitial alloying is where the alloying atoms fit between the metal atoms, such as carbon in steel. Substitutional alloying is where the alloying atoms replace the other metal atoms, such as in Brass with Copper and Zinc.

Decreasing the grain size

Grain size can be decreased through chemical treatment, such as an acid wash, or through the use of ultrasound as the metal solidifies. Smaller grains notmally lead to stronger metals, although in high temperature applications, such as in a jet turbine, small grains are actually unwanted. This is because a T-induced slip or failure can occur along grain boundaries. For these applications, it is better to reduce the density of grain boundaries, ideally aiming for a single crystal microstructure, meaing the metal is a single crystals, therefore has no grain boundaries.

5.2 Advanced Materials

Metallic Glass

This is a metal but with a disordered, non-crystalline structure, the same as glass. This provides high strength, high elastic limit, high corrosion resistance, resistance to scratches, dents, or wear. It does however make the metal brittle, although less brittle than mineral glass (normal glass, SiO₂).

Shape-Memory Alloys

This is an alloy that 'remembers' its original shape, so that when it is deformed it returns to its original shape upon heating. These alloys have applications in industries such as automobile, aerospace, and robotics.

5.3 Choosing a Metal

There are five main things to consider when deciding if a metal is appropriate for use. These are:

- Is it suitable for the task (strength, chemical stability)?
- Is it abundant as an ore?
- Is it easy to extract and purify?
- Is it cheap (This is a combination of the above two)?

6 The Chemical Behaviour of Metals 26/10/17

How stable and how easy to extract a metal is is mainly determined by oxidation and reduction. These are the most common types of chemical reaction and they normally occur together, with one chemical oxidising while another reduces. This is a redox reaction, and the system hosting both the reactions is called a redox system

6.1 Oxidation

Oxidation is a chemical reaction associated with a loss of electrons (remember OIL RIG). Within our environment this normally involves oxygen, although not always. Any chemical which causes oxidation is known as an oxidising agent. Metal corrosion is an oxidation reaction.

Examples:

$$Metal \rightarrow Metal^{n+} + ne^{-}$$

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-}$$

6.2 Reduction

Reduction is a chemical reaction associated with the gain of electrons (again, remember OIL RIG). Any chemical which causes the reduction of another is known as a reducing agent. The extraction of metals from ores is done through the reduction of metals.

Examples:

$$\begin{aligned} \operatorname{Metal}^{n+} + \operatorname{ne}^{-} &\to \operatorname{Metal} \\ \operatorname{Cu}^{2+} + 2\operatorname{e}^{-} &\to \operatorname{Cu} \\ \operatorname{Al}^{3+} + 3\operatorname{e}^{-} &\to \operatorname{Al} \end{aligned}$$

7 Electrochemical Potential

Electrochemical potential is an alternative way of measuring the oxidising/reducing power of elements. It is a measure (J/ mol) of the chemical potential of a compound which takes electrostatic forces into account.

It can be used to understand; the use of electricity to extract metals, corrosion, batteries, and fuel cells. It also provides another way to predict the occurrence of redox chemical reactions.

7.1 Standard Potential

The standard potential is an electrochemical potential which measure the ability of compounds to oxidize/ reduce other compounds in comparison to the $\mathrm{H^+/H_2}$ redox couple under standard conditions. Standard potential ($\mathrm{E^0}$) is in volts and the sign and magnitude is an indication of a substance to act as a reducing or oxidizing agent.

$$2 H^{+} + 2 e^{-} \rightarrow H_{2}(g) = 0V$$

	Standard	Potentials at 25 °C		
	Reduction Half-Reaction		E° (V)	
Stronger	F ₂ (g) + 2 e ⁻	> 2 F⁻(aq)	2.6/	Weaker
oxidizing	H2O2(aq) + 2H*(aq) + 2e*	> 2 H ₂ O(I)	1.78	reducing
agent	MnO (ag) + 8 H*(ag) + 5 e-	Mn2+(aq) + 4 H2O(I)	1.51	agent
A	Cl ₂ (g) + 2 e ⁻		1.36	
4	Cr20,2 (aq) + 14 H*(aq) + 6 e		1.33	
	O2(g) + 4H*(aq) + 4e*	> 2 H ₂ O(I)	1.23	
	Br ₂ (aq) + 2 e ⁻	> 2 Br*(ag)	1.09	
	Ag *(aq) + e*	→ Ag(s)	0.80	
	Fe3*(aq) + e*	> Fe ²⁺ (aq)	0.77	
	O2(g) + 2H*(aq) + 2e-	> H ₂ O ₂ (ag)	0.70	
	12(s) + 2 e-	> 2 l⁻(aq)	0.54	
	O2(g) + 2 H2O(l) + 4e-	> 4 OH - (aq)	0.40	
	Cu 2*(aq) + 2 e*	→ Cu(s)	0.34	
	Sn**(aq) + 2 e*	> Sn²+(aq)	0.15	
	2 H*(ag) + 2 e-	$\longrightarrow H_2(g)$	0	
	Pb3+(aq) + 2e-	→ Pb(a)	- 0.13	
	Ni 2+(aq) + 2 e-	→ Ni(s)	- 0.26	
	Cd2+(aq) + 2e-	> Cd(s)	- 0.40	
	Fe ³⁺ (aq) + 2 e ⁻	→ Fe(s)	- 0.45	
	Zn2+(ag) + 2 e-	→ Zn(s)	- 0.76	
	2 H 2O(I) + 2 e-	→ H ₂ (g) + 2 OH ⁻ (aq)	- 0.83	_
	Al 31(ag) + 3 e-	> AI(s)	- 1.66	
Weaker	Mg24(aq) + 2 e"	→ Mg(s)	- 2.37	Stronger
oxidizing	Na+(aq) + e-	> Na(s)	- 2.71	reducing
agent	Li*(aq) + e*	→ Li(s)	- 3.04	agent

By convention, the standard potential is associated to a reduction reaction: $M^{n+} + ne^- \to M$ where M represents a metal. $E^0 = E^0_{red(uction)}$. This equation can be shown as $E^0_{red}(M^{n+}/M) = \text{Standard potential (V)}$. For example:

$$\begin{split} E_{\rm red}^0(Cu^{2+}/Cu) &= +0.34\,\mathrm{V} \\ E_{\rm red}^0(Zn^{2+}/Zn) &= -0.76\,\mathrm{V} \end{split}$$

If
$$E_{red}^0 > 0$$
 Then M^{n+} tends to be reduced by $H_2(g)$: $M^{n+}(aq) + H_2(g) \rightarrow M(s) + 2H^+(aq)$

If
$$E^0_{red}$$
; 0 Then M^{n+} tends to reduce $H^+(aq)$: $M(s) + 2H^+(aq) \rightarrow M^{n+}(aq) + H_2(g)$

For example:

$$Cu^{2+} + H_2 \rightarrow H^+ + Cu$$

 $Zn^{2+} + H^+ \rightarrow Zn + H_2$

For a redox reaction the total voltage produced is $E_{red} - E_{ox}$

7.2 Group Metals

Group 1

Very reactive, strong reducing agent, and soft with low melting points

Group 2

Less reactive than group 1, weaker reducing agents, they are harder and have higher melting points.

Group 3

Weaker reducing agents than group 2 and not very reactive. They are harder and have higher melting points (due to more "drude glue")

7.3 Transition Metals

Transition metals are metals with partially filled d-orbitals. This controls many properties of transition metals and make the elements all behave similarly. They generally engage in strong bonding as atoms are small and heavy. They are also not very reactive due to their valence electrons having a high

ionization energy. They have more than one oxidation state and often show catalytic activity.

8 Aluminium

Aluminium is a light-weight metal that is mechanically stronger than group one and two metals, has a higher melting point and is less reactive (as there is more 'Drude Glue'). It is the most common metallic element in the Earth's crust, and the third most abundant of all the elements, after oxygen and silicon.

8.1 Aluminium Extraction vs Iron Extraction

Aluminium is a good reducing agent, better than iron, meaning it is difficult to reduce it chemically in an economic way

$$Al^{3+} + 3e^{-} \rightarrow Al$$
 $E = -1.66v$

$$Fe^{2+} + 2e^{-} \rightarrow Fe$$
 $E = -0.44v$

For aluminium it is more economically viable to use electrolysis, in which electricity is used to force the reduction reaction.

8.2 Electrolysis

Electrolysis uses a direct current to force a non-favourable reaction to occur. Cations migrate to the cathode where they are reduced while anions migrate to the anode where they are oxidised.

Electrolysis requires the reacting material to allow movement of charged ions, however solid ${\rm Al_2O_3}$ (alumina) doesn't allow this as the atoms are in a fixed position. A solution of the material would normally be used, but alumina doesn't easily dissolve in anything. Melting the material would also work, although the metling point of alumina is 2050 °C, so this is impractical.

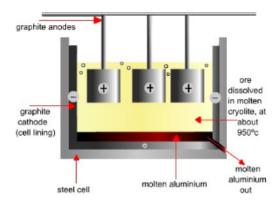
The solution is to decompose the alumina into molten cryolite (Na_3AlF_6), which occurs at about 950 °C. The flouride here lowers the melting point of the cryolite-alumina mix, allowing the alumina to dissolve in the molten cryolite, meaning it can conduct electricity.

At the graphite cathode:

$$2 \text{ Al}_2 \text{O}_3 \rightarrow {}_4 \text{Al} + 3 \text{ O}_2 \qquad E_{red} = -1.66v$$

At the graphite anode:

$$6 \,\mathrm{O}^{2-} \to {}_{3}\mathrm{O}_{2} \,(\mathrm{g}) + 12 \,\mathrm{e}^{-} \qquad E_{ox} = -0.3v$$



The lifetime of these graphite anodes is only 20-28 days, meaning that they need to be replaced every 28 days as the carbon gradually burns away and reacts with oxygen. Modern cells operate between 4.0-4.5 volts, and between 150,000 and 300,000 amps! A single cell can normally produce 1-2 tonnes of aluminium per day.

8.3 Economical considerations

Aluminium extraction is very expensive as it requires a lot of electrical power (3 moles of e⁻ to produce 1 mol of Al), meaning the plants are normally located nearby cheap electricity, such as hydroelectric. It is also costly due to the replacing of the graphite rods, the fabrication of cryolite, and the transport of bauxite (aluminium ore).

Recycling Al requires around 5% of the energy needed to extract it from bauxite, making recycling incredibly valuable. Unfortunately 58% of cans go to landfill in Europe, around 45000 tonnes of Aluminium cans go to landfill in the UK per year.

8.4 Properties of Aluminium

Aluminium has stronger bonds than group one or two metals as the atom is smaller and there is more Drude glue. This means it is harder, has a higher melting point, is more dense, and is a good conductor of heat and electricity.

9 Extraction and Corrosion of Other Metals 14/11/17

The more reactive a metal the higher its tendancy to bond with other elements, so the harder it is to extract

9.1 Group One and Two

Group one and two metals are very reactive, having only one or two valence electrons, meaning they tend to occur as salts such as sodium chloride and magnesium chloride. These metals are extracted using electrolysis as they are some of the strongest reducing agents so they can't be chemically reduced. When electrolysising these salts we must start with molten salt, not just a salt solution, such as sea water in the case of sodium chloride. This is becaise the easiest reaction (the one which requires less energy) will always occur first, so using sea water we would just reduce the water to hydrogen, not reduce the sodium.

$$Na^{+} + e^{-} \rightarrow Na$$
 $-2.71v$
 $2 H_2O + 2 e^{-} \rightarrow H_2 + 2 OH^{-}$ $0.00v$

These metals also corrode incredibly easily because of how reactive they are.

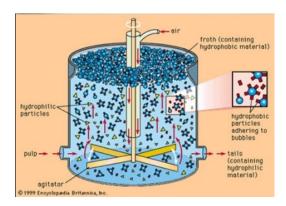
9.2 Transition Metals

Iron is the most important because of how much it is used. Nearly all of these can be etracted by chemical reduction of an ore.

Copper

Copper occurs mainly as sulphides (Cu₂S and CuFeS₂) and has a ccp structure, making it very maleable. It is also an excellent electrical and thermal conductor.

In extraction, crushed ore is separated from excess rock using froth flotation. In this process, the copper ore is mixed with water and stirred by a agitator. Air is then bubbled through, along with a small amount of alcohol which binds to the copper sulphide, allowing it to bind to the air bubbles and float to the surface where it can then be scraped off. The process is shown below.



This copper is then extracted from its ore using either high temperatures (air roasting) or using an aqueous solution with electrolysis.

Copper has catalytic properties and slowly corrodes to form a green outer later which then protects it from further corrosion. It can be used to make various alloys:

- Brass (10-50% Zinc)
- Bronze (22% Tin, 9-16% Aluminium)
- Cupro-nickel coins (with Nickel)
- Gold blends (5-30% Copper in Gold to lower the carat, making it cheaper and harder

Titanium

Titanium is a relatively abundant element, but on its own it is not very strong, although is quite light. When alloyed with tin, aluminium or vandium it has high strength and is quite ductile, meaing it's widely used for strong, tough and light alloys. However, because of the extraction process it is quite expensive.

The main titanium ores are rutile (TiO_2) and ilmenite $(FeTiO_3)$, although rutile is scarcer and more expensive than ilmenite it is more commonly used as it doesn't contain iron compounds so is easier to process. When processing rutile it is first converted to titanium(IV) chloride, which is then reduced to titanium using either magnesium or sodium.

Like copper, titanium has catalytic properties. It also should corrode but, like aluminium, forms a thin stable, self-healing, corrosion-resisitant layer of

 ${
m TiO_2}$ that protects the metal.

 ${\rm TiO_2}$ is very white so is widely used as a pigment and whitener in paint. It is as strong as steel but less dense, and can withstand very high temperatures. This gives it a lot of uses in the fabrication of aircraft, space craft and missiles.

10 Non-Metallic Elements and Compounds 19/11/17

10.1 Primary and Secondary bonds

Atoms have two types of bonds, primary and secondary bonds. Primary bonds are strong, short range and include Covalent, Ionic and Metallic bonds, while secondary bonds are weak, long range and include Polar/ Hydrogen bonds and Van der Walls bonds. Primary bonds are rarely pure bonds, and most compounds are partially one type of bonding and partially another type.

Pure Covalent

Between atoms of the same group or element

Very strong, directional bonds

Insoluble in water

Some form giant structures with

very high melting points

Others form isolated molecules with

very low melting points

Pure Ionic

Between group one, two and seven

Strong, non-directional bonds

Soluble in water

High(ish) melting points

Ionic with some Covalent

Between groups two, three (metals) and five and six (non-metals) Higher strength bonds than Ionic More directional bonds than pure Ionic

Less soluble than pure Ionic Higher metling points than pure Ionic solids

Covalent with some Ionic

Between different atoms (non-

metals)

Quite strong directional bonds

Partially soluble in water

Polar molecules

11 Secondary Bonding

The behaviour of gases is often non-ideal, meaning that the relationships between pressure, volume and temperature are not accurately described by the ideal gas law, PV = nRT.

Cohesion is used when describing intermolecular forces while adhesion is used to describe when a foreign object interacts with the molecules in a substance. These forces explain capillary action.

Surface Tension - The elastic tendency of liquids which makes them acquire the least surface area possible

Capillary Action - The ability of a liquid to flow in narrow spaces without the assistance of external forces, such as gravity

Vapor Pressure - The pressure exerted by a vapor in thermodynamic equilibrium with its condensed phases at a certain T in a closed system

Miscibility - The property of substances to mix in all proportions to form a homogenous solution (for example water and oil are immiscible as they wont mix)

Solubility - The ability for a substance, called the solute, to dissolve in a solvent

11.1 Bonding Strength

Primary Bonding

Force	Basis of Attraction	$rac{ m Energy}{ m (Kj/mol)}$	Example
Ionic	Cation-anion	400-4000	NaCl
Covalent	Nuclei-shared e ⁻	150-1100	$H\!-\!H$
	pair		
Metallic	Cations-	75-1000	Fe
	delocalised		
	electrons		

Secondary Bonding

Force	Basis of Attraction	Energy (Kj/mol)
Ion-dipole	Ion charge - dipole	40-600
	charge	
H bond	Polar bond to H ⁻	10-40
	dipole charge	
Dipole - dipole	Dipole charges	5-25
Ion-induced dipole	Ion charge- polarised	3-15
	e ⁻ cloud	
Dipole-induced dipole	Dipole charge - polariz-	2-10
	able e^- cloud	
Dispersion	polarizable e ⁻ clouds	0.05 - 40