Content

Lattice Energy

Definitions

Lattice Energy ΔH^{θ}_{latt} :

Lattice energy is the enthalpy change involves when one mole of an ionic compound is formed from its gaseous ions.

$\Delta H^{\theta}_{latt}[\mathrm{NaCl}]$ $\quad \mathrm{Na^+_{(g)}} + \mathrm{Cl^-_{(g)}} \rightarrow \mathrm{NaCl_{(s)}}$

$\Delta H^{\theta}_{latt}[\mathrm{MgO}]$ $\quad \mathrm{Mg^{2+}_{(g)}} + \mathrm{O^{2-}_{(g)}} \rightarrow \mathrm{MgO_{(s)}}$

Lattice energy is always negative because ionic bond formed while no bond is broken during the reaction.

The stronger ionic bond formed; the more negative lattice would be. $\Delta H^{\ominus}_{\mathrm{latt}}[\mathrm{MgO}]$ is more negative than $\Delta H^{\ominus}_{\mathrm{latt}}[\mathrm{NaCl}]$, because magnesium ion has higher charge density than sodium ion

Ionic bond is the electrostatic force between cation and anion. The strength of electrostatic force follows the following equation:

$$F = k\frac{Qq}{r^2} = k \times \frac{Q}{r} \times \frac{q}{r}$$

Q and q is the charge of cation and anion while r is the distance between the ions which can be considered as the size of the ions. Thus, $\frac{Q}{r}$ or $\frac{q}{r}$ can be considered as charge density of the ion.

First Electron Affinity ΔH^{θ}_{ea} :

First electron affinity is the enthalpy change involves when one mole of electrons is added to 1 mole of gaseous atoms to form one mole of gaseous -1ve ions under standard conditions.

ΔH^{θ}_{1ea} $\quad \mathrm{O_{(g)}} + \mathrm{e} \rightarrow \mathrm{O^-_{(g)}}$

Second electron affinity is the enthalpy change involves when one mole of electrons is added to 1 mole of gaseous -1ve ions to form one mole of gaseous -2ve ions under standard conditions.

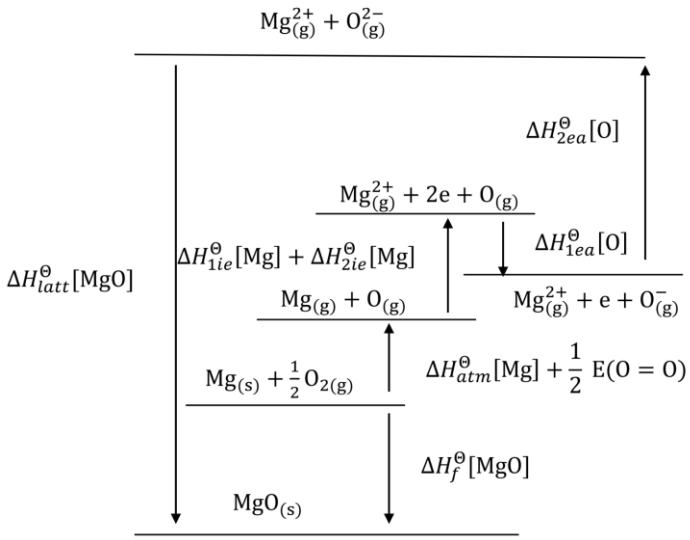
ΔH^{θ}_{2ea} $\quad \mathrm{O^-_{(g)}} + \mathrm{e} \rightarrow \mathrm{O^{2-}_{(g)}}$

First electron affinity of non-metal is usually negative because attraction between electrons and nucleus forms when adding electrons to the atoms.

Second electron affinity is always positive because repulsion need to be overcome when adding electrons to negatively charged ions.

Born-Haber Cycle

Give Born-Haber cycle of MgO and show how to calculate its lattice energy.



$$\Delta H^{\Theta}_{latt}[\mathrm{MgO}] = \Delta H^{\Theta}_{f}[\mathrm{MgO}] - (\Delta H^{\Theta}_{atm}[\mathrm{Mg}] + \tfrac{1}{2}\,\mathrm{E(O=O)} + \Delta H^{\Theta}_{1ie}[\mathrm{Mg}] + \Delta H^{\Theta}_{2ie}[\mathrm{Mg}] + \Delta H^{\Theta}_{1ea}[\mathrm{O}] + \Delta H^{\Theta}_{2ea}[\mathrm{O}])$$

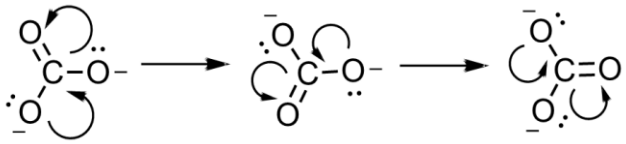
Thermal stability

State and explain the trend of thermal stability of group II carbonate.

Thermal decomposition takes place as group II carbonates are heated.

$$\mathrm{MCO_3} \rightarrow \mathrm{MO} + \mathrm{CO_2}$$

Without group II cation, electrons are evenly distributed in carbonates.



As the size of cation increases down the group, the anions become less polarized. Thus, thermal stability increases down the group.

In the presence of cation, electrons may concentrate on one of the oxygen atoms that is close to the cation. When both electrons move to cation, C-O bond breaks and thermal decomposition takes place.

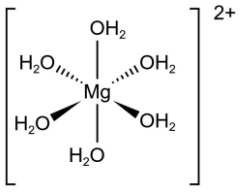
Solubility of Group II Hydroxides and Sulfate

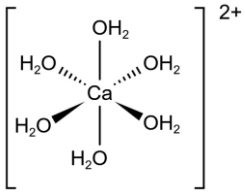
Enthalpy Changes of Hydration

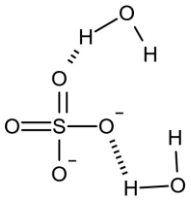
Enthalpy change of hydration is the energy released when dissolving one mole gaseous ions into excess water.

$\Delta H_{hyd}[Mg^{2+}]$ $\Delta H_{hydr}[Ca^{2+}]$ $\Delta H_{hyd}[SO_4^{2-}]$

$Mg^{2+}(g) + aq \rightarrow Mg^{2+}(aq)$ $Ca^{2+}(g) + aq \rightarrow Ca^{2+}(aq)$ $SO_4^{2-}(g) + aq \rightarrow SO_4^{2-}(aq)$



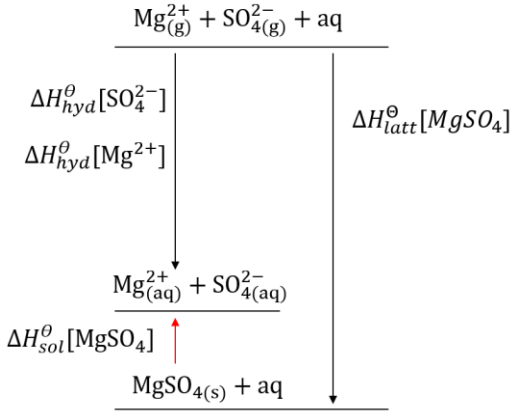


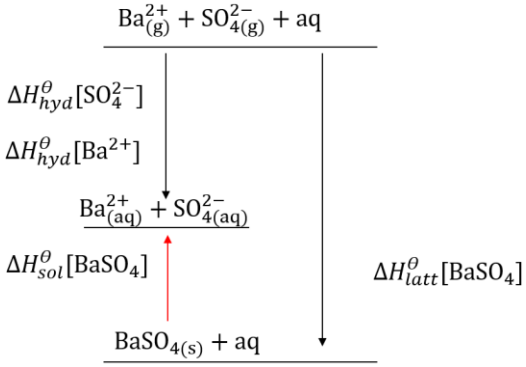


Enthalpy change of hydration is always negative because dative bond or intermolecular force, such as hydrogen bond, form between ions and water molecules.

$\Delta H_{hyd}[Mg^{2+}]$ is more negative than $\Delta H_{hydr}[Ca^{2+}]$ because Mg^{2+} has smaller ionic radius, thus forms stronger coordinate bonds with water.

State and explain the solubility of group II sulfate down the group.



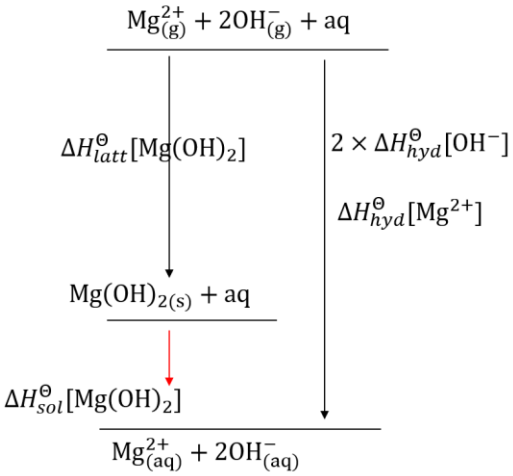


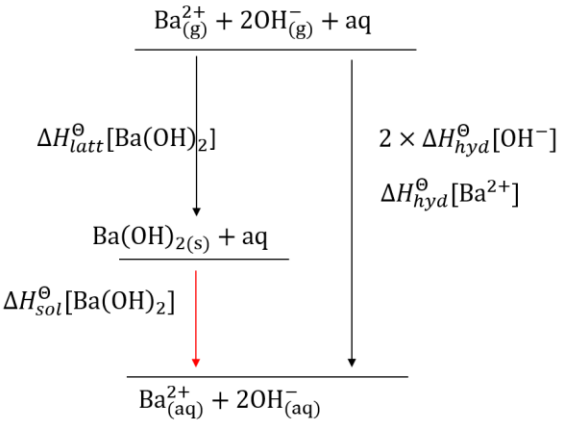
$$\Delta H_{sol}^{\theta} = \Delta H_{hyd}^{\theta} - \Delta H_{latt}^{\theta}$$

As the size of metal cation increase down the group, charge density decreases.
Both lattice energy and enthalpy change of hydration decrease while hydration decreases more.
Thus, enthalpy change of solution becomes more endothermic and *solubility decreases down the group.*

Hydration decreases more than lattice energy because water has much smaller size than sulfate. Thus, water is more sensitive the change of charge density.

State and explain the solubility of group II hydroxide down the group.





As the size of metal cation increase down the group, charge density decreases.
Both lattice energy and enthalpy change of hydration decrease while lattice energy decreases more. Thus, enthalpy change of solution becomes more exothermic and *solubility increase down the group.*

If group II hydroxides, lattice energy decreases more than hydration because hydroxide ion has smaller size than water. Thus, hydroxide ion is more sensitive the change of charge density.

Entropy

Basic Concepts

Define entropy

The number of possible arrangement of particles and their energy in a given system.

Compare entropy values

Low entropy values	High entropy values	Explanation
Solid $CaCO_3$(s)	Gas CO_2(g)	Gas molecules move freely.
Ionic compound NaCl	Solution of ionic compound NaCl(aq)	Ions in solution can move.
Cold substance	Hot substance	Particles gain more kinetic energy at higher temperature

Entropy Changes ΔS^{θ}

Entropy changes in reactions

Chemical Reaction	Entropy Change	Reasons
$\mathrm{CaCO_3(s) \rightarrow CaO(s) + CO_2(g)}$	Increase	Gas produced
$\mathrm{2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)}$	Increase	More gas at RHS
$\mathrm{N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)}$	Decrease	Less gas at RHS

How to calculate entropy change of system?

$$\Delta S^{\theta} = \sum S^{\theta}_{product} - \sum S^{\theta}_{reactants}$$

Calculate entropy change of system of the following reaction

$$\mathrm{2Ca(s) + O_2(g) \rightarrow 2CaO(s)}$$

The entropy values are

$S^{\theta}[\mathrm{Ca(s)}] = 41.40\ \mathrm{J\ K^{-1}mol^{-1}}$ $S^{\theta}[\mathrm{O_2(g)}] = 205.0\ \mathrm{J\ K^{-1}mol^{-1}}$ $S^{\theta}[\mathrm{CaO}] = 39.70\ \mathrm{J\ K^{-1}mol^{-1}}$

$$\Delta S^{\theta}_{system} = \Delta S^{\theta}_{product} - \Delta S^{\theta}_{reactants} = 2 \times S^{\theta}[\mathrm{CaO}] - 2 \times S^{\theta}[\mathrm{Ca(s)}] - S^{\theta}[\mathrm{O_2(g)}]$$

$$= 2 \times 39.7 - 2 \times 41.40 - 205.0$$

$$= -208.4\ \mathrm{J\ K^{-1}mol^{-1}}$$

Gibbs Free Energy

Give expression of Gibbs free energy and suggest what kind information it conveys.

$$\Delta G = -T\Delta S$$

$$\Delta G = \Delta H_{reaction} - T\Delta S$$

In standard condition $\Delta G^{\theta} = \Delta H^{\theta} - T\Delta S^{\theta}$

Reaction only takes place when ΔG^{θ} is negative.

Calculate the Gibbs free energy change for the decomposition of zinc carbonate at 298K.

$\mathrm{ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)}$ $\Delta H_r^{\theta} = 71.0\ \mathrm{kJ\ mol^{-1}}$

$S^{\theta}[\mathrm{ZnCO_3(s)}] = 82.4\ \mathrm{J\ K^{-1}\ mol^{-1}}$ $S^{\theta}[\mathrm{CO_2(g)}] = 213.6\ \mathrm{J\ K^{-1}\ mol^{-1}}$

$S^{\theta}[\mathrm{ZnO}] = 43.6\ \mathrm{J\ K^{-1}\ mol^{-1}}$

$\Delta S^{\theta} = \sum \Delta S^{\theta}_{product} - \sum \Delta S^{\theta}_{reactants}$

$= 213.6 + 43.6 - 82.4 = +174.8\ \mathrm{J\ K^{-1}\ mol^{-1}}$

$\Delta G^{\theta} = \Delta H^{\theta} - T\Delta S^{\theta}$

$= 71 - \frac{298 \times 174.8}{1000} = +18.9\ \mathrm{kJ\ mol^{-1}}$

ΔG^{θ} is positive at 298K, thus it does not take place at room temperature.

Entropy Change and Temperature

Equilibrium condition

Gibbs can be zero when suitable temperature is used, which suggests that reaction can go both directions.

$$\Delta G = \Delta H - T\Delta S$$

ΔS_{system}	$\Delta H_{reaction}$	Reaction spontaneous	comments
+	-	at any temperature	If reaction become more disordered and is exothermic, it happens at any temperature.
-	+	at no temperature	If reaction become less disordered and is endothermic, it never happens.
+	+	at high temperature	If reaction become more disordered and is endothermic, it only happens at high temperature
-	-	at low temperature	If reaction become less disordered and is exothermic, it only happens at low temperature

$$\Delta G = \Delta H - T\Delta S$$

$\Delta H_{reaction}$ is the total energy that is released by the reaction. $T\Delta S$ is the energy used for the change of entropy in the system while ΔG is the energy that can be used to do work.

Electrode Potential

Cell

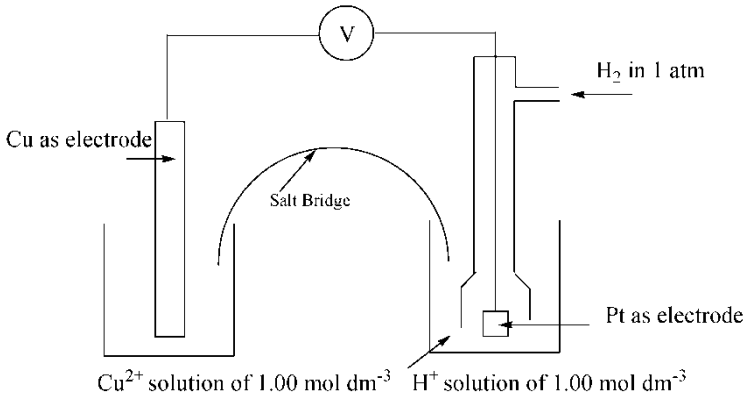
SEP (Standard Electrode Potential):

Definition

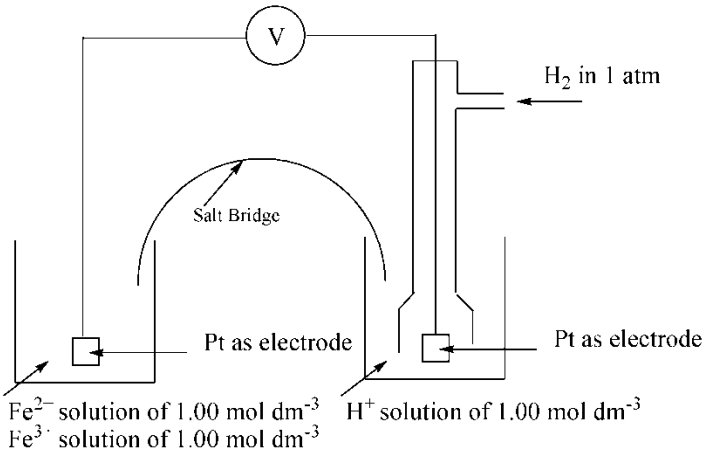
The e.m.f. measured under standard conditions with a standard hydrogen electrode as the other half-cell.

Using a diagram to show how to measuring the electrode potential of following half-cell.

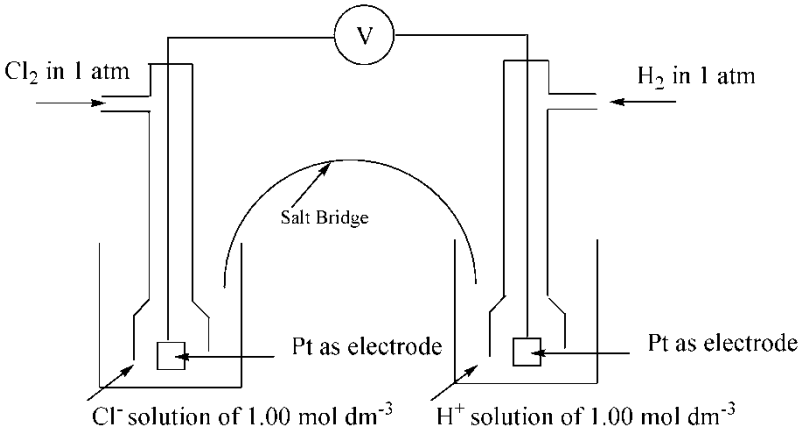
Cu^{2+}/Cu



Fe^{3+}/Fe^{2+}



Cl_2/Cl^-



Prediction of Redox Reaction

How can you predict the oxidizing power or reducing power of a substance using the E value provided in data booklet?

The more positive the E value, the stronger oxidant the substance on the LHS would be. The more negative the E value, the stronger reductant the substance on the RHS would be.

Use E value to show whether Cl_2 will oxidize Fe^{2+} to Fe^{3+} or not?

At first, we need to find the standard electrode potential involves $\mathrm{Cl_2}$ as oxidant while $\mathrm{Fe^{2+}}$ as reductant

$\mathrm{Cl_2 + 2e \rightleftharpoons 2Cl^-}$ $\quad E^o = +1.36\ \mathrm{V}$

$\mathrm{Fe^{3+} + e \rightleftharpoons Fe^{2+}}$ $\quad E^o = +0.77\ \mathrm{V}$

For the reaction to take place, the half-cell of Cl_2 will be reduced while Fe^{2+} will be oxidized

$$E^{\mathrm{o}}_{cell} = E^{\mathrm{o}}_{reduced} - E^{o}_{oxidized}$$

$E^{\mathrm{o}}_{reduced}$ is the E value of the half-cell gaining electrons while $E^{o}_{oxidized}$ is the E value of the half-cell losing electrons.

$$E^{\mathrm{o}}_{cell} = 1.36 - 0.77 = +0.59\ \mathrm{V}$$

Because E^{o}_{cell} is positive, thus the reaction is feasible.

<u>Calculate Gibbs Free Energy from E^{o}_{cell}</u>

In last chapter, we know that reaction is feasible when Gibbs free energy is negative. The value shows the ability of the reaction to do work. In cell, the chemical energy is released as electrical energy. Thus E^{o}_{cell} and ΔG^{o} has following relationship:

$$\Delta G^{\mathrm{o}} = -nE^{\mathrm{o}}_{cell}F$$

n is the number of electrons transferred in the equation.

F the charged carried by one mole electrons $\quad 96500\ \mathrm{C\ mol^{-1}}$

The E^{o} value for two electrode reaction are given

$$\mathrm{H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2\ H_2O} \qquad E^o = +1.77\ \mathrm{V}$$

$$\mathrm{Cr^{3+} + e^- \rightleftharpoons Cr^{2+}} \qquad E^{\mathrm{o}} = -0.41\ \mathrm{V}$$

Calculate the value of $\Delta\ G^{\mathrm{o}}$ for the cell reaction that occurs, per mole of $\mathrm{H_2O_2}$.

$$E^{o}_{cell} = 1.77\ V - (-0.41\ V) = 2.18\ V$$

$$\Delta G^{\mathrm{o}} = -nE^{\mathrm{o}}_{cell}F = 2 \times 2.18 \times 96500 = 420740 = 420.7\ kJ\ mol^{-1}$$

Show how will E value of the following reaction change

$$2Fe^{3+}(aq) + Zn(s) \rightarrow 2Fe^{2+}(aq) + Zn^{2+}(aq)$$

Divide the reaction into two half equation,

$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ $\quad$ $Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$ $\quad$ $E^o = +0.77$

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $\quad$ $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ $\quad$ $E^o = -0.76$

$$E^{\Theta}_{cell} = +0.77 - (-0.76) = +1.53\ \text{V}$$

	Effect on Fe^{2+}/Fe^{3+} electrode	Effect on Zn^{2+}/Zn electrode	Effect on E_{cell}
Conditions	$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	
$[Zn^{2+}]$ increase	No change	More positive	More negative
$[Zn^{2+}]$ decrease	No change	Less Positive	More positive
$[Fe^{2+}]$ increase	More negative	No change	More negative
$[Fe^{2+}]$ decrease	More positive	No change	More positive

For a given reactions such as: $2Fe^{3+}(aq) + Zn(s) \leftrightharpoons 2Fe^{2+}(aq) + Zn^{2+}(aq)$

If equilibrium moves to RHS, the Gibbs free energy would be more negative. Remember the relation between Gibbs free energy and E^{θ}_{cell}

$$\Delta G^o = -nE^{\theta}_{cell}F$$

Thus, if equilibrium moves to RHS, the E^o_{cell} would be more positive. Otherwise, more negative.

Nernst Equation

$$E = E^{\theta} + \frac{0.059}{n}\log\frac{[\text{oxidized form}]}{[\text{reduced form}]}$$

Calculation the E_{cell} of the following reaction in which the concentration of Ag^+ is 1.47×10^{-5}mol dm^{-3} and that of Cu^{2+} is 1mol dm^{-3}

$$2Ag^+ + Cu \rightarrow Ag + Cu^{2+}$$

$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$ $\quad$ $E^o = +0.8\ \text{V}$

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $\quad$ $E^o = +0.34\ \text{V}$

For Ag^+/Ag electrode

$$E = 0.8 + \frac{0.059}{1}\log_{10} 1.47\times10^{-5} = 0.57\text{V}$$

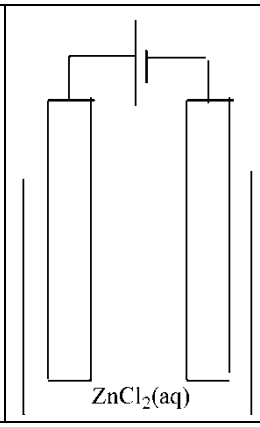
$E_{cell} = 0.57 - 0.34 = 0.17\ \text{V}$

Electrolysis

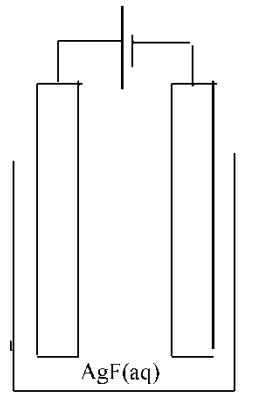
Qualitative Electrolysis

Show the half equations at both cathode and anode. Show why these half-equations are chosen.
Reduction takes place at cathode while oxidation takes place at anode. Species with more positive E value are more likely to be reduced while species with more negative E value are more likely to be oxidized.

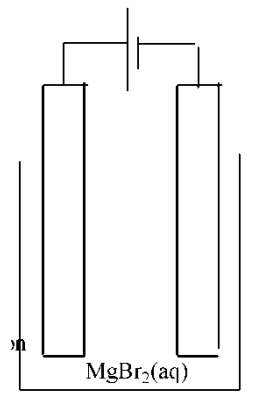
$ZnCl_2$(aq)

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $2Cl^- \rightarrow Cl_2 + 2e^-$ $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ 1.23V $Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ 1.37V In dilute $ZnCl_2$ solution, oxygen would be produced In concentrated $ZnCl_2$ solution, chlorine would be produced		$2H^+ + 2e^- \rightarrow H_2$ $Zn^{2+} + 2e^- \rightarrow Zn$ $2H^+ + 2e^- \rightleftharpoons H_2$ 0V $Zn^{2+} + 2e^- \rightleftharpoons Zn$ -0.76V Hydrogen would be produced whatever concentration of zinc chloride is used.

AgF(aq)

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $2F^- \rightarrow F_2 + 2e^-$ $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ 1.23V $F_2 + 2e^- \rightleftharpoons 2F^-$ 2.87V Oxygen would be produced no whatever concentration is used.		$2H^+ + 2e^- \rightarrow H_2$ $Ag^+ + e^- \rightarrow Ag$ $2H^+ + 2e^- \rightleftharpoons H_2$ 0V $Ag^+ + e^- \rightleftharpoons Ag$ +0.80V Silver would be produced no whatever concentration is used.

$MgBr_2$(aq)

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $2Br^- \rightarrow Br_2 + 2e^-$ $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ 1.23V $Br_2 + 2e^- \rightleftharpoons 2Br^-$ 1.07V Bromine would be produced usually.		$2H^+ + 2e^- \rightarrow H_2$ $Mg^{2+} + 2e^- \rightarrow Mg$ $2H^+ + 2e^- \rightleftharpoons H_2$ 0V $Mg^{2+} + 2e^- \rightleftharpoons Mg$ -2.83V Hydrogen would be produced whatever concentration is used.

Quantitative Electrolysis

Calculate the mass of lead deposited at the cathode during electrolysis when a current of 1.50A flows through molten lead(II) bromide for 20 minutes.

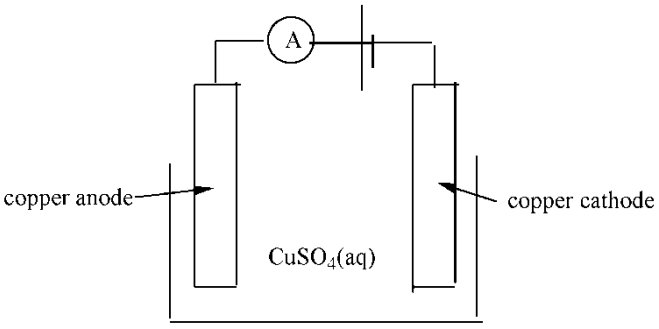
$Q = I \times t = 1.5 \times 20 \times 60 = 1800\text{C}$

$n_{(\text{e})} = \frac{Q}{F} = \frac{1800\text{C}}{9.65 \times 10^4} = 1.87 \times 10^{-2}\ \text{mol}$

$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$

$m_{(\text{Pb})} = \frac{1}{2} \times n_{(\text{e})} \times A_r = \frac{1}{2} \times 1.87 \times 10^{-2} \times 207.2 = 1.94\text{g}$

Show how Avogadro Constant can be calculated by electrolysis of copper (II) sulfate.



Set up an electrolysis device with copper as both electrodes and copper sulfate as electrolyte. Measure the mass of copper anode m_1 before electrolysis and the mass of the anode m_2 afterwards. Record current I and time t in the experiment.

$\text{n}_{(\text{Cu})} = \frac{m_{(\text{Cu})}}{A_r} = \frac{m_2 - m_1}{A_r}$

$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$

$n_{(\text{e})} = 2 \times n_{(\text{Cu})}$

$F = \frac{Q}{n_{(\text{e})}} = \frac{I \times t}{n_{(\text{e})}}$ F is Faraday constant which also can be represented by L

$A = \frac{F}{\boldsymbol{e}} = \frac{L}{\boldsymbol{e}}$ A is Avogadro constant

Equilibria

K_w and pH

Concepts

Give the expression of K_w and state its value at standard condition.

$$H_2O(l) \leftrightharpoons H^+(aq) + OH^-(aq)$$

$K_w = [H^+][OH^-]$

$K_w = 1.0 \times 10^{-14}\ \text{mol}^2\text{dm}^{-6}$ at 298K

What is pH?

$pH = -\log_{10}[H^+]$

Calculations

How to calculate pH if the concentration of acid is given?

Calculate the pH of a solution whose $[H^+]$ is 3.00×10^{-4}mol dm^{-3}

$pH = -\log_{10}[H^+] = -\log_{10}[3.00 \times 10^{-4}] = 3.52$

The free proton in the solution is contributed by both acid and water. Acid gives much more proton compared with water. Thus, the contribution made by water is ignored.

How to calculate pH if the concentration of alkali is given?

Calculate the pH of 0.1 mol dm^{-3} NaOH

$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}\ \text{mol}^2\text{dm}^{-6}$

$$[H^+] = \frac{1.0 \times 10^{-14}}{0.1} = 1.0 \times 10^{-13}\ \text{mol dm}^{-3}$$

The free hydroxide in the solution is contributed by both base and water. base gives much more hydroxide compared with water. Thus, the contribution made by water is ignored.

$pH = -\log_{10}[H^+] = -\log_{10}[1.0 \times 10^{-13}] = 13$

or it can be also calculated in this way

$$pH = -\log_{10}[H^+] = -\log_{10}\frac{K_w}{[OH^-]} = -\log_{10} K_w + \log_{10}[OH^-] = 14 + \log_{10}[OH^-] = 13$$

K_a and Calculations

Concept and Basic Calculation

Give the expression of K_a and pK_a in the following reaction.

$$\mathrm{HA(aq)} \leftrightharpoons \mathrm{H^+(aq) + OH^-(aq)}$$

$$K_a = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

$$\mathrm{p}K_a = -\log_{10} K_a = -\log_{10} \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]} = -\log_{10}[\mathrm{H^+}] - \log_{10} \frac{[\mathrm{A^-}]}{[\mathrm{HA}]} = \mathrm{pH} - \log_{10} \frac{[\mathrm{A^-}]}{[\mathrm{HA}]}$$

How K_a can be calculated when pH of a weak acid solution is given?

Calculate the value of K_a for methanolic acid. A solution of 0.010 mol dm^{-3} methanolic acid, HCOOH, has a pH of 2.90

$$HA(aq) \leftrightharpoons H^+(aq) + OH^-(aq)$$

$$[\mathrm{A^-}] = [\mathrm{H^+}] = 10^{-2.9} = \ 1.26 \times 10^{-3}\ \mathrm{mol\ dm^{-3}}$$

$$K_a = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]} = \frac{(1.26\times10^{-3})^2}{0.01} = 1.59 \times 10^{-4}\ \mathrm{mol\ dm^{-3}}$$

At the equilibrium, [HA] is actually smaller than its original concentration due to the dissociation. However, the dissociated acid is much smaller than the undissociated. Thus, the amount of dissociation is ignored.

How pH of a weak acid solution can be calculated when K_a is given?

Calculate the pH of 0.100 mol dm^{-3} ethanoic acid, CH_3COOH. ($K_a = 1.74 \times 10^{-5}\ \mathrm{mol\ dm^{-3}}$)

$$K_a = \frac{[\mathrm{H^+}][A^-]}{[\mathrm{HA}]} = \frac{[\mathrm{H^+}]^2}{[\mathrm{HA}]}$$

$$[\mathrm{H^+}] = \sqrt{K_a[\mathrm{HA}]} = \sqrt{1.74 \times 10^{-5} \times 0.10} = 1.32 \times 10^{-3}\ \mathrm{mol\ dm^{-3}}$$

Buffer Solution

Concepts

Definition of buffer solution

A solution that resists the change in pH when small amounts of acids or alkalis are added

Explain how the solution of a weak acid HA and its salt NaA can act as buffer.

In solution $\mathrm{HA} \rightleftharpoons \mathrm{H^+ + A^-}$

$\mathrm{NaA \rightarrow Na^+ + A^-}$

When acid is added equilibrium moves to LHS and $\mathrm{A^-}$ act as proton acceptor.

$\mathrm{A^- + H^+ \rightarrow HA}$

When base is added equilibrium moves to RHS and HA acts as proton donor

$\mathrm{HA + NaOH \rightarrow NaA + H_2O}$

pH only changes when the concentration of H^+ or OH^- changes. Buffer solution maintains its constant pH by changes H^+ or OH^- into molecules.

The following substances can also act as buffer solution

Weak base and its salt $\mathrm{NH_4Cl + OH^- \rightarrow NH_3 + H_2O}$

$\mathrm{NH_3 + H^+ \rightarrow NH_4^+}$

Carbonate and carbonic acid $\mathrm{H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O}$

$\mathrm{HCO_3^- + H^+ \rightarrow H_2CO_3}$

Amino acids $\mathrm{H_3N^+CH_2COO^- + OH^- \rightarrow NH_2CH_2COO^- + H_2O}$

$\mathrm{H_3N^+CH_2COO^- + H^+ \rightarrow NH_3^+CH_2COOH}$

Calculation

How to calculate the pH of buffer solution?

Calculate the pH of a buffer whose $[\mathrm{HA}]$ is 0.05 mol dm^{-3} and $[\mathrm{NaA}]$ of 0.1 mol dm^{-3}.

(K_a of HA = 1.60 × 10^{-4} mol dm^{-3})

$$K_a = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

$$[\mathrm{H^+}] = \frac{K_a[\mathrm{HA}]}{[\mathrm{A^-}]} = \frac{1.6 \times 10^{-4} \times 0.05}{0.1} = 8 \times 10^{-5}\ \mathrm{mol\ dm^{-3}}$$

$[\mathrm{A^-}]$ should be higher than 0.1, because the dissociate of HA also gives $\mathrm{A^-}$. However, the dissociation of HA is too small compared with the $\mathrm{A^-}$ contributed by $[\mathrm{NaA}]$. Thus, the contribution made by HA is ignored.

$$\mathrm{pH} = -\log_{10} 8 \times 10^{-5} = 4.1$$

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{salt}]}{[\mathrm{acid}]}$$

K_{sp}

Concept and Calculation

Give the expression of K_{sp} of the following dissociation.

$$A_xB_y(s) \leftrightharpoons xA^{y+}(aq) + yB^{x-}(aq)$$

$K_{sp} = [A^{y+}]^x[B^{x-}]^y$

*At equilibrium, $[A^{y+}]$ and $[B^{x-}]$ reaches its maximum. **Solubility** is the maximum concentration that can be reached when A_xB_y dissolved in water. Thus, at equilibrium, $[A^{y+}]$ and $[B^{x-}]$ is the solubility of A_xB_y.*

How K_{sp} can be calculated from solubility?

When the ratio of cation and anion is 1:1

A saturated aqueous solution of cadmium sulfide, CdS, whose solubility is 1.46×10^{-11} mol^2 dm^{-6}

$$CdS(s) \leftrightharpoons Cd^{2+}(aq) + S^{2-}(aq)$$

$[Cd^{2+}] = [S^{2-}] = 1.46 \times 10^{-11}$ mol dm^{-3}

$K_{sp} = [Cd^{2+}][S^{2-}] = (1.46 \times 10^{-11})^2 = 2.13 \times 10^{-22}$ mol^{2}dm^{-6}

When the ratio of cation and anion is not 1:1

A saturated solution of magnesium fluoride, MgF_2, whose solubility is 1.22×10^{-3} mol dm^{-3}

$$MgF_2(s) \leftrightharpoons Mg^{2+}(aq) + 2F^{-}(aq)$$

$[Mg^{2+}] = [MgF_2] = 1.22 \times 10^{-3}$ mol dm^{-3}

$[F^{-}] = 2[MgF_2] = 2.44 \times 10^{-3}$ mol dm^{-3}

$K_{sp} = [Mg^{2+}][F^{-}]^2 = [MgF_2](2[MgF_2])^2 = 4([MgF_2])^3$

$= 4 \times (1.22 \times 10^{-3})^3 = 7.26 \times 10^{-9}$ mol^{3}dm^{-9}

How solubility can be calculated from K_{sp}?

When the ratio of cation and anion is 1:1

Calculate the solubility in mol dm^{-3} of zinc sulfide, ZnS, whose K_{sp} is 1.6×10^{-23} mol^{2}dm^{-6}

$$ZnS(s) \leftrightharpoons Zn^{2+}(aq) + S^{2-}(aq)$$

$[ZnS] = [Zn^{2+}]=[S^{2-}]$

$K_{sp} = [Zn^{2+}][S^{2-}] = [ZnS]^2$

$[ZnS] = \sqrt{K_{sp}} = \sqrt{1.6 \times 10^{-23}} = 4.0 \times 10^{-12}$ mol dm^{-3}

When the ratio of cation and anion is not 1:1

Calculate the solubility of silver carbonate Ag_2CO_3 whose $K_{sp}$is 6.3×10^{-12} mol^{2}dm^{-6}

$$Ag_2CO_3(s) \leftrightharpoons 2Ag^{+}(aq) + CO_3^{2-}(aq)$$

$[Ag_2CO_3] = \frac{1}{2}[Ag^{+}] = [CO_3^{2-}]$

$K_{sp} = [Ag^{+}]^2[CO_3^{2-}] = (2[Ag_2CO_3])^2[Ag_2CO_3] = 4([Ag_2CO_3])^3$

$[Ag_2CO_3] = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{6.3 \times 10^{-12}}{4}} = 1.16 \times 10^{-4}$ mol dm^{-3}

Prediction for Precipitation

How to predict precipitation?

Will a precipitate form if we mix equal volumes of solutions of $1.00 \times 10^{-4}\ \text{mol dm}^{-3}\ \ \text{Na}_2\text{CO}_3$ and $5.00 \times 10^{-5}\ \text{mol dm}^{-3}\ \ \text{BaCl}_2$ the K_{sp} of BaCO_3 is $5.5 \times 10^{-10}\ \text{mol}^2\text{dm}^{-6}$)

The volume of mixed solution doubles the previous solutions, thus the concentration of each ion halves.

$[\text{CO}_3^{2-}][\text{Ba}^{2+}] = 0.50 \times 10^{-4} \times 2.50 \times 10^{-5} = 1.25 \times 10^{-9} > K_{sp}(5.5 \times 10^{-10})$

Precipitate will be formed when two solutions mixed together

What is common ion effect?

Reduction in the solubility of a dissolved salt achieved by adding a solution of a compound which has an ion in common with the dissolved salt. This often results in precipitation.

K_{sp} shows the maximum value of the products of ionic concentrations.

If the product of ionic concentration is smaller than K_{sp}, this means equilibrium is not achieved and ions stay in aqueous state.

If the product exceeds K_{sp}, this means equilibrium has reached and precipitate formed, so as to keep the product equals K_{sp}.

K_{pc} and Its Calculation

State what is partition coefficient K_{pc}

Equilibrium constant that relates the concentration of a solute partitioned between two immiscible solvents at a particular temperature.

How to calculate K_{pc} if the concentration of solute in both solvents are given?

When a solution of 1.00 g of X in 100 cm^3 of water was shaken with 10 cm^3 of ether, 0.80 g of X was transferred to the ether layer. Calculate the partition coefficient of X between ether and water.

$$K_{pc} = \frac{[\mathrm{X}]_{\mathrm{ether}}}{[\mathrm{X}]_{\mathrm{water}}} = \frac{\frac{0.8\ \mathrm{g}}{10\ \mathrm{cm}^3}}{\frac{(1.00-0.8)\ \mathrm{g}}{100\ \mathrm{cm}^3}} = 40$$

If the K_{pc} is bigger than 1, X has higher solubility in ether.

If the K_{pc} is smaller than 1, X has higher solubility in water.

The solubility of a substance in a given solvent depends on the interaction between solutes and solvent. Polar solutes have higher solubility in polar solvent while non-polar solutes have higher solubility in non-polar solvents.

How to use K_{pc} to predict the concentration of solute in both solvents?

How much of X would you extract in total by using the ether as two separate lots of 5 cm^3 instead of the 10 cm^3 in one go?

Suppose a g X is extracted in the first lot

$$K_{pc} = \frac{[\mathrm{X}]_{\mathrm{ether}}}{[\mathrm{X}]_{\mathrm{water}}} = \frac{\frac{\mathrm{a\ g}}{5\ \mathrm{cm}^3}}{\frac{(1.00-\mathrm{a})\mathrm{g}}{100\ \mathrm{cm}^3}} = 40$$

$$\mathrm{a} = \frac{2}{3} = 0.66\mathrm{g}$$

Then there is 1-0.66=0.34g X in water

Suppose b g X is extracted in the second lot

$$K_{pc} = \frac{[\mathrm{X}]_{\mathrm{ether}}}{[\mathrm{X}]_{\mathrm{water}}} = \frac{\frac{\mathrm{b\ g}}{5\ \mathrm{cm}^3}}{\frac{(0.34-\mathrm{b})\mathrm{g}}{100\ \mathrm{cm}^3}} = 40$$

$$\mathrm{b} = \frac{2 \times 0.34}{3} = 0.23\mathrm{g}$$

Totally there will be 0.66+0.23=0.89 g X been extracted if the extraction is carried in two separated lots.

Reaction Kinetics

Basic Concepts

Rate of Reaction

The change in concentration of substance in the reaction over a period of time.

$$\text{rate of reaction} = \frac{\text{change in concentration}}{\text{time taken for this change}}$$

Rate equation

Mathematical expression which describes how reaction rate change as concentration of substance changes.

$$\text{rate of reaction} = k[\text{A}]^{\text{m}}[\text{B}]^{\text{n}}$$

k is rate constant, which only changes when temperature changed. k increases as temperature increases.

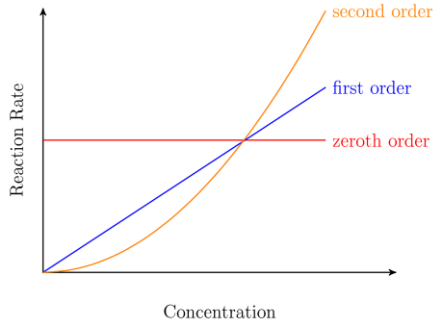
Order of Reaction

The order of reaction with respect to a particular reactant is the power to which the concentration of that reactant is raised in the rate equation

Graphs

Graphs of reaction rate against concentration

Show graphs of zero, first and second order reaction



Zeroth order Rate=$k[\text{A}]^0$

If the reaction rate is independent of its concentration, we say this reactant is zeroth order.

The gradient of zeroth order curve is zero.

First order Rate= $k[\text{A}]$

If the rate is proportional to its concentration, we say this reactant is first order.

The gradient of first order curve is a constant.

Second order Rate=$k[\text{A}]^2$

If the rate is proportional to the square of its concentration, we say this reactant is second order.

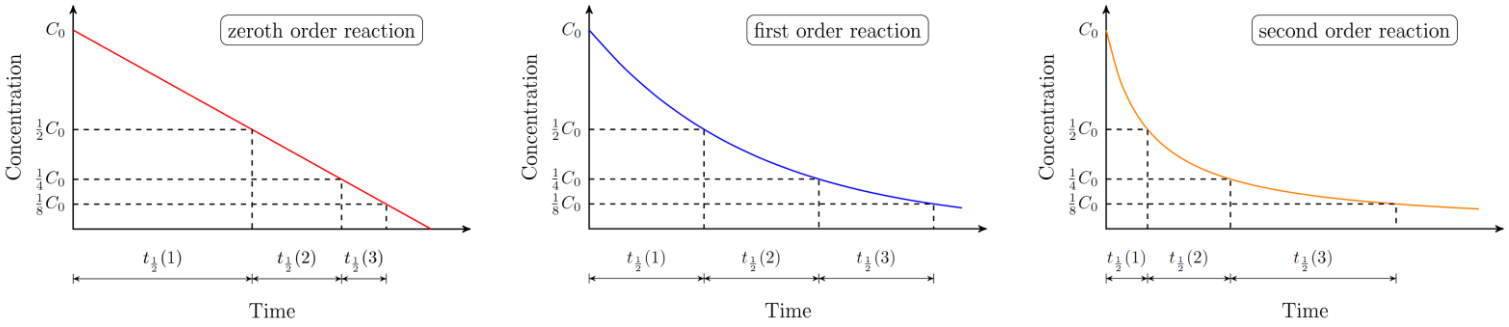
The gradient of second order curve increases as its concentration increases.

Orders of Reaction

Half-life

Define what is half-life and show how to find half-life in concentration-time graphs.

Half-life is the time taken for concentration of substance in interest decrease to half of its original concentration.



For zeroth order, half-life halves as reaction proceeds.

For first order, half-life stays the same.

For second order, half-life doubles as reaction proceeds.

Half-life and Rate Constant

A **first order reaction** depends on the concentration of only one reactant (a **unimolecular reaction**).

The rate law for a reaction that is first order with respect to a reactant A is:

$$\text{rate} = k[\text{A}]^1$$

k is rate constant.

$$t_{\frac{1}{2}} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

$$k = \frac{0.693}{t_{\frac{1}{2}}}$$

Initial Rate

Find Order by Initial Rate

$$CH_3COCH_3 + I_2 \xrightarrow{H^+} CH_3COCH_2I + HI$$

Experiment	[HCl] mol dm^{-3}	[C_3H_6O] 10^{-3} mol dm^{-3}	[I_2] 10^{-3} mol dm^{-3}	Initial Rate 10^{-6} mol dm^{-3} s^{-1}
1	1.25	0.50	1.25	10.9
2	0.625	0.50	1.25	5.4
3	1.25	0.25	1.25	5.1
4	1.25	0.50	0.625	10.1

Find the order of the reaction with respect to each reactant, explaining how you arrive at your answer.

For row 1 and row 2, initial rate halves as [HCl] halves, HCl is first order

$\frac{\text{row1 [HCl]}}{\text{row2 [HCl]}} = \frac{1.25}{0.625} = \frac{2}{1}$, $\frac{\text{row1 initial rate}}{\text{row2 initial rate}} = \frac{10.9}{5.4} = \frac{2}{1}$. HCl is first order

For row 1 and row 3, initial rate halves as [C_3H_6O] halves, C_3H_6O is first order

$\frac{\text{row1 [C}_3\text{H}_6\text{O]}}{\text{row2 [C}_3\text{H}_6\text{O]}} = \frac{0.50}{0.25} = \frac{2}{1}$, $\frac{\text{row1 initial rate}}{\text{row2 initial rate}} = \frac{10.9}{5.1} = \frac{2}{1}$. C_3H_6O is first order

For row 1 and row 4, initial rate stay constant when [I_2] halves, I_2 is zero order.

Calculate K

Rate equation rate = k[HCl][C_3H_6O]

Thus $k = \frac{\text{rate}}{[\text{HCl}][\text{C}_3\text{H}_6\text{O}]}$

Data from row 1 $k = \frac{10.9\times10^{-6}}{1.25\times0.5\times10^{-3}} = 0.0174\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$

Rate Determine Step

For reaction below, four scenarios of mechanism it may proceeds are proposed. If the rate equation of this reaction is $r = k[\text{Cr(CO)}_6$. Choose the mechanism that is consistent with its rate equation.

$$\text{Cr(CO)}_6 + \text{PR}_3 \longrightarrow \text{Cr(CO)}_5\text{PR}_3 + \text{CO}$$

Scenario A	$\text{Cr(CO)}_6 \longrightarrow \text{Cr(CO)}_5 + \text{CO}$	Fast
	$\text{Cr(CO)}_5 + \text{PR}_3 \longrightarrow \text{Cr(CO)}_5\text{PR}_3$	Slow
Scenario B	$\text{Cr(CO)}_6 \longrightarrow \text{Cr(CO)}_5 + \text{CO}$	Slow
	$\text{Cr(CO)}_5 + \text{PR}_3 \longrightarrow \text{Cr(CO)}_5\text{PR}_3$	Fast
Scenario C	$\text{Cr(CO)}_6 + \text{PR}_3 \longrightarrow \underset{\text{transition state}}{[\text{OC}\cdots\text{Cr(CO)}_4\cdots\text{PR}_3]} \longrightarrow \text{Cr(CO)}_5\text{PR}_3 + \text{CO}$	
Scenario D	$\text{Cr(CO)}_6 + \text{PR}_3 \longrightarrow \text{Cr(CO)}_6\text{PR}_3$	Slow
	$\text{Cr(CO)}_6\text{PR}_3 \longrightarrow \text{Cr(CO)}_5\text{PR}_3 + \text{CO}$	Fast

Only $Cr(CO)_6$ present in rate equation, which suggest that it should be the only reactant that involves in slow step which is also called rate determine step. Thus, B can be the right mechanism

Catalysis

Homogeneous Catalysis

Reaction 1

$$S_2O_8^{2-}(aq) + 2\,I^-(aq) \longrightarrow 2\,SO_4^{2-}(aq) + I_2(aq)$$

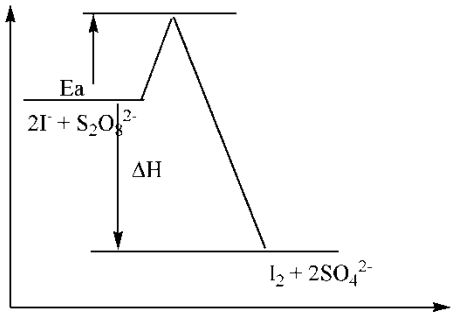
The reaction between $S_2O_8^{2-}$ and I^- is slow because both reactants are negatively charged. Repulsion makes it difficult for two particles to collide.

Fe^{3+} can be served as catalyst for this reaction, because both iron ions are positively charged and attractions between the reactants make collision takes place much easier.

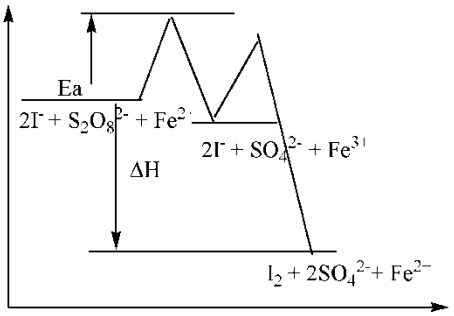
$$2I^-(aq) + 2Fe^{3+}(aq) \rightarrow I_2(aq) + 2Fe^{2+}(aq)$$

$$S_2O_8^{2-}(aq) + 2Fe^{2+}(aq) \rightarrow 2SO_4^{2-}(aq) + 2Fe^{3+}(aq)$$

Uncatalyzed reaction



Catalyzed reaction



Reaction 2

$$2\,SO_2 + O_2 \longrightarrow 2\,SO_3$$

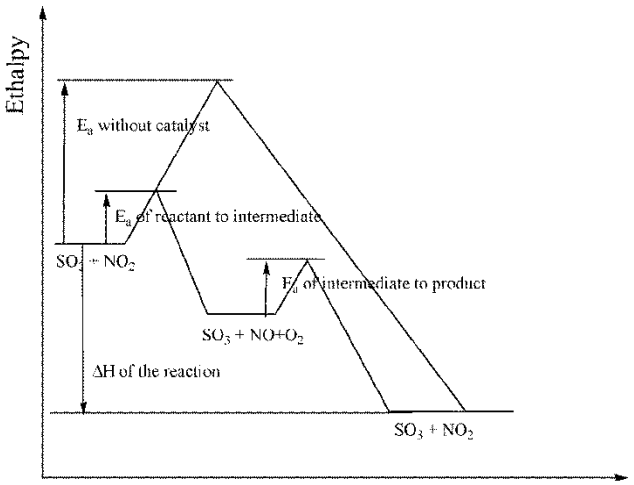
NO_2 can be served as catalyst for this reaction.

$$SO_2 + NO_2 \longrightarrow SO_3 + NO$$

$$SO_3 + NO \longrightarrow SO_3 + NO_2$$

Nitrogen oxide served as catalyst for the conversion of sulfur trioxide which reaction with water to form acid rain.

That's how oxides of nitrogen contribute to acid rain.



Heterogeneous Catalysis

Reaction 1

$$\mathrm{N_2 + 3\,H_2 \overset{Iron}{\rightleftharpoons} 2\,NH_3}$$

Haber Process is served as industrial manufacture of ammonia.

Four Steps in Heterogeneous Catalysis

Adsorption	reactant molecule chemically adsorbed onto the surface of iron
Reaction	adsorbed reactant react on the surface of catalyst
Desorption	bonds between products and catalyst are broken

Reaction 2

$$\mathrm{CO + N_xO \xrightarrow{platinum} CO_2 + \frac{x}{2}N_2}$$

Catalytic conversion is used to remove CO and NO from car exhaust. It is also a heterogeneous catalysis.

Transition Metal

Basic Concepts

Definition

Elements that can form stable ions with incomplete d orbitals.

Give electronic configuration of following atoms or ions.

$_{29}Cu$ $1s^2 2s^2 2p^2 3s^2 3p^6 \mathbf{4s^1 3d^9}$ $_{29}Cu^+$ $1s^2 2s^2 2p^2 3s^2 3p^6 \mathbf{3d^9}$

$_{24}Cr$ $1s^2 2s^2 2p^2 3s^2 3p^6 \mathbf{4s^1 3d^5}$ $_{24}Cr^{3+}$ $1s^2 2s^2 2p^2 3s^2 3p^6 \mathbf{3d^3}$

Special Property of Transition Element

How and why transition metal differs from conventional metal in its physical property?

Melting point

Transition metal usually has higher melting point than conventional metal due to its abundant delocalized electrons which usually means stronger metallic bond.

Density

Transition metal usually has higher density than conventional metal which is resulted by both smaller atomic radius and larger atomic mass.

How and why transition metal differs from conventional metal in its chemical property?

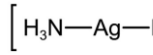
Oxidation number

Transition metals usually have more than one oxidation number. Because energy gap between 4s and 3d orbitals is small.

Ligands and Complex Ions

Use an equation to show how silver chloride dissolved in ammonia water.

$$AgCl(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$$



Nitrogen atoms fill their lone pairs into d orbital of silver ion, forming a complex ion.

Definitions and Conventional Complex Ions

Give definitions of the following terms

Complex ions Ions formed by binding cations with ligands through coordinate bond.

Ligand Species with lone pair and be able to bind with metal cations.

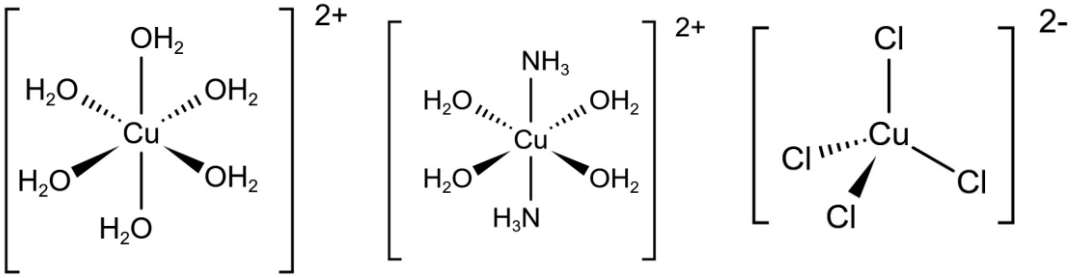
Monodentate ligands that form only one coordinate bond with central ion

bidentate ligands that form only two coordinate bonds with central ion

Cation	Ligand	Formula	Color	Shape
Cu^{2+}	H_2O	$[Cu(H_2O)_6]^{2+}$	Blue	Octahedral
	H_2O & OH^-	$Cu(H_2O)_4(OH)_2$	Pale blue	Octahedral
	H_2O & NH_3	$[Cu(H_2O)_4(NH_3)_2]^{2+}$ or $[Cu(H_2O)_2(NH_3)_4]^{2+}$	Deep blue	Octahedral
	Cl^-	$[CuCl_4]^{2-}$	Yellow	Tetrahedral
Co^{2+}	H_2O	$[Co(H_2O)_6]^{2+}$	Pink	Octahedral
	NH_3	$[Co(NH_3)_6]^{2+}$	Blue	Octahedral
	Cl^-	$[CoCl_4]^{2-}$	Blue	Tetrahedral
	En $H_2NCH_2CH_2NH_2$	$[Co(en)]^{4-}$		Octahedral
Ni^{2+}	CN-	$[Ni(CN)_4]^{2-}$	Yellow	Square planar
	H_2O	$[Ni(H_2O)_6]^{2+}$	Green	Octahedral
Pt	Cl^-&NH_3	Pt $(NH_3)_2$ Cl_2		Square planar
Ag	NH_3	$[Ag(NH_3)_2]^+$	Colorless	Linear

Only the colors of copper and cobalt complex are required by the syllabus.

Give the diagram of the following complex ions



$[Cu(H_2O)_6]^{2+}$ $[Cu(H_2O)_4(NH_3)_2]^{2+}$ $[CuCl_4]^{2-}$

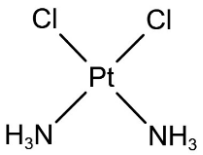
Stereoisomerism of Complex Ions

Give stereoisomers of the following complex ions

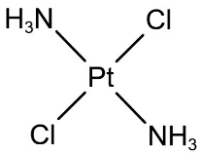
Geometrical Isomer

$Pt(NH_3)_2Cl_2$

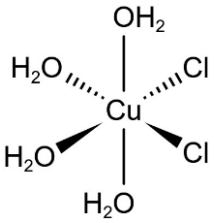
Cis

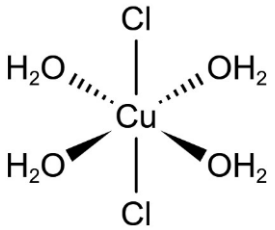


Trans

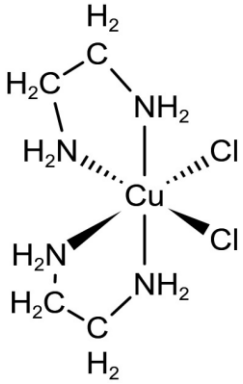


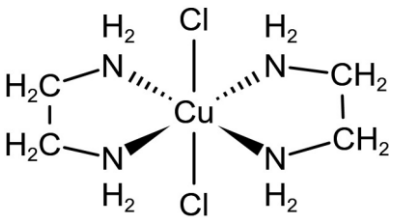
$Cu(H_2O)_4Cl_2$





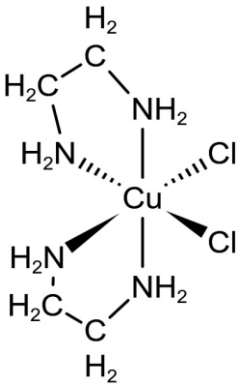
$Cu(NH_2CH_2CH_2NH_2)_2Cl_2$

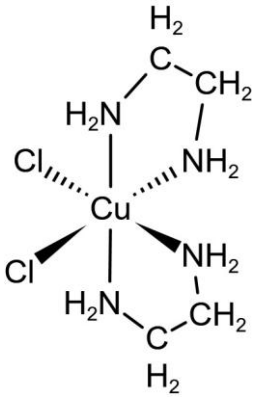




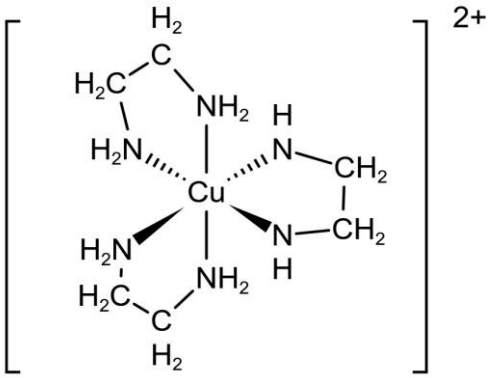
Optical Isomer

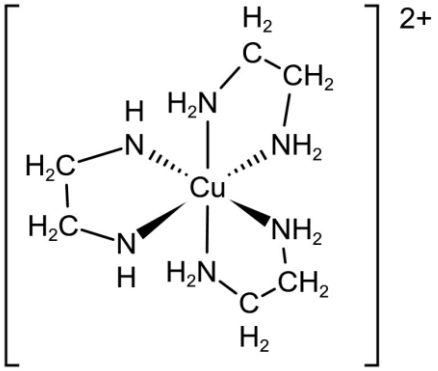
$Cu(NH_2CH_2CH_2NH_2)_2Cl_2$





$[Cu(NH_2CH_2CH_2NH_2)_3]^{2+}$





Substitution of Ligands

Describe and explain what happens when ammonia water is added to copper sulfate solution.

Ammonia water is weakly basic $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

Pale blue precipitate is produced when small amount ammonia water is added.

$$[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(H_2O)_4(OH)_2(s) + 2H_2O(l)$$

blue solution — pale blue precipitate

Precipitate dissolves when excess ammonia is added and give a deep blue solution.

$$Cu(H_2O)_4(OH)_2(s) + 2H_2O(l) \rightarrow [Cu(H_2O)_4(NH_3)_2]^{2+}(aq) + 2OH^-(aq)$$

pale blue precipitate — deep blue solution

Give an equation to describe what happened when concentrated hydrochloric acid is added to copper sulfate solution and give the expression of stability constant.

$$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightarrow [CuCl_4]^{2-}(aq) + 6H_2O(l)$$

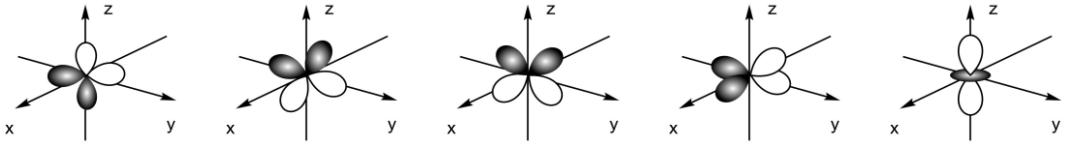
blue solution — yellow solution

$$K_{stab} = \frac{[CuCl_4]}{[Cu(H_2O)_6][Cl^-]^4}$$

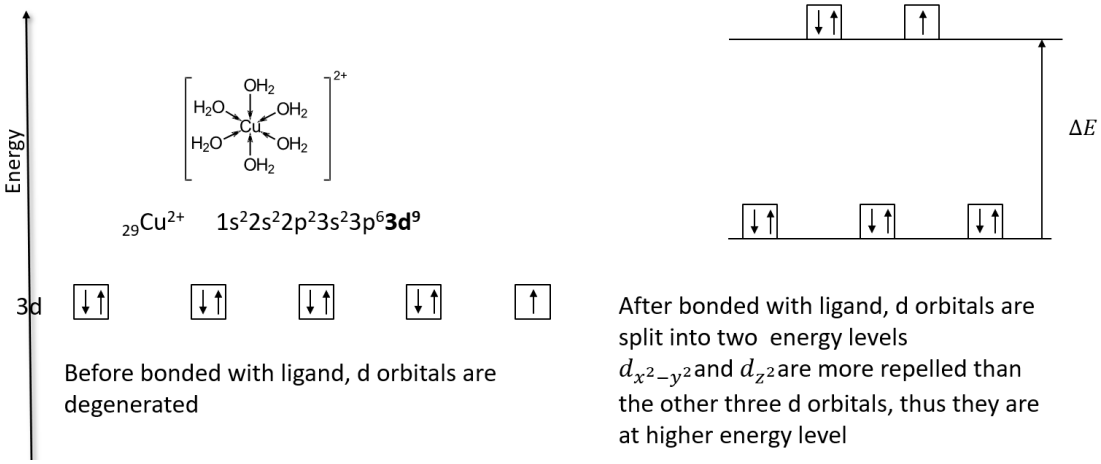
K_{stab} can be used to predict the complex ions formed when various ligands exist at solution. K_{stab} with higher value suggests higher likelihood of existence of the complex ions in interest while K_{stab} with lower value suggests the opposite.

Color of Complex Ions

Use diagram to show how d orbitals of transition elements split into two energy group when combined with ligands.



d_{xy} d_{xz} d_{yz} $d_{x^2-y^2}$ d_{z^2}



$_{29}Cu^{2+}$ $1s^2 2s^2 2p^2 3s^2 3p^6 \mathbf{3d^9}$

Before bonded with ligand, d orbitals are degenerated

After bonded with ligand, d orbitals are split into two energy levels $d_{x^2-y^2}$ and d_{z^2} are more repelled than the other three d orbitals, thus they are at higher energy level

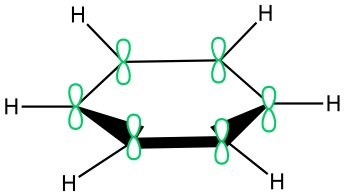
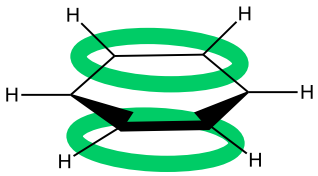
In octahedral complex, $d_{x^2-y^2}$ and d_{z^2} orbitals would experience higher repulsion, thus at higher energy level.
In tetrahedral complex, $d_{x^2-y^2}$ and d_{z^2} orbitals would experience lower repulsion, thus at lower energy level.

Before binding with ligands, five orbitals in d subshell are at same energy level. These 5 orbitals split into two energy group after forming coordinate bonds with ligands because of the repulsion of lone pairs in ligands. The energy gap between these two groups is within the range of energy carried by photons.

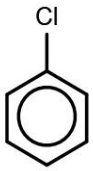
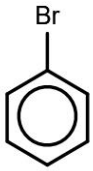
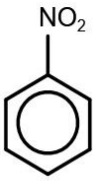
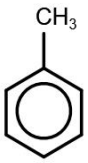
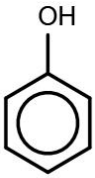
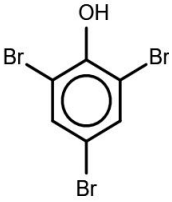
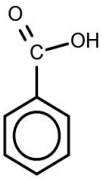
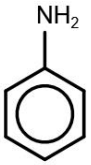
Explain why complex ions of transition metal always colored and why color would change when ligands changed, use Cu^{2+} as example.

The energy of d orbitals split into two groups when binding with ligands. Electrons at lower energy level can flip into higher energy level by absorbing photons. Only photons carrying energy that is the same with the energy gap will be absorbed. The color we see is the complementary color of the photon that is absorbed.
Different ligands produce different energy gap due to its different repulsion. Thus, different photons will be absorbed and different color will be observed.

Benzene

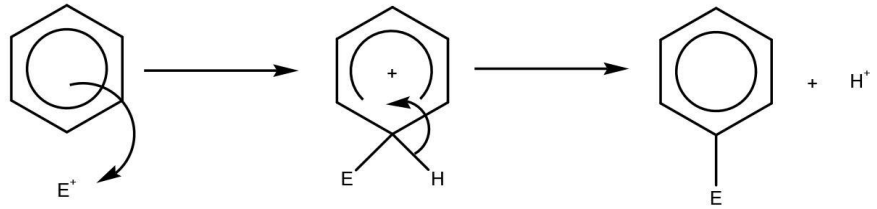
Structure	
Diagram	Description
	Each carbon is sp^2 hybridized. It forms 3 σ bond, 2 with neighboring carbons and 1 with hydrogen. Unhybridized p orbital of each carbon form a big π bond, with 6 delocalized electrons in it.
 	

Give the structures of the compounds according the name given below

Chlorobenzene	Bromobenzene	Nitrobenzene	Methylbenzene
			
Phenol	**2,4,6-tribromophenol**	**Benzoic acid**	**Phenylamine**
			

Electrophilic Substitution of Benzene

Draw the mechanism of electrophilic substitution of benzene using E^+ to represent electrophile

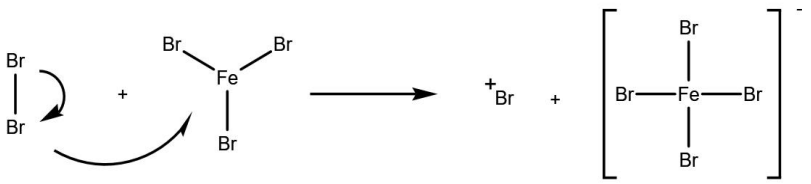
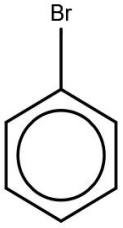
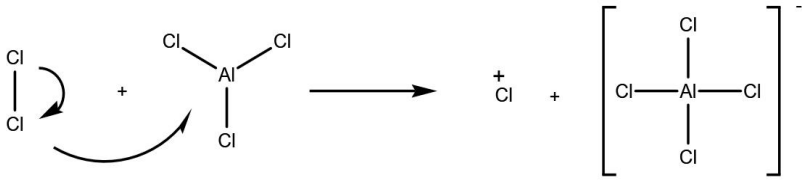
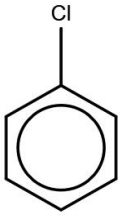
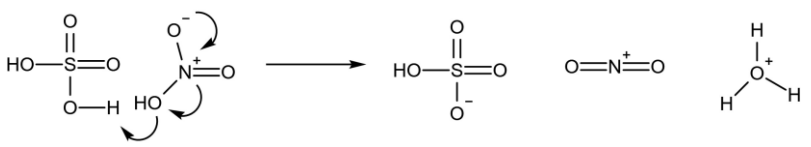
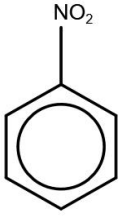


E^+ represents electrophile (lone pair acceptor), which is usually positively charged.

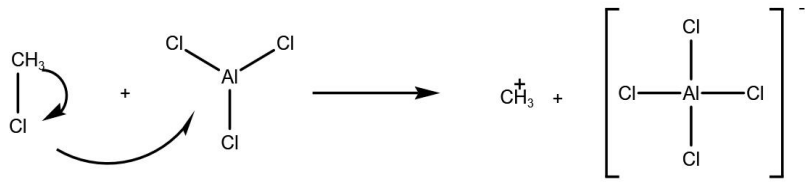
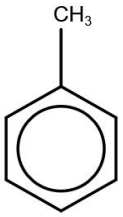
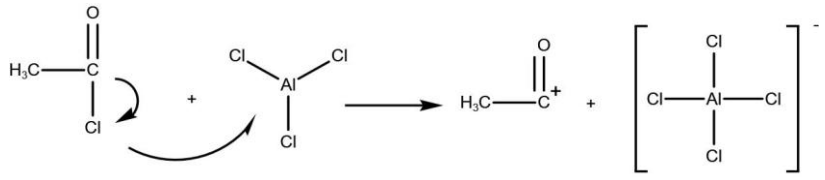
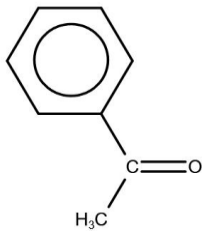
A pair of electrons from π bonding system is used to form a bond between carbon and E^+.

Four electrons remain in π bonding system and the benzene ring is positively charged.

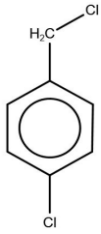
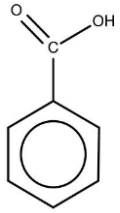
Bonding pair between C-H goes back to π bonding system and a proton is released.

Reagent/ Catalyst	Preparation of Electrophile	Product
Br_2/ $FeBr_3$	 $Br_2 + FeBr_3 \rightarrow [FeBr_4]^- + Br^+$ Catalyst would be regenerated in this way $H^+ + [FeBr_4]^- \rightarrow HBr + FeBr_3$	
Cl_2/ $AlCl_3$	 $Cl_2 + AlCl_3 \rightarrow [AlCl_4]^- + Cl^+$ Catalyst would be regenerated in this way $H^+ + [AlCl_4]^- \rightarrow HCl + AlCl_3$	
Conc. HNO_3 Conc. H_2SO_4 Heat	 $H_2SO_4 + HNO_3 \rightarrow HSO_4^- + NO_2^+ + H_2O$	

Friedel-Crafts Alkylation

Reagent/ Catalyst	Preparation of Electrophile	Product
CH_3CH_2Cl $AlCl_3$ heat	 $CH_3Cl + AlCl_3 \rightarrow [AlCl_4]^- + CH_3^+$	
CH_3COCl $AlCl_3$ heat	 $CH_3COCl + AlCl_3 \rightarrow [AlCl_4]^- + CH_3CO^+$	

Methylbenzene

Reaction of Methylbenzene		
Electrophilic Substitution	Free Radical Substitution	Oxidation
Reagent: Cl_2 Condition: $AlCl_3$ as catalyst Product 	Reagent: Cl_2 Condition: UV Light Product 	Reagent: $KMnO_4$ Condition: Reflux Product 

In electrophilic substitution, only the H on 1st, 3rd and 5th carbon of the benzene will be substituted, because alkyl group is electron-donating.

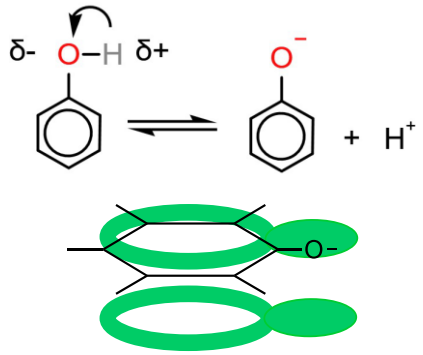
Phenol

Acidity

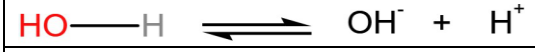
Acidity Comparison

Give structures of the following compounds and try to compare their acidities.

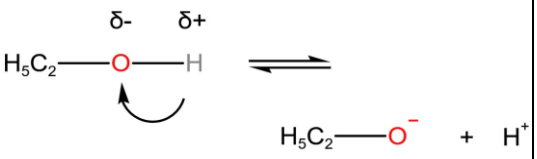
phenol



Water



Ethanol



Comparison between phenol and water

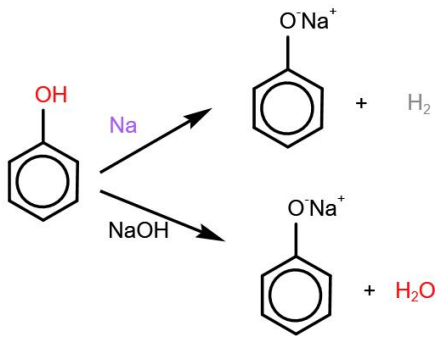
Phenol is more acidic than water. The phenoxide ion, $C_6H_5O^-(aq)$, has its negative charge spread over the whole ion as one of the lone pairs on the oxygen atom overlaps with the delocalized π bonding system in the benzene ring. Benzene serves as electron withdrawing group, making it easier for OH bond to break.

Comparison between water and ethanol

Ethanol is a weaker acid than water because of the electron-donating alkyl (ethyl) group attached to the oxygen atom in the ethoxide ion. This has the effect of concentrating more negative charge on this oxygen atom, which more readily accepts an H^+ ion. Alkyl group is electron donating, making it harder for OH bond to break.

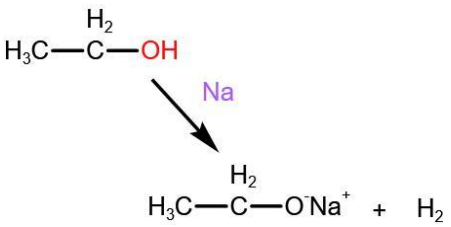
Chemical Reaction Involves Its Acidity

Phenol



Sodium hydroxide is usually used to increase the solubility of phenol.

Alcohol



The acidity of alcohol is too weak to react with hydroxide.

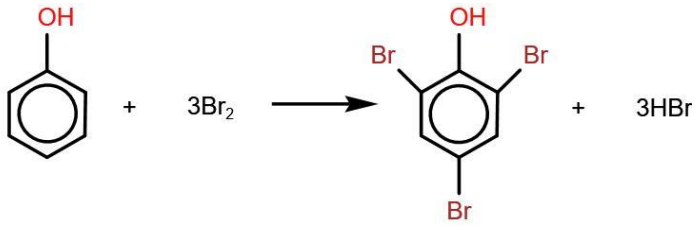
Compounds with benzene ring are insoluble in water unless they form salt and carry charge.

Electrophilic Substitution

The electrophilic substitution of bromine with phenol is much easier than that with benzene.

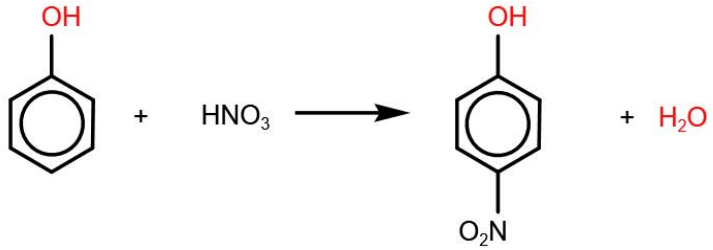
The overlap of one lone pairs of the oxygen atom in hydroxyl group with the π bonding system increases the electron density of the benzene ring in phenol. This makes the benzene ring more likely to be attacked by electrophiles. It 'activates' the benzene ring, especially at positions 2, 4 and 6.

Substitution with bromine

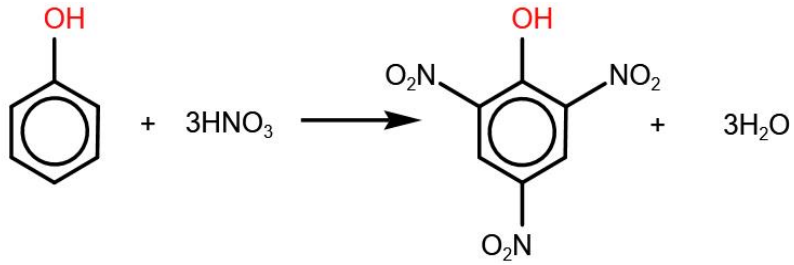


This reaction is usually used to show the presence of phenol, white precipitate would be produced

Substitution with dilute HNO_3



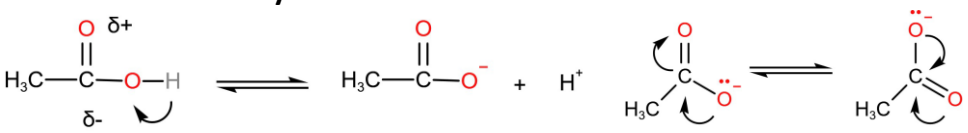
Substitution with concentrated HNO_3



Carboxylic Acid

Acidity Comparison

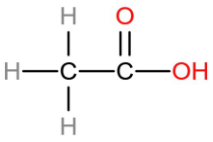
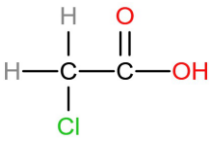
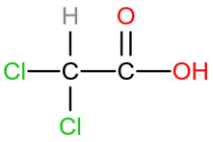
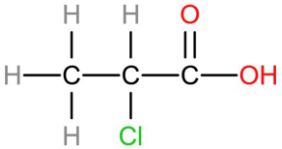
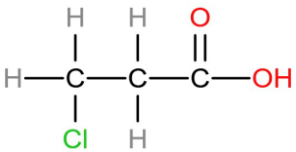
Give the displayed formula of ethanoic acid and ethanoate, trying to suggest the reasons for its acidity



C=O is electron withdrawing group, making OH bond more likely to break.

The carboxylate ion is stabilized by the delocalization of electrons around the COO^- group. This delocalization spreads out the negative charge on the carboxylate ion, reducing its charge density and making it less likely to bond with an $H^+(aq)$ ion to re-form the undissociated acid molecule.

Give structures of the following compounds and try to compare their acidities.

Ethanoic acid	Explanation
	Acidity: $CHCl_2COOH > CH_2ClCOOH > CH_3COOH$ Chlorine has much higher electronegativity than carbon, thus it is electron-withdrawing group. The O-H bond in acid is weakened by its presence. Furthermore, chlorine can also elevate the negative charge on $–COO^-$. The more chlorine atoms found on the acid; the higher acidity is expected.
Chloroethanoic acid	
	
Dichloroethanoic acid	
	
2-chloropropanoic acid	Acidity: $CH_3CHClCOOH > CH_2ClCH_2COOH$ The closer of Cl to –COOH group, the more influence it can exert on it. Thus, higher acidity is expected when Cl is at the neighboring carbon of –COOH group.
	
3-chloropropanoic acid	
	

Oxidation

Carboxylic Acid	Oxidant	Observation	Equation
Methanolic acid	$KMnO_4/H^+$	Purple to colorless	$3HCOOH + Cr_2O_7^{2-} + 8H^+ \rightarrow 3CO_2 + Cr^{3+} + 7H_2O$ The oxidation number of carbon in HCOOH is +2 while in CO_2 is +4. Two electrons of carbon are transferred to chromium as one HCOOH molecule is oxidized. The oxidation number of chromium in dichromate (VI) is +6, six electrons are transferred as one chromate is reduced. Three HCOOH react with one dichromate (VI).
	$K_2Cr_2O_7/H^+$	Orange to green	
	Tollens' reagent	Silvery mirror	
	Fehling's reagent	Red precipitate	
Ethanoic acid	$KMnO_4/H^+$	Purple to colorless	$2MnO_4^- + 6H^+ + 5H_2C_2O_4 \rightarrow 2Mn^{2+} + 10\ CO_2 + 8H_2O$
	$K_2Cr_2O_7/H^+$	Orange to green	

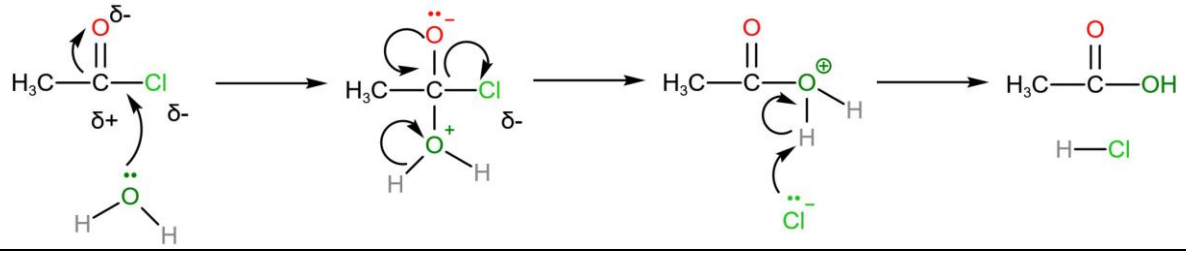
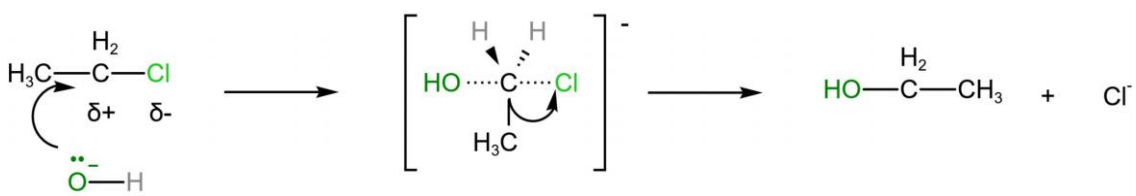
Acyl Chloride

Preparation of Ethanoyl Chloride and Benzoyl Chloride

Reagent	Condition	Equation	Observation
PCl_3	Heat	$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$	
PCl_5	r.t.p	$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3$	Fume
$SOCl_2$	r.t.p	$CH_3COOH + SOCl_2 \rightarrow CH_3COCl + SO_2 + HCl$	Fume

Nucleophilic Substitution

Compare the hydrolysis of the following compound

compound	Nucleophile	Equation	Condition or Observation
Ethanoyl Chloride	H_2O		No special condition Due to the production of HCl, white fume is observed
Chloro-ethane	OH^-		Reflux in aqueous solution
Chloro benzene	None		

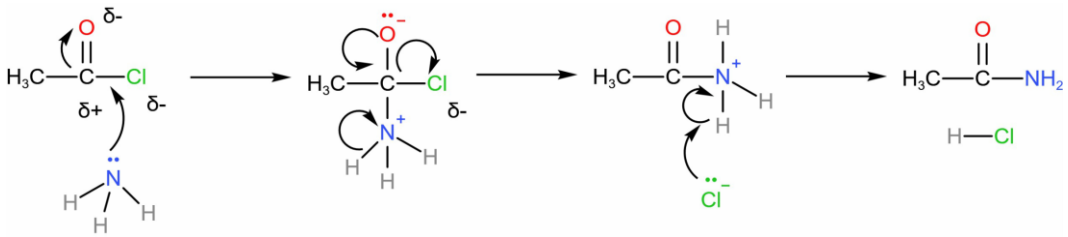
Try to suggest the difference of the ease of hydrolysis.

Acyl chlorides are very reactive compounds. The carbonyl carbon has electrons drawn away from it by the Cl atom as well as by its O atom, and both are strongly electronegative atoms. This gives the carbonyl carbon a relatively large partial positive charge and makes it particularly open to attack from nucleophile. Thus, its hydrolysis is much more vigorous than that of chloroalkane which needs to be heated and a much stronger nucleophile, OH^-.

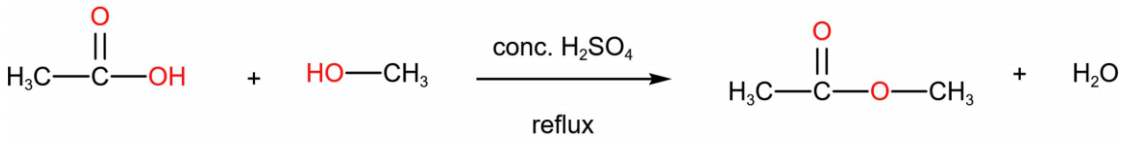
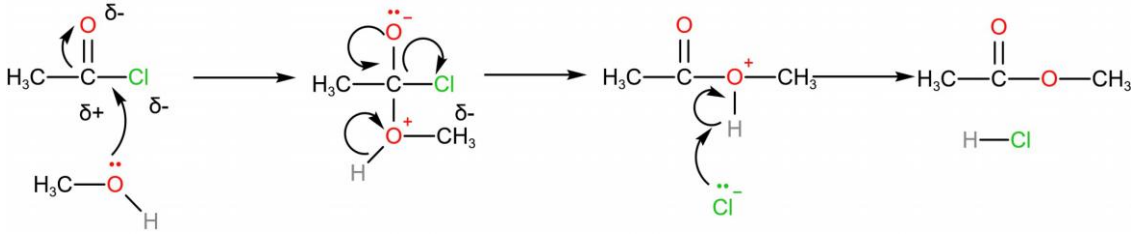
Chlorobenzene cannot be hydrolyzed anyway. Because lone pair of Cl atom is apt to delocalized into π system of benzene, C-Cl bond in chlorobenzene will therefore much stronger than the one in chloroalkane.

Condensation Reaction of Acyl Chloride

Formation of Amide

Reagent	Nucleophile	Equation	Condition or Observation
Acyl chloride	Amine		No special condition White fume is observed

Formation of ester

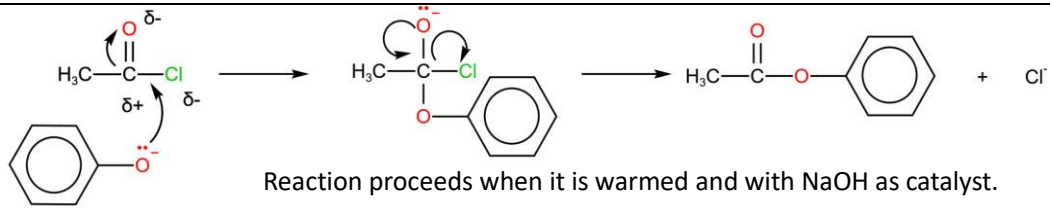
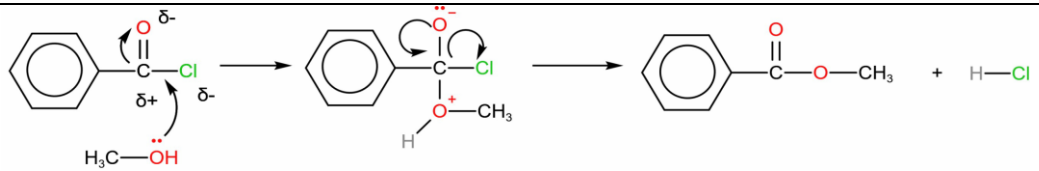
Product	Reagent	Equation	Condition or Observation
Ethyl propanoate	Propanoic acid		
	Propanoyl chloride		Vigorous reaction with white fume produced

Try to suggest the ease of esterification with acyl chloride.

The formation of ester or amide is condensation reaction as well as nucleophilic substitution. The partial positive charge is much more concentrated on the carbon of acyl chloride than that of alcohol, making it more open to the attack of nucleophile, amine or alcohol.

Formation of Ester with Benzene Ring

The ester with benzene ring must be formed by acyl chloride.

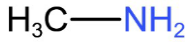
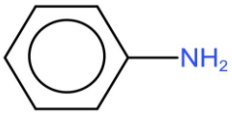
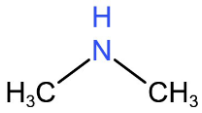
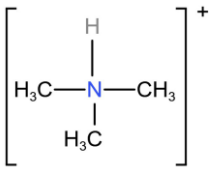
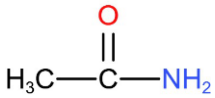
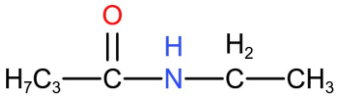
Product	Reagent	Equation	Condition or Observation
Phenyl propanoate	Propanoyl chloride	 Reaction proceeds when it is warmed and with NaOH as catalyst.	Esterification involves phenol must be proceeded with acyl chloride under alkaline condition.
Ethyl benzoate	Benzoyl chloride		

Because the lone pair on oxygen in phenol delocalize into π bonding system, making it less likely to form ester with carboxylic acid.

Organic Nitrogen Compounds

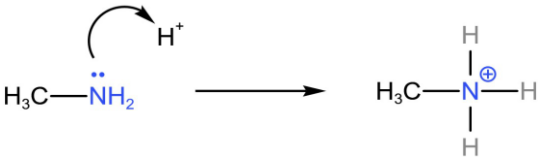
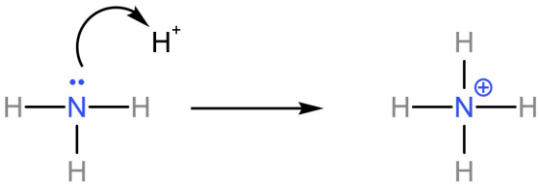
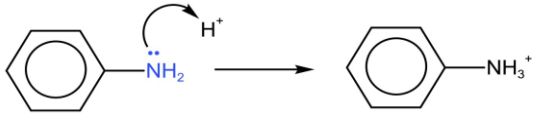
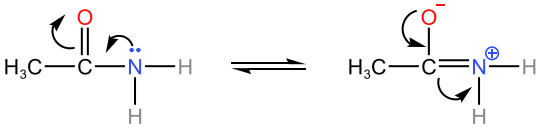
Structure

Give the structures of the compounds according the name given below

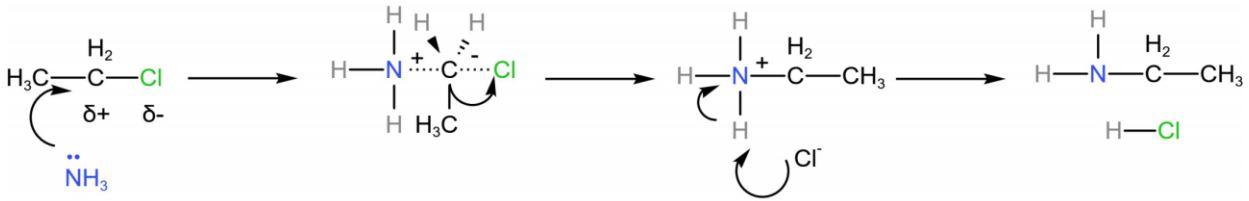
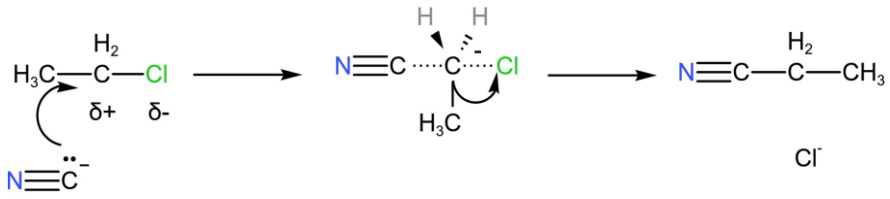
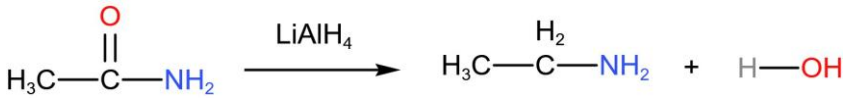
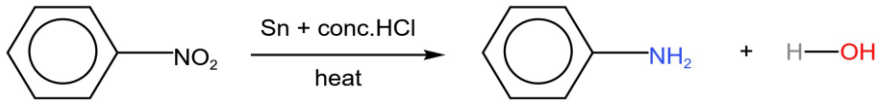
Amine			
Methylamine	Phenylamine	Dimethylamine	Trimethylammonium
			
Amide			
Ethanamide		*N*-ethyl butanamide	
			

Basicity

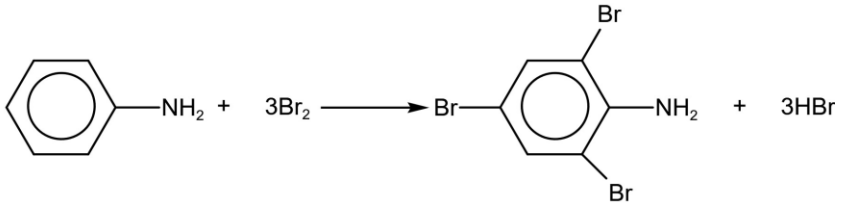
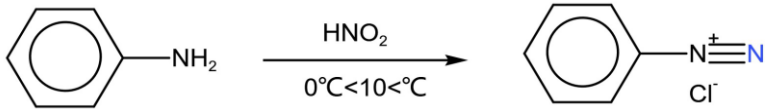
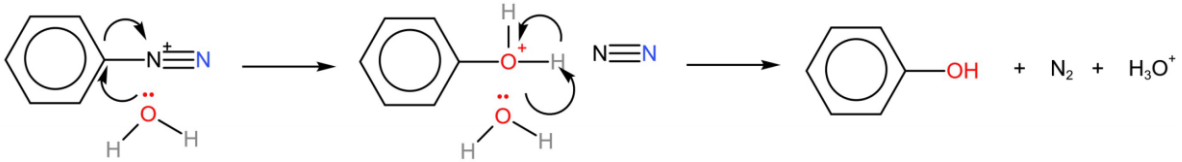
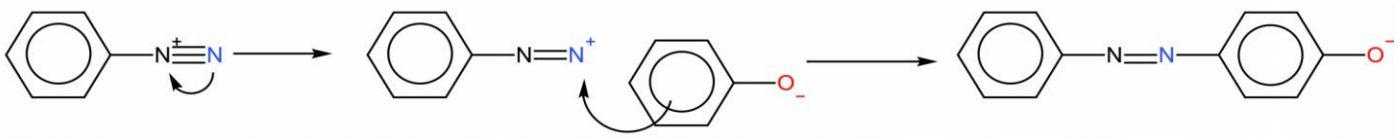
Give structures of the following compounds and try to compare their acidities.

Methylamine	Comparison between Methylamine and ammonia Methylamine is more basic than ammonia. Because alkyl group has positive inductive effect, its presence would increase the availability of lone pair on N atom to proton.
	
ammonia	
	Comparison between phenylamine and ammonia. Phenylamine is less basic than ammonia. Because the lone pair on N atom tend to delocalized into π bonding system of benzene, making it less available to accept proton.
phenylamine	
	
amide	
	Lone pair on N delocalized by C=O, thus cannot accept proton

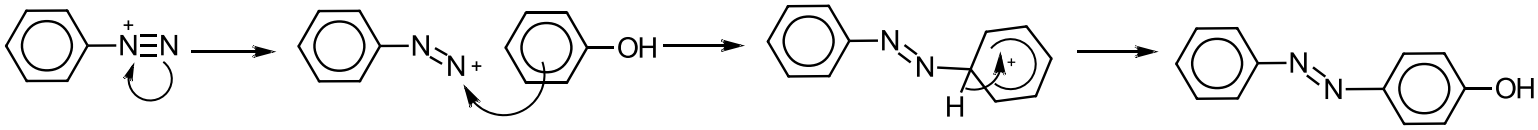
Preparation of Ethylamine or Phenylamine

Reagent	Condition	Equation
RX NH_3	Reflux in alcohol	$R\text{-}X + NH_3 \rightarrow R\text{-}NH_2 + HX$ 
RX CN^-	Reflux in alcohol	$R\text{-}X + CN^- \rightarrow R\text{-}CN + X^-$  Further Reaction and conditions $R\text{-}CN + 4[H] \rightarrow R\text{-}NH_2$ H_2/nickel & $LiAlH_4$ can serve as reductant in above reaction
Amide	Reductant	$R\text{-}CONH_2 + 4[H] \rightarrow RCH_2NH_2 + H_2O$ Only $LiAlH_4$ can serve as reductant in above reaction 
Nitro-benzene	reductant	 no other reductant can be used

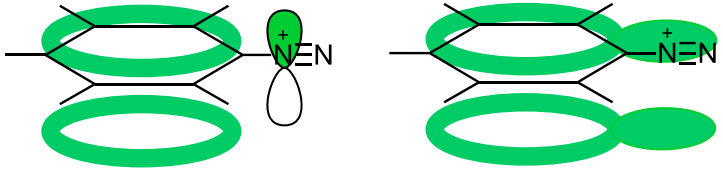
Electrophilic Substitution of Phenylamine

reaction	Reagent/ Condition	Equation	Observation
	Br_2		White ppt
Diazoti-sation	Nitrous acid < 10℃	$NaNO_2 + HCl \rightarrow HNO_2 + NaCl$ produce nitrous acid  Benzene diazonium chloride would hydrolyze into phenol if temperature gets too high 	
Coupling	Phenol in alkaline solution	 Orange dye produced at the end of reaction. The π bond between nitrogen atoms joints two π bonding system of benzene ring. This creates energy gap and color.	

Coupling is actually an electrophilic substitution. Diazonium ion act as electrophile to attack phenoxide ion.



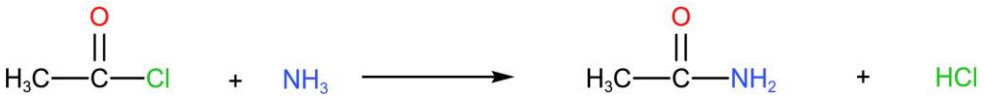
π bond in diazonium delocalize into the π bonding system of benzene, stabilizing the structure.



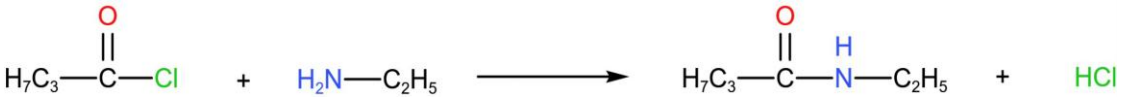
Formation of Amide and Its Hydrolysis

Give the equations of the formation of the following amides from suitable acyl chloride.

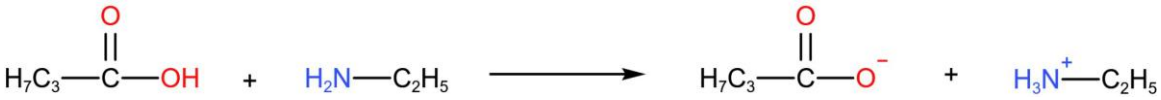
Ethanamide



N-ethylbutanamide

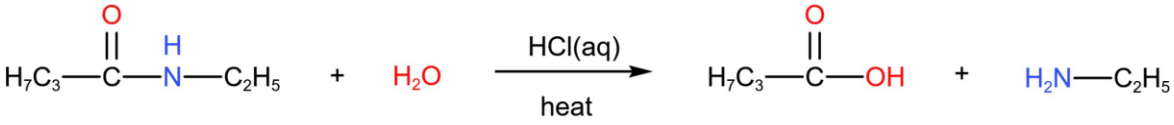


Note that amide has to be synthesized by acyl chloride and amine. If we put carboxylic acid and amine together, a neutralization may take place instead.



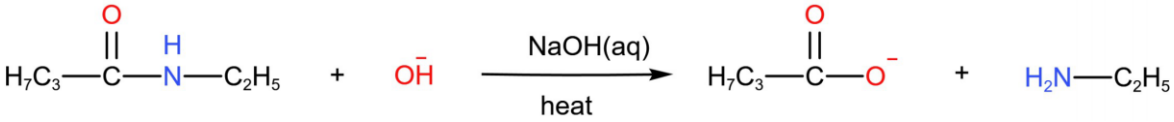
Give the equations of the hydrolysis of *N*-ethylpropanamide in both acidic and basic conditions.

In acidic condition



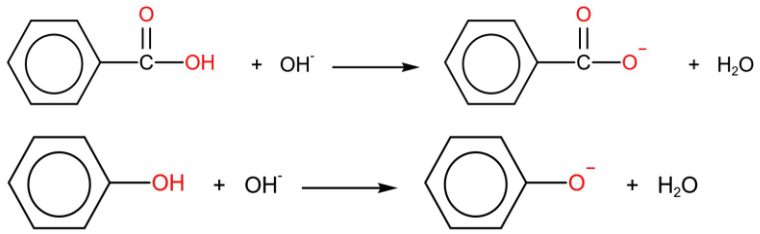
Normally, in acidic hydrolysis, amine is produced instead of its salt. If the acid is in large excess, ethylammonium will be produced.

In basic condition

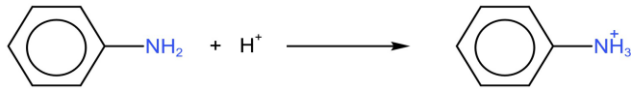


Provided with *cold alkaline or acidic* solution, neutralization may take place.

Phenol or carboxylic acid react with strong base



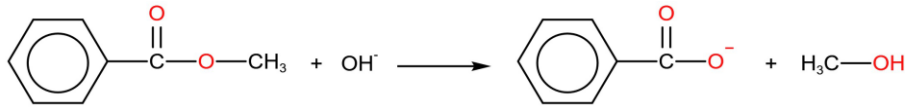
Amine reacts with strong acid



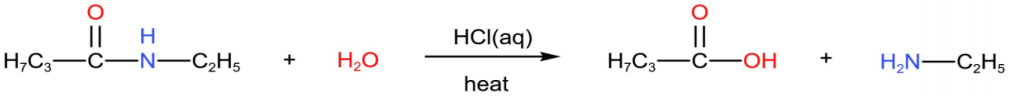
Note that compound with benzene only dissolve when it has at least one net charge.

Provided with *hot alkaline or acidic solution*, hydrolysis may take place.

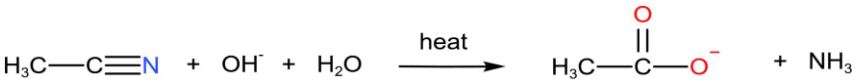
Ester hydrolyzes into acid and alcohol



Amide hydrolyzes into acid and amine

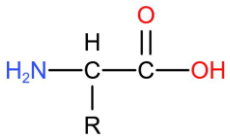
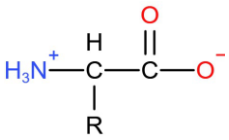
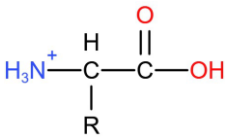
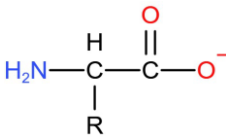
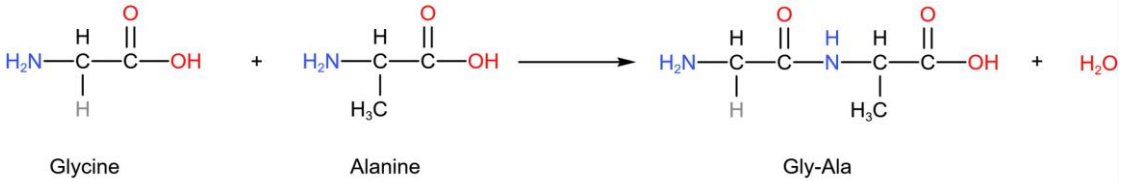
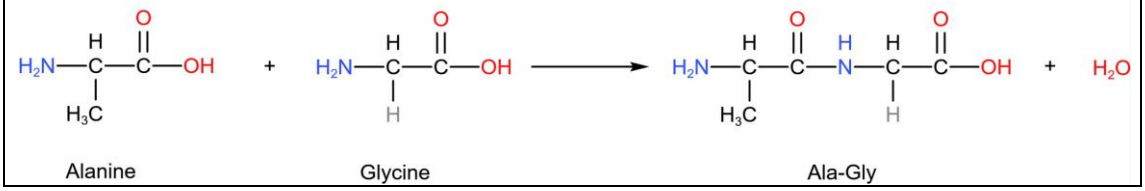


Nitrile hydrolyze into acid or its salt



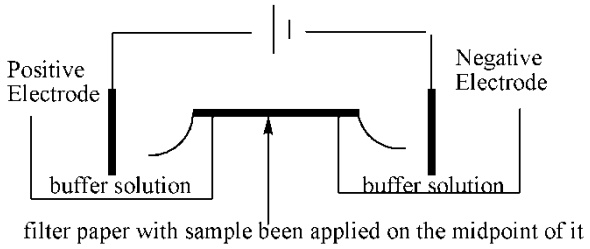
Amino Acid and Peptide Bond

Give the structures of the compounds according the name given below

Amino Acid			
General Structure	Zwitterion form	In acidic solution	In basic solution
			
Peptide bond			
Show the formation of dipeptide			
			
Glycine	Alanine	Gly-Ala	
			
Alanine	Glycine	Ala-Gly	

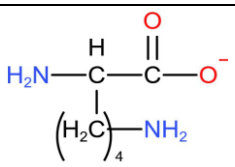
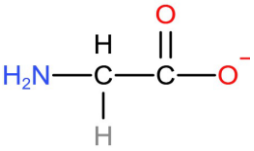
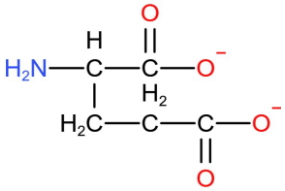
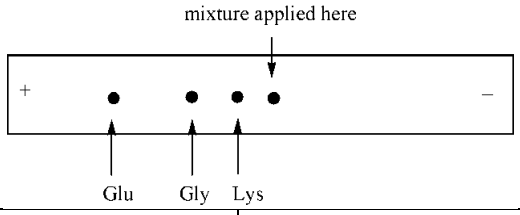
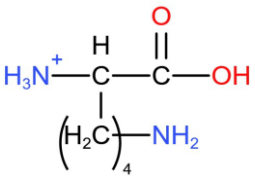
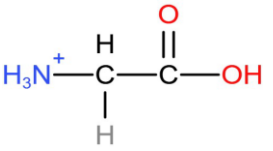
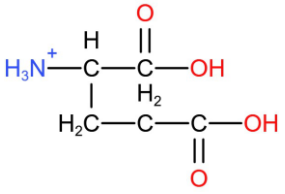
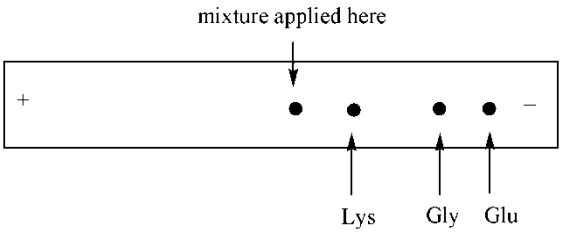
Electrophoresis

Draw a diagram to show how electrophoresis is carried out.

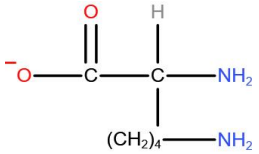
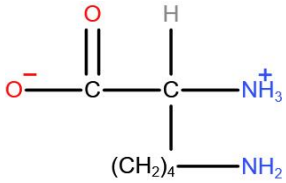
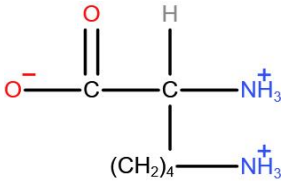
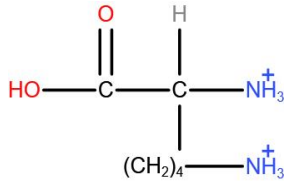
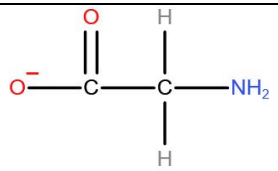
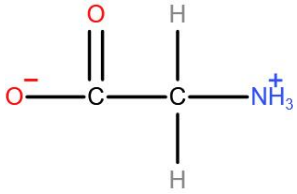
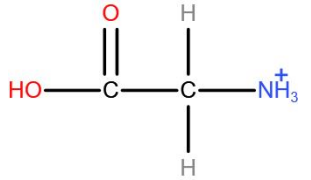
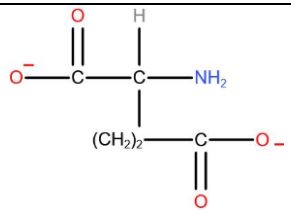
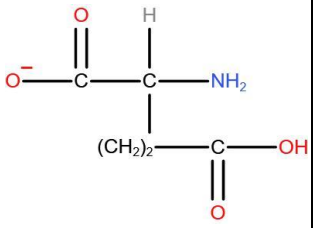
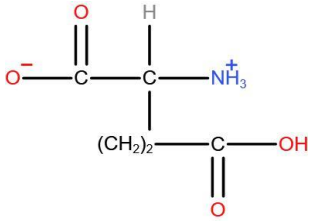
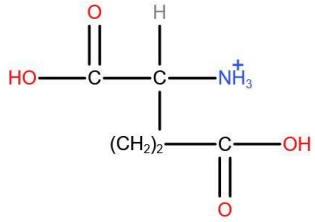


State two factors that decide the position of amino acid in the electropherogram

1. Charge of amino acid
2. Mass of amino acid
3. pH of buffer solution

pH of Buffer Solution	lysine	Glycine	Glutamic Acid
10			
Electropherogram			
pH of Buffer Solution	lysine	Glycine	Glutamic Acid
3			
Electropherogram			

Isoelectric Point is the pH in which amino acid exists as zwitterion form (no overall charge). Note that amino acid in zwitterion form has no net charge.

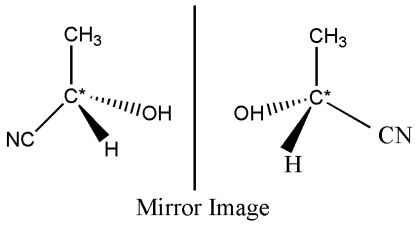
pH of Buffer Solution	Very basic	Basic	Isoelectric Point	Acidic	Very Acidic
lysine			 pH: 9.74		
Glycine			 pH: 5.97		
Glutamic Acid			 pH: 3.22		

At a buffer solution whose pH is maintained around 6: Glycine would have almost no net charge

Lysine would be positively charged while Glutamic acid would be negatively charged

Optical Isomerism

Enantiomer is a pair of optical isomers. They have the same physical and chemical properties. Polarized light rotates as they encounter one isomer of the enantiomer. Enantiomer rotate polarized light in different direction.



Give definitions of the following terms

Optically active:

Compound that is able to rotate plane of polarized light

Enantiomer/ Optical isomer:

Molecules that rotate plane of polarized light to opposite direction.

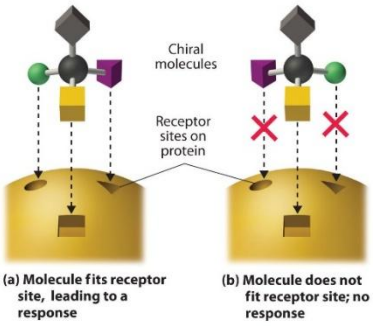
Stereoisomers that are non-superimposable mirror images.

Racemic mixture:

The mixture that has a pair of enantiomers with the same proportion is called **racemic mixture**. The chemical synthesized in lab are usually racemic mixture and they do not rotate polarized light. This is because plane of polarized light will be rotated by both isomers by the same angle of equal amounts but in different directions.

Enantiomer Drug

Enantiomers also show different biological activity as they have different spatial structure. The active ingredient of drug usually acts as inhibitor that binds to specific enzyme, disturbing biological pathway. The chemical must have complementary shape with the enzyme so as to bind with it. Usually only one of the enantiomers can bind with drug. The other isomer is either useless or toxic.



This picture is from internet

The advantage of produce drug with the only effective enantiomer

1. the other enantiomer may have different biological activity thus giving rise to side effect
2. avoids the need to separate the optical isomers to form the pure active isomer
3. lower dosage required
4. higher yield of biologically-active molecule

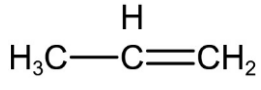
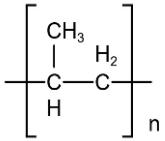
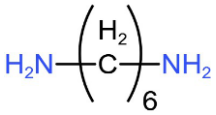
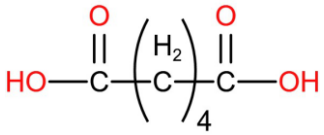
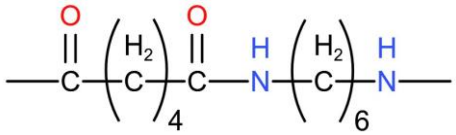
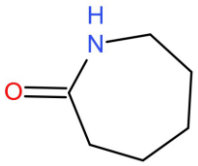
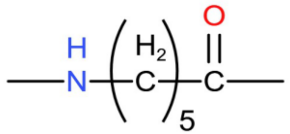
Suggest methods of adapting the synthesis to produce a single enantiomer

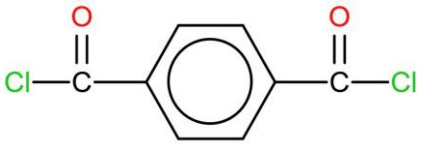
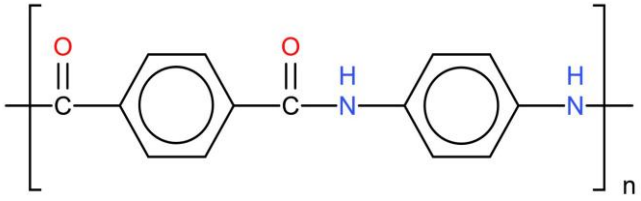
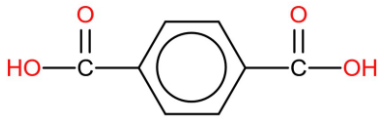
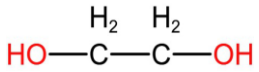
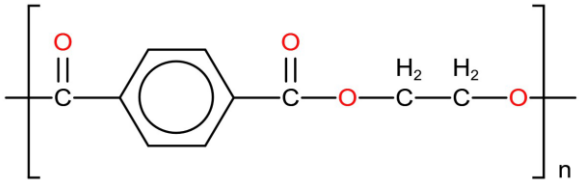
1. use chiral catalyst
2. use enzyme

Polymer

Synthetic Polymer

Structure of Polymers

<table>
<tr><td rowspan="2">Additional</td><td colspan="2">Monomer</td><td>Polymer</td></tr>
<tr><td colspan="2"> 
Propene</td><td> 
polypropene</td></tr>
<tr><td rowspan="5">Condensational</td><td colspan="3">Polyamide (nylon 6, 6)</td></tr>
<tr><td>Monomer1
1,6-diaminohexane</td><td>Monomer2
Hexanedioic acid</td><td>Polymer</td></tr>
<tr><td>  </td><td>  </td><td>  </td></tr>
<tr><td colspan="3">Polyamide (nylon 6)</td></tr>
<tr><td colspan="2">Caprolactam</td><td>Polymer</td></tr>
<tr><td colspan="2">  </td><td>  </td></tr>
</table>

Condensational	Polyamide (Kevlar)		
	Monomer1 1,4-phenylene-diamine	Monomer2 terephthaloyl chloride	Polymer
			
	Polyester (terylene)		
	Monomer1 Benzene-1,4-dicarboxylic acid	Monomer2 Ethane-1,2-diol	Polymer
			

Describe the differences between additional polymerization and condensational polymerization.

	Additional Polymerization	Condensational Polymerization
Monomer	Must have "C=C"	-OH, -COOH, -COCl, $-NH_2$ Functional groups that can condense
Product	Only polymer	Polymer and small molecules
Polymer	Only carbon in its main chain	Ester, amide or other linkages can be found on its main chain

Environmental Problem of Synthetic Polymers

State the environmental problem caused by polyalkenes. Do similar problems present with polyamide and polyester?

1. Most plastics such as polyethene, PVC are not biodegradable.
2. In polyamides, such as nylon, the amide links, CO-NH, can be broken down by hydrolysis in acidic conditions found in land-fill waste dumps with rotting vegetation. For polyesters, the ester links are similarly broken down by acid hydrolysis, forming alcohols and carboxylic acids. This susceptibility to hydrolysis makes both polyamides and polyesters biodegradable, unlike the non-biodegradable polyalkenes.
3. The polymer breaks into smaller fragments by UV light. The plastic will biodegrade much more quickly if it is not chemically inert.

Analytical Chemistry

Chromatography

Chromatography is a laboratory technique for the separation of a mixture. The mixture is dissolved in a fluid called the *mobile phase,* which carries it through a structure holding another material called the *stationary phase.* The various constituents of the mixture travel at different speeds, causing them to separate. The separation is based on differential partitioning between the mobile and stationary phases. Subtle differences in a compound's partition coefficient result in differential retention on the stationary phase and thus affect the separation

Partition Coefficients

Definition

The ratio of the concentration of a solute between two immiscible solvents at equilibrium

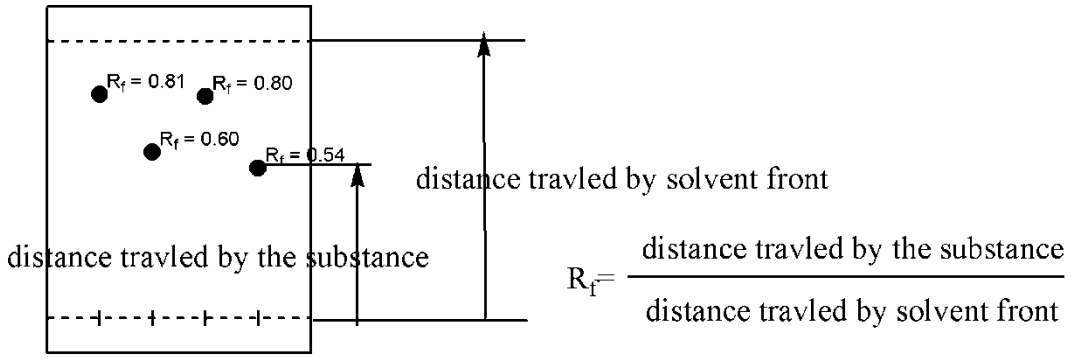
Expression

$$K_{pc} = \frac{[\text{concentration in solvent 1}]}{[\text{concentration in water}]}$$

K_{pc} can be used to predict how much time is needed for certain substance to be washed out. If mobile phase is solvent 1 while stationary phase is solvent 2, then higher K_{pc} suggests shorter retention time while lower K_{pc} suggests the opposite.

Principle of Chromatography

In paper chromatography, R_f value is used to distinguish different substance. Show how R_f value can be calculated.



Partition

separation due to their different solubility in mobile phase.

Adsorption

Separation due to their adhesion to stationary phase.

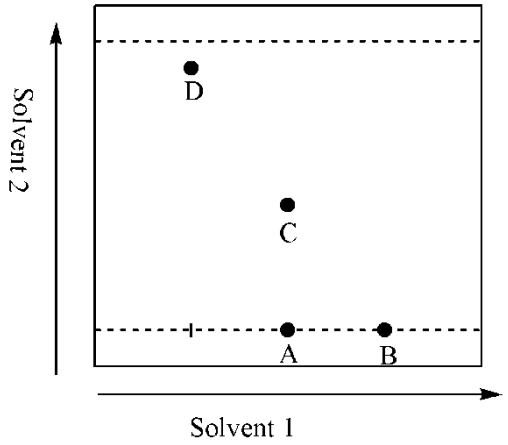
Types of Chromatography

Fill the forms regarding different chromatography techniques.

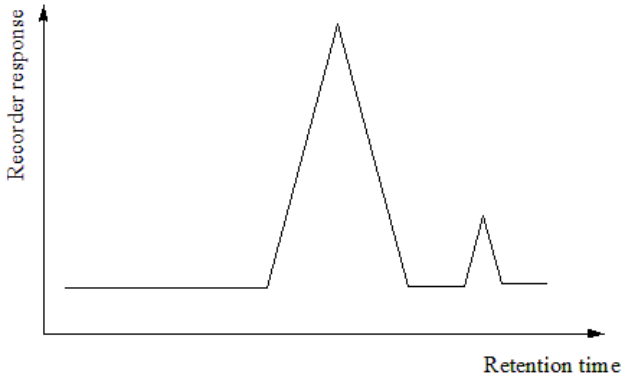
chromatography	*stationary phase*	*mobile phase*	*value*	*separation principle*	*comments*
Paper Chromatography	solvent trapped on the paper	solvent moving across paper	R_f	partition	easy to be carried out yet resolution is low
TLC **Thin Layer Chromatography**	SiO_2 or Al_2O_3	organic solvent usually non-polar	R_f	adsorption	
HPLC **High Performance Liquid Chromatography**	non-volatile liquid bonded onto solid support	polar solvent (e.g. H_2O or CH_3OH)	retention time	partition	excellent separation and can be used medical and environmental research
GLC **Gas Liquid Chromatography**	non-volatile liquid bonded onto solid support	inert carrier gas	retention time	partition	volatile substance like gas dissolved in blood

Draw a chromatogram of two ways chromatography with 4 substances lists below

substance	*solubility in solvent 1*	*solubility in solvent 2*
A	soluble	insoluble
B	very soluble	insoluble
C	soluble	soluble
D	insoluble	very soluble



Draw a chromatogram of HPLC or GLC with two substances, A and B being separated. A has much larger amount more soluble in mobile phase.



Retention time is the time between injection and retention.

Recorder response records the amount of substance being washed out at specific time.

Area under the curve is the amount of substance.

For substance with stronger interaction with mobile phase will take less time to be washed out while substance with stronger interaction with stationary phase will take more time to be washed out.

Proton (^{1}H) NMR (Nuclear Magnetic Resonance)

Analyze NMR Spectrum

Chemical shift

Chemical shift is used to refer to the energy carried by radio wave. ^{1}H with different chemical environment absorbs radio wave at different chemical shift.

Absorption

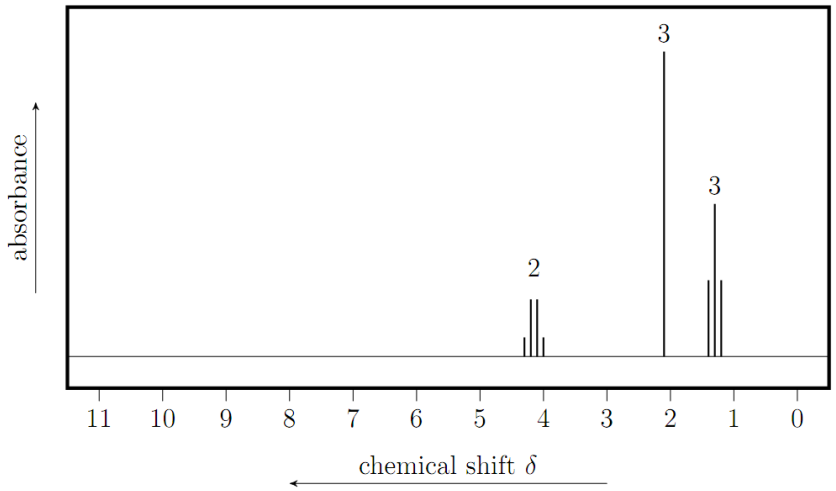
The height of absorption suggests the number of ^{1}H at that chemical environment.

Splitting pattern

For high resolution chromatography, neighboring ^{1}H also interfere the energy gap created by two spinning states. The exact splitting pattern of a peak depends on the number of hydrogen atoms on the adjacent carbon atoms.

number of adjacent ^{1}H atom	splitting pattern	relative intensity	spectrum
0	singlet	1	
1	doublet	1:1	
2	triplet	1:2:1	
3	quartet	1:3:3:1	

Give the structure of a molecule ($C_4H_xO_2$) whose ^{1}H NMR spectrum was shown below.



The triplet at δ1.3 suggests a –CH_3 adjacent to a –CH_2

The quartet at δ4.2 suggests a –CH_2 connecting with O and adjacent to a –CH_3

The singlet at δ2.0 suggests a –CH_3 connecting with C=O and no carbon around it bond with H

So the compound is $CH_3CH_2CO_2CH_3$.

Carbon-13 NMR (Nuclear Magnetic Resonance)

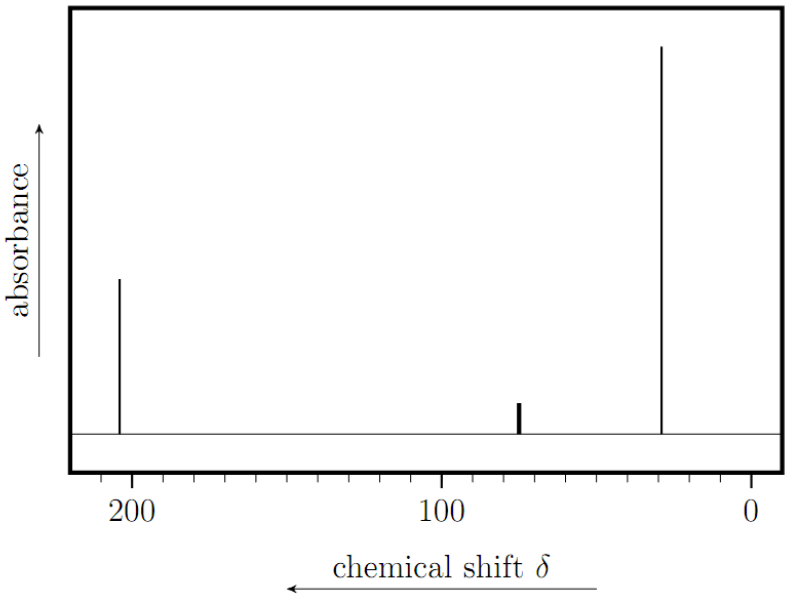
Principle

About 1% of the carbon atoms in any sample of an organic compound will be the carbon-13 isotope. Its nuclei will interact with the magnetic field applied in the NMR analysis so can produce a NMR spectrum.

The signal produced in carbon-13 NMR appear as discrete vertical lines on the spectra. Different from the spectrum produce by H-1, no complicate splitting pattern will be produced and the height of the line is not always corresponding to the number of carbon atoms involved.

Analyze NMR Spectrum

Give the structure of a molecule (C_3H_6O) whose ^{13}C NMR spectrum was shown below.



Only two chemical environments are found in this compound.

The absorbance at δ30 suggest carbons next to C=O.

The absorbance at δ200 suggest carbon on C=O

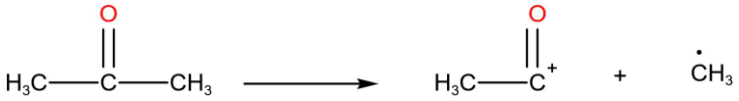
Thus the structure should be CH_3COCH_3.

The absorbance at 80 is produced by the solvent used in the analysis.

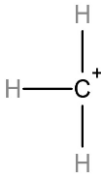
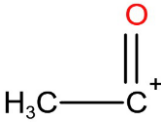
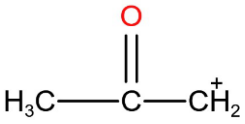
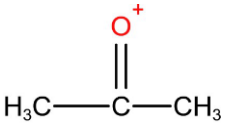
Mass Spectrometry

Principle

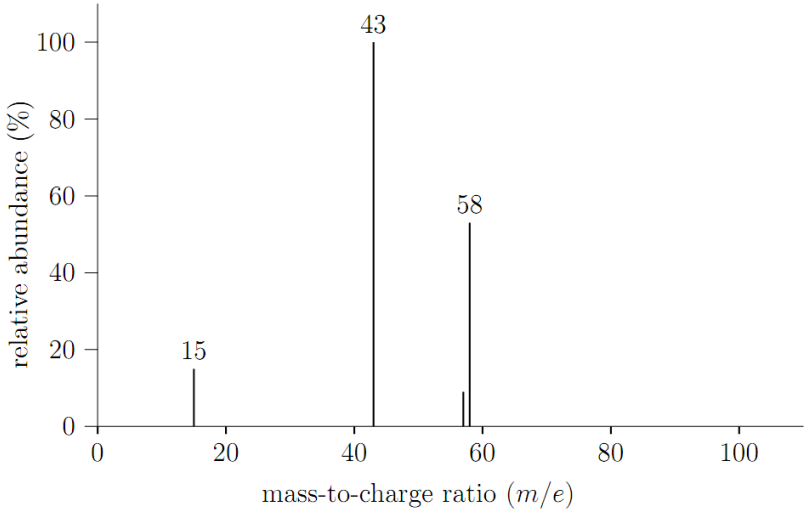
In mass spectrometer the sample is first vaporized. When vapor from the sample enters the machine, it is bombarded by high energy electrons. This knocks electrons from the molecules and breaks covalent bonds, fragmenting the molecules.



Fragments produced by propanone and their mass-to-charge ratio (m/e)

Fragments				
m/e	15	43	57	58

Mass spectrum produced by those fragments



X-axis shows the mass per charge of the fragments, the y-axis shows the relative abundance of each fragment.

The peak at the higher mass-to-charge ratio is caused by the molecular ion (M^+). This ion is formed by the sample molecule with one electron knocked out. It gives us the relative molecular mass of the sample.

Mass Spectrum of Isotopes ^{13}C

There will always be a very small peak just beyond the molecular ion peak at a mass of [M+1]. This is caused by molecules in which one of the carbon atoms is ^{13}C whose chance of occurrence is 1.10%. The abundance of M+1 peak increases as number of carbon increases.

Molecules	Species responsible for		Relative abundance
	M peak	M+1 peak	[M+1] : [M]
HCOOH	$H^{12}COOH$	$H^{13}COOH$	$1.1 : 100$
CH_3COOH	$^{12}CH_312COOH$	$^{13}CH_3{}^{12}COOH$ $^{12}CH_3{}^{13}COOH$	$(1.1 \times 2) : 100$
CH_3CH_2COOH	$^{12}CH_3{}^{12}CH_2COOH$	$^{13}CH_3{}^{12}CH_2{}^{12}COOH$ $^{12}CH_3{}^{13}CH_2{}^{12}COOH$ $^{12}CH_3{}^{12}CH_2{}^{13}COOH$	$(1.1 \times 3) : 100$

Thus, the number of carbon atoms (n) in a molecule can be deducted

$$n = \frac{\frac{[\mathrm{M}+1]}{[\mathrm{M}]}}{\frac{1.1}{100}} = \frac{100}{1.1} \times \frac{\text{abundance of } [\mathrm{M}+1]^{+}\text{ion}}{\text{abundance of } \mathrm{M}^{+}\text{ion}}$$

For a molecule whose M peak has relative abundance of 54.5% and M+1 peak of 3.6%, calculate the number of carbon atoms in it.

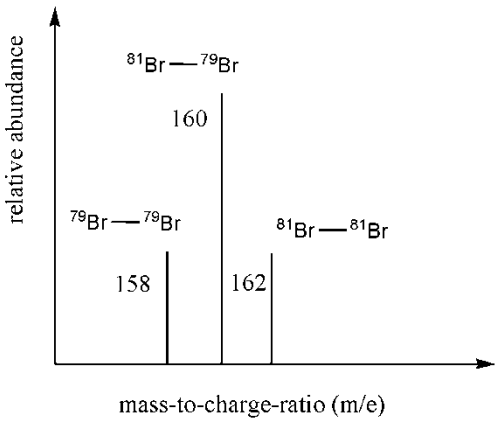
$$n = \frac{100}{1.1} \times \frac{3.6}{54.5} = 6.0$$

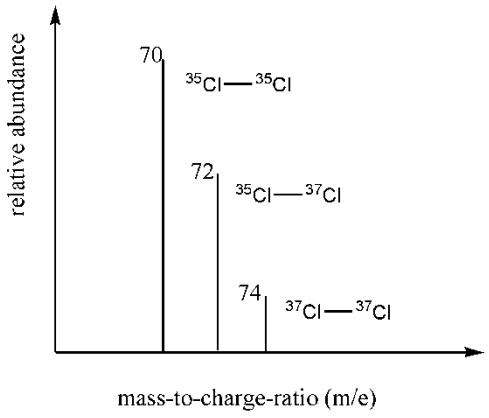
There are 6 carbon atoms in this molecule.

Mass Spectrum of Isotopes Br and Cl

If the sample compound contains chlorine or bromine atoms, we also get peaks beyond the molecular ion peak because of the isotopes of chlorine and bromine.

Element	Isotopes	Approximate %
chlorine	^{35}Cl	75
	^{37}Cl	25
bromine	^{79}Br	50
	^{81}Br	50





Element	number of atoms per molecule	peaks present and their height ration	
Chlorine	1	M:[M+2]	= 3:1
	2	M:[M+2]: [M+4]	= 9:6:1
Bromine	1	M:[M+2]	= 1:1
	2	M:[M+2]: [M+4]	=1:2:1