A2 CHEMISTRY

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Feasibility of reactions

CHANGE	EXO/ ENDOTHERMIC	$\Delta S_{surroundings}$	ΔS_{system}	ΔS_{total}	WHY IS THE CHANGE SPONTANEOUS?
DISSOLVING SODIUM NITRATE IN WATER	Endothermic	Decreases	Increases because the crystalline lattice is destroyed	+ve	ΔS_{system} is larger
SODIUM METAL BURNING IN CHLORINE	Exothermic	Increases	Decreases because crystalline lattice is formed	+ve	$\Delta S_{surroundings}$
AMMONIA GAS AND HYDROGEN CHLORIDE GAS COMBINE TO GIVE SOLID AMMONIUM CHLORIDE	Exothermic	Increases	Decreases because a lattice forms	+ve	$\Delta S_{surroundings}$ is larger

Feasibility, stability and inertness

The key factors for the feasibility of a reaction are:

- The entropy change in the system
- le.co.uk The temperature measured in kelvin. This is why a cher man action that doesn't occur at room temperature may become feasible as temper
- The enthalpy change with the surroundings



Some reaction on be highly exother in the source of the so methane and oxygen, which don't ignite spontaneously at room temperature. There are different kinds of stability that can affect chemical reactions. The thermodynamic stability of a compound relative to its elements depend on the enthalpy level of the products relative to the reactants. An energy level profile diagram for an exothermic reaction can show the products as more thermodynamically stable than the reactants. A negative enthalpy of formation indicates that a compound is more stable that its elements- it must form exothermically from its elements. The ΔS_{total} tells us nothing about the rate of reaction. A high activation energy barrier may prevent a reaction starting, in such cases the reactants are said to kinetically stable or kinetically inert. Energy first must be provided to start such reactions:

- A spark
- Heat (thermal decomposition)
- Light (visible or UV)

Using entropy to explain the effect of temperature on an equilibrium constant

Exothermic and endothermic reactions both affect the entropy of the surroundings.

- For an exothermic reaction the ΔS_{surr} would be positive, i.e. entropy increases
- So $\Delta S_{total} = R \ln K$ can be written as $\ln K = \left(\frac{1}{R}\right) \times \left(\Delta S_{sys} + \Delta S_{surr}\right)$ that can then be written as: $\ln K = \left(\frac{1}{R}\right) \times \left(\Delta S_{sys} + \frac{\Delta H}{T}\right)$
- As temperature increases the magnitude of $\frac{\Delta H}{T}$ decreases
- For an exothermic reaction as T increases, $\ln K$ becomes smaller .
- For an endothermic reaction as T increases, ln K becomes larger
- The increase of ΔS_{surr} becomes less significant and the position of equilibrium shifts
- When the temperature is increases for an endothermic reaction the increase in ΔS_{sys} is the significant factor

Hence,

- Exothermic T increases K decreases
- Endothermic T increases K increases

Rates and equilibria in industry

Many of the important industrial reactions are reversible. Hence equilibrium yield, equilibrium constant Catalysts on equilibrium and rate Catalysts speed up both the forwards and backwards repeties ale.co.uk They lower the activation energy Reduce time taken to establish equilibrium and rate constant are affected by changes in reaction conditions.

Effect of catalysts on equilibrium and rate

 Reduce time taken to establish equilibrium
Effect of temperature changes on equilibrium and rate Reversible matterns are endothered in the other direction. The temperature effects on yield can be summarized as follows:

- When the enthalpy of reaction is positive, k (equilibrium constant) increases with temperature, giving more of the product
- When change is negative, k falls with temperature increase, giving more product
- Increased temperature increases rate constant k, so rate increase with increasing temperature

Effect of concentration and pressure changes on equilibrium and rate

- Adding more reactant to an equilibrium mixture accelerates the forward reaction
- As the amounts of products increase, the reverse reaction starts to speed up. A new position of equilibrium is established and the equilibrium constant remains unchanged
- The change is pressure is the same as concentration but for gases

The atom economy in industry

$atom \ economy \ (\%) = \frac{mass \ of \ atoms \ in \ desired \ product}{total \ mass \ of \ atoms \ in \ reactants} \times 100\%$

Improvement in atom economy can be done by:

- Developing an alternative more efficient synthesis, such as a catalyst with better atom economy
- Finding uses for waste products

Fuel cell breathalysers

- This device detects the chemical reaction of ethanol inside a fuel cell
- Exhaled air flows through one side of the fuel cell- platinum electrode oxidises any ethanol to ethanoic acid, releasing protons and electrons
- A meter measures the current flow
- Protons combine with oxygen on the other side of the cell, forming water



• The more alcohol in the exhaled breath the more is oxidised and the greater the current measured

Fuel cells like this still aren't as effective as IR spectroscopy and blood alcohol content from a blood sample.

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Nitration

The reaction is most effective at approximately 50° C in the formation of nitrobenzene. The electrophile is the nitronium ion, NO_2^+ formed from a mixture of conc. Nitric and sulphuric acids:

$$HNO_{3(l)} + 2H_2SO_{4(l)} \rightarrow NO_{2(sol)}^+ + 2HSO_{4(sol)}^- + H_3O_{(sol)}^+$$

Sulphuric is reformed and hence acts as the catalyst.



Above 50°C gives rise to multiple substitutions:



Sulfonation

This reaction is carried out with fuming sulphuric acid (conc. Sulphuric acid and additional sulphur trioxide). This very string acid reacts under reflux with benzene to give benzenesulfonic acid, the electrophile being sulphur trioxide. Sulfonic acids contain SO₃H group and are important computed ially in



These introduce a side chain into the benzene ring.

Alkylation

A halogenoalkane and aluminium chloride catalyst is used to add a hydrocarbon side chain to the ring. The electrophile is generated: $CH_3CH_2Cl + AlCl_3 \rightarrow CH_3CH_2^+ + AlCl_4^-$.



The catalyst is the reformed by reacting with the additional proton that is produced $H^+ + AlCl_4^- \to HCl + AlCl_3$

The reaction is endothermic and 1:7 mole ratio. What would increase yield and decrease equilibrium constant?

To increase the yield, increase the temperature so it would favour the forwards reaction to oppose the change and decrease the pressure as the reaction would favour the side with the most moles. To decrease constant, a decrease in pressure as endothermic forwards as T increase K increases.

Acid/ base equilibria

REMEMBER – look to see if it's diol, UNITS

State two approximations made in the calculations of pH.

The ionisation of the acid is negligible hence the concentration of the acid initially and the concentration of acid at equilibrium are equivalent. The concentration of H⁺ is equivalent to HA, as ionisation of water is negligible.

Why is the pH calculation of a stronger acid less accurate?

The assumption that there is negligible dissociation of the acid become invalid. As the stronger acid dissociates more

What is an appropriate indicator for a weak acid strong base reaction?

Phenolphthalein, colour change from colourless to red. As there is a vertical section on the PH curve between 6-11 and the indicator lays within that range at (8.2-10)

How does phenolphthalein at as an indicator?

It remains colourless in acidic condition and turn pink in an alkaline solutions as it forms a pink anion by loss of H⁺ ions.

pH of a strong acid decrease by I unit when diluted by scale factor of ten very decrease acid behave differently?

Equilibrium of the weak acid; $HA + H_2O \rightleftharpoons A^- + H_2O^+$, and the diduction of the acid, increase water, equilibrium shifts right resulting in a greater than expected concentration of hydrogen ions and therefore the decrease in concentration of hydrogen ion is less than expected and change in pH isn't as dramatic. **Explain how a buffer of thin works, using equations comport explanation.**

The burge contents a large reservation A and A. In the equation $HA \rightleftharpoons A^- + H^+$. On the addition of alkali the OH⁻ reacts with H⁺ to produce water and hence shifts equilibrium right producing more acid to dissociate and replaces the H⁺. On the addition of acid the H⁺ react with large reservoir of A⁻ (shifts equilibrium left to oppose the change) and hence the ration of A⁻ to HA hardly changes.

Further organic chemistry

Explain the term chiral and what feature of the molecule makes it chiral.

A chiral molecule is non-superimposable on its mirror image. The carbon atom had four different groups bonded to it.

What's the difference between the two mixtures containing chiral molecules giving rise to a different in optical activity?

In the mixture A it would contain only one enantiomer or an unequal mixture of the two enantiomers. Mixture B is a racemic mixture, hence wouldn't show any optical activity.

When the mechanism occurs between an optically active isomer to produce another optically active isomer. What does this indicate about the first stage of the mechanism?

This means that only one enantiomer is formed, meaning it must have occurred via a $S_N 2$ mechanism where a 5-bonded intermediate carbocation is produced. This is because the nucleophile can only attack

from one side of the molecule, which is opposite to the side of the leaving group.

How can an optically active isomer produce a mixture showing no optical activity?

Why would a fewer step synthesis be 'greener'?

There are less reactants required, less waste at the end of each step.

Why would the use of a catalyst be 'greener'?

Reactions can therefore be carried out at a lower temperature, which requires less energy input and hence less fossil fuels be burnt for the process to occur.

Briefly describe how you would use chromatography to identify amino acids in a hydrolysed protein mixture. Spot mixture on paper, maker spots of amino acids and measure Rf values. Run in a solvent in one

direction, then rotate and repeat. Spray with ninhydin and heat to permanently mark amino acid

movement on the paper. Compare amino acid Rf values to known values and identify.

Why is the enthalpy of hydrogenation of benzene less exothermic than expected?

The pi system, from electrons delocalised around the ring gives the molecules greater stability which

required more energy to break the bonds. Hence less exothermic and more energy required in the

system to break the bonds so less is given into the surroundings.

What features on methyl orange make is water-soluble?

The –SO₃⁻ are hydrated, as negative ion bonds attract to water. Nitrogen/oxygen atom hydrogen bond to the water molecules.

What's the purpose of sulphuric acid in the nitrating mixture?

It protonates the nitric acid to act as a base.

What's the distinguishing characteristic of combinatorial chemistry?

It allows simultaneous synthesis of many products that are different but related compounds.

How would increasing mass of a compound added to solution give a more accurate result? CO Using a larger mass reduces the percentage error in weighing.

Why does benzene undergo substitution reactions rather than addition?

The delocalisation of the pi system electrons of the ring makes table that an equivalent 1, 3, 5-100

cyclohexatriene, and so substitution retains this stalle ngement

What does the stabilisation energy file zen mean?

The enthalpy change for the output of benzene

What does steam distillation depend on?

The use of the technique depends on the cerepound forming two layers with water.

Suggest why catalytic activity decreases over time

The surface area of the catalyst may decrease.

- f. The natural direction is an increase in entropy. Such as a gas spreading spontaneously through a room, a consequently increase disorder so positive entropy change
- g. Experiments relation to disorder and enthalpy changes:
 - i. Dissolving a solid, so change is state from solid to liquid increase in an entropy change
 - ii. When a gas is evolved in a reaction there is a change in state and hence an increase in entropy
 - iii. There is a decrease in entropy as a reactants were gas and solid to produce a solid decreases disorder and hence a decrease in entropy
 - iv. In mixing two solids, the entropy change will depend on the physical state of product of produce or the number of moles of product produced
- h. The total entropy change of reaction is depending on the entropy change in the system and the entropy change of the surroundings hence:

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$$

- i. The entropy change if the system is given in the entropy data
- j. The entropy change of the surroundings: $\Delta S_{surroundings} = \frac{-\Delta H}{T}$, which can be substituted and used to calculate the total entropy change using the expression above
- k. The feasibility of a reaction depends on both these entropy changes and the greater the temperature the smaller the value of entropy change of surroundings is and hence effects the total entropy change less. The reaction occurs if the total entropy change is positive disregarding if one of the values is in fact negative
- I. Thermodynamic stability is dependent on the enthalpy change of a reaction. Cregative enthalpy change of formation indicates a greater stability than it elements if ovever a high activation energy may prevent a spontaneous reaction occurring static as combustion requiring an ignition, this is where reactants are kinetically in r
- m. The total entropy change of an underthermic being positive shows it's possible to occur at room temperature. As the dual of feasible if the entropy change of the system is greater than the value of entropy change of stropy page.
- n. Lattice energy is the enthalpy of formation when one mole of ionic compound forms from gaseous ions. Hydration enthalpy is the enthalpy change when one mole of gaseous ions dissolve in sufficient water to form an infinitely dilute solution. The enthalpy of solution is when one mole of a compound dissolves in water to form an infinitely dilute solution.

 $\Delta H_{solution} = -\Delta H_{lattic\,energy} + \Delta H_{hydration}$

- o. Lattice enthalpy; larger charges increases forces of attraction, smaller ions fit closer together increasing attraction, degree of covalent character. Hydration enthalpy; smaller ions have a greater charge density and larger charges increase charge density, which attracts more polar water molecules which are exothermic.
- p. A positive $\Delta H_{solution}$ is overall endothermic and therefore isn't favoured in term of enthalpy, however from a very low entropy value for the ionic lattice upon dissolving the liquid increase the entropy and the entropy change favours the reaction.

Equilibria

- a. Dynamic equilibrium is when the rate of the forwards reaction is equal to the reverse and the concentration of reactants and products remains constant.
- b. Many industrial processes are reversible reactions, such as Haber process

CHEMISTRY UNIT 5

Application of redox equilibria

- An oxidation number is the value assigned to an element representing the number of electrons lost or gained in the atom. Redox is where oxidation and reduction occurs in the same reaction. A half-reaction is the reduction or oxidation component that occurs in the overall redox reaction. L,
- b. Using the changes in oxidation numbers i.e. gain and loss in electrons, can help relate to determine at what ratio for example titrations occur at.
- c. Standard electrode potential is the potential difference measured between electrode system and a hydrogen half-cell under standard conditions. A standard hydrogen electrode is an equilibrium of hydrogen gas and H⁺ ions, with hydrogen gas at 1atm pressure, solution at 1moldm⁻³ and at 298K. This is used as a reference cell for which is defined as zero and all other electrode systems are measure against to find their stand electrode potentials.
- d. $E_{cell} = RHS LHS$, if the e-cell value is greater than zero then reaction is considered thermodynamically feasible. Where the RHS is the most positive value and the most powerful oxidising agent. The more positive the value suggest the further reaction is likely to favour greater production of the products.
- e. The e-cell value is directly proportional to the total (Prop) mange and ln *K*(equilibrium constant)
- f. Hence since promotional to entry y even if it is greater the zero, reaction may not occur spontaneously due to kinetic inertness, a clisco see in unit 4 entropy.
- g. Using the value of electrode potent are of elements with various oxidation states, and reagents such as iron experiments can be undertaken to successively reduce or oxidising observing colour changes such as with vanadium
- h. Procedures of redox titrations:
- a. The potassium manganate (VII) titration, is a redox reaction between MnO₄⁻ and Fe²⁺, which is self indication (if manganate is in burette then colourless to purple). Due to the 1:5 ration at which magnate and iron react respectively, a solution of unknown iron concentration can be calculated for the titre and the percentage mass of iron in an anaemia tablet for example can be calculated. There is an excess of sulphuric acid added so the titration isn't greater than expected and end point masked by the MnO₂ that would be produced which is a brown precipitate.
- b. Thiosulfate redox is between I₂ and S₂O₃²⁻, which uses a starch indicator, added towards the end as otherwise a blue complex form with high concentrations of iodine which is insoluble and doesn't redissolve upon excess thiosulfate so indeterminate endpoint. Using known iodine concentration reacted can be used using molar ratio to determine unknown masses of a metal in an alloy for example.

- j. Hydrogen and ethanol fuel cells (alcohol fuel cell) uses the energy from the reaction in the cell to create a voltage. They produce a continuous voltage as fresh reactants are fed in, maintaining a constant concentration. Advantages include less pollution since ethanol can be produced from fermentation of biomass (effectively carbon neutral) and hydrogen from electrolysis of water. Has greater efficiency, since direct conversion to electric. Limitations however are that it's expensive, very difficult transporting and storing hydrogen, cells have limited life span and uses toxic chemicals in their production.
- k. Early breathalysers analysed the extent of colour change of the oxidation of dichromate from alcohol on the breath, fuel cells are used to generate a current form the alcohol on breath, greater current means more alcohol. IR is also used which can determine amounts of alcohol from its spectrum, more alcohol greater absorbance. IR doesn't use OH group absorption as bonds are also present in water on the breath. The use of fuel cells and IR can be used in prosecution in many countries.

Transition metals and their chemistry

- a. A d block element is defined as having its outer shell electron in the d subshell, where as a transition metal is also a d block element but also forms one or more stable ions with a partially filled 3-d orbital.
- b. Across the 3-d block the electronic configuration follows the expected pattern of filing the 4S subshell then consecutively filling the 3d. However the exception to the rule is chromute and copper, which instead have a half filled 4s subshell and a half filled and full 3c subshell respectively. This is a more stable arrangement by minimising results or between paired electrons.
- c. Electronic structure or the elements cance backed up y looking at the successive ionisation energies of elements, i.e. a big junch indicates where the electron is the last removed form a half filled or empty subtrain equiring more energy theoto the increase in nuclear change to attraction attraction.
- d. General properties of transition metal elements include:
 - i. They have variable oxidations states as they are able to form one or more stable ions
 - ii. They can form coloured ions in solution, as the d subshell spilt visible light region of electromagnetic spectrum is absorbed at that specific wave length the light is absorbed and the remaining colour that can be seen is its complimentary colour
 - iii. The transition metal ion can form complexes by forming dative covalent bonds to ligands, where if more than bond is formed from the same compounds, it's defined as a bi/poly dentate ligand.
 - iv. They can also acts as effective catalysts, due to their variable oxidation states and availability of d orbitals.
- e. shapes of complex ions include; linear $[CuCl_2]^-$, planar $[Pt(NH_3)_2Cl_2]$, tetrahedral $[CrCl_4]^-$ and octahedral $[Cr(NH_3)_6]^{3+}$, $[Cu(H_2O)_6]^{2+}$ and other aqua complexes
- f. the chemistry of chromium and copper, including properties and reactions:
 - i. following reactions from a range of compounds:
- Chromium (VI) oxide reacts with water to give a strong acid:

$$CrO_3 + H_2O \to H_2CrO_4. [Cu(H_2O)_3(OH)_3]_{(s)}$$

- Reacts with an acid to form $[Cr(H_2O)_6]^{3+}_{(aq)}$ and with a base to give $[Cr(OH)_6]^{3-}_{(aq)}$.

- iii. Samples of a complex such can be prepared for example producing chromium ethanoate uses a tap funnel, which drips HCl into he round bottom flask containing sodium dichromate (VI) the pressure of hydrogen building up forces solution over into the sodium ethanoate, a red precipitate of chromium (II) ethanoate is formed and solution contains dissolved red chromium (II) ethanoate also.
- h. Transition metals make for very useful catalyst due to their variable oxidation states. They can use 3d and 4s electrons of atoms on the metals surface to form weak bonds to the reactants (how reactants are absorbed onto catalyst active sites). They are able to be reduced and oxidised easily as an intermediate in the reaction before returning to its initial state to be reused.
- i. Catalysts are important to develop in order to improve high economy/yield processes to be more feasible in industry, for example ethanoic being made from carbon monoxide and methanol has a high atom economy which is made possible using an iridium/ iodine based catalyst. The scientific community validates new discoveries by peer reviewed published journals.
- J. Transition metals react with sodium hydroxide and ammonia to from various complexes, with a little added or when in excess. These produce specific colours from select transition metals. Consult table for specific detail.
- k. Amphoteric behaviour can be seen in reactions as an equilibrium of acid and alkaline, whereas a ligand exchange goes to completion and the ligands become permanently exchanged.
- I. Transition metals have other applications that include photochromic sun glas \bigcirc which sunlight shifts the equilibrium $Cu^+_{(s)} + Ag^+_{(s)} \rightleftharpoons Cu^{2+}_{(s)} + Ag_{(s)}$. Transition metals for chemotherapy treatments, cis-platin binds to DNA of a \bigcirc reals and stops cancer cells dividing.
- a. The structure of he ceremas a delocalised pi with as opposed to the alternating double bond stricture with the original holes the be, called the Kekule structure. Several pieces of evidence support this structure. This includes; hydrogenation of benzene has a lower enthalpy change than expected if it were to contain three double bonds, suggesting a more stable structure i.e. the delocalised pi system. X-ray diffraction shows bond lengths between carbon atoms are all equal in benzene where as double bonds are shorter than single that wouldn't be true for Kekule structure. Benzene doesn't decolourise bromine water at room temp. indicating there's not a double bond present
- b. Reactions of benzene include:
 - i. Combustion, which burns yellow with a smoky flame, this is due to a high carbon to hydrogen ration in the molecule, which lends itself readily to incomplete combustion.
 - ii. Reaction with bromine occurs rapidly in presence of UV light:

