

Kinetics

- Changing [reactants] will affect the rate.
- Rate expression can only be determined experimentally

Order of Reaction

Rate Expression = $k [A]^m \times [B]^n$

(*Units are in mol / dm^{-3} , **K has no unit**)

- The exponent is the order. Order of A is m; Order of B is n
- The overall order of the reaction is $m + n$
- If the order of a reactant is **zero**, **do not** write it down in the expression

=Know how to find the order from a data table

(e.g. doubling the concentration would double the rate; order = 1)

=K can be found by plugging known rate and concentrations into a given rate expression

-Graphs of **initial rate** vs. **initial concentration**:

-Graphs of **time** vs. **concentration**

-Cutting the concentration by **a half**:

-First order, the rate becomes **a half**

-There is a constant half-life

-The time for the reactants to remain half as before always takes the same amount of time

Concentration: ($t_{1/2} \dots \frac{1}{2} \cdot t_{1/2} \dots \frac{1}{4}$, etc)

-Second order, the rate becomes $\frac{3}{4}$

Reaction Mechanism = The simple steps by which a reaction actually occurs

-Rate law for an elementary process follows directly from its molecularity

Isomerism

Isomerism

Isomer = Different compounds with the **same molecular formula** but with **different physical and chemical properties**

Structural = Same atoms joined together in a different order

3 Types of isomer

1. Position isomer

=same hydrocarbon skeleton but function group attached to different place

e.g.

-propan-1-ol as compared to propan-2-ol

2. HC chain isomer

e.g.

-CCCC as compared to CCC
C

3. Functional group isomer

e.g.

CCOH as compared to COC*

*=methoxymethane belongs to alkoxyalkane family

Chemical properties differences:

For types 1 and 2, if the functional group is not changed, the chemistry is not changed

For type 3, the chemistry is changed when the functional group is change

e.g.

CCOH : liquid at room temperature. Hydrogen bonding is present.

COC : gas at room temperature

Structural: Geometric enantiomers = stereoisomer

=same atoms, attached in the same order, but the 3d structure is different

Enantiomers

-chiral C (carbon attached to 4 different groups)

-produce 2 isomers

-they are mirror images

-cannot be superimposed on each other no matter how it is rotated

Equilibrium

Phase Equilibrium:

* **Not a chemical equilibrium**

Evacuated container with a volatile liquid on the bottom:

1. gaseous molecules exert pressure
2. some gaseous molecules return to the liquid
3. eventually the rate of vaporization drops and the rate of condensation increases
4. Rate of vaporization = rate of condensation

-The system that is in a state of **dynamic equilibrium** is similar to a **chemical equilibrium**

=A liquid boils when vapor pressure = pressure on the surface of the liquid

What factors affect this phase equilibrium?

-Surface area

-affects forward and reverse rate = speeds up the time to equilibrium

-Increase temperature

-to escape the intermolecular forces between the molecules (endothermic)
-vaporization requires bonds to be broken (? $H_{\text{vaporization}}$)
-similar to activation energy in a chemical reaction

=Things that are easy to evaporate:

- weak bonds
- high vapor pressure
- low ? $H_{\text{vaporization}}$
- non-polar

=Non-polar molecules have van der Waals

Van der Waals = all intermolecular forces

=Increasing the temperature increases vapor pressure

→ temperature increases → more molecules escape liquid → more molecules need to condense to match this rate → vapor pressure increases

Haber Process

Haber Process

=steam is reacted with CH₄ from natural gas over a heated catalyst

1. CH₄ + steam + catalyst → H₂ + CO₂ + excess CH₄

2. Air is added:



=This then reacts with more CH₄ to form H₂ + CO₂

3. The CO₂ is removed to leave N₂ + H₂ in a 1:3 ratio

4. N₂ and H₂ are compressed and passed over a heated Fe catalyst. This equilibrium is established:

Conditions for Haber Process

-high pressure (200 atm)

-shifts equilibrium towards the products

-the temperature is compromised 400°C

-also a finely powdered Fe catalysts

-still only about 15% products

-gases are cooled and the gases are recycled

-NH₃ is cooled and removed

Reduction and Oxidation Reaction

Balancing Redox Equations

= "Major OH electrons"

Standard conditions (E^{\ominus}):

T = 298K

[] = 1 mol / dm³

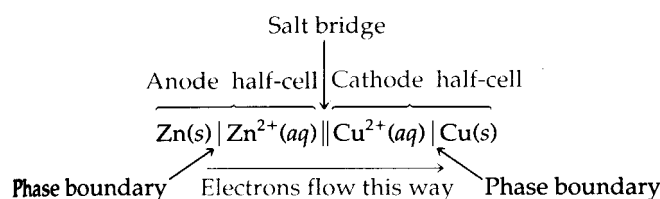
p = 101.3 kPa

Electrochemical cell

-Can be presented using short-hand notations:

/ : **phase boundary**

|| : **salt bridge**



-Know the movement of ions:

anions → anode
cations → cathode

=Hydrogen half cell has a potential of **zero**

-1 atm H₂(g)

-pt coated electrode (with finely powdered pt black)

-1M HCl

Standard Electrode Potential

=A metal is in a solution of its ions

-if the metal is reactive, a Le Chatelier's shift to the right occurs



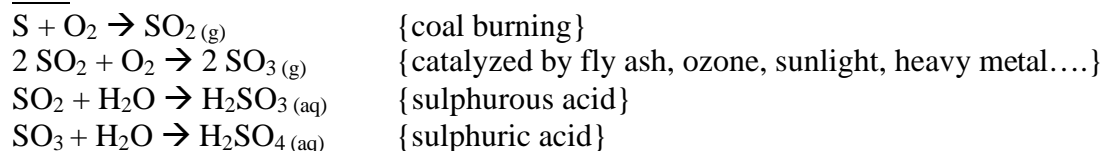
(When the metal dissolves, the remaining metal has an excess of electrons)

Acid Rain

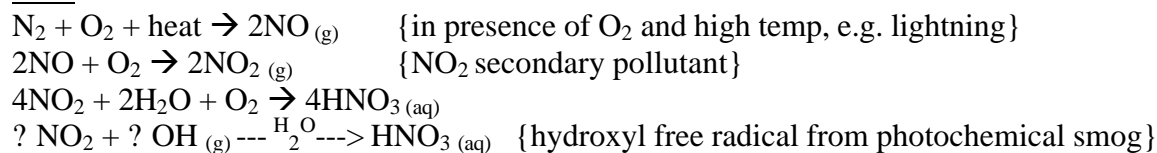
Normal rain in pH 5.6 due to carbonic acid: $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3(\text{aq}) \leftrightarrow \text{H}^+ + \text{HCO}_3^-$
In industrialized areas, pH 4-5 is common

Sources

SO_x

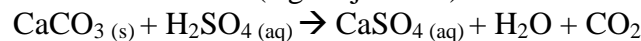


NO_x



Harm

- 1) *Human*: - acid droplets irritates respiratory tract
- 2) *Aquatic life*: salmon cannot survive pH 5.5; fish in general cannot tolerate pH 4
- 3) *Soil*: removes basic nutrients
- 4) *Materials*: corrosion of marble (e.g. Taj Mahal)



Carbonates convert to more soluble sulfates, which induce “stone leprosy”

Bleaching and weakening of fabrics and leather

Discolouration and embrittlement of paper

- 5) *Iron and Steel*: $4 \text{Fe} + 3 \text{O}_2 \rightarrow 2 \text{Fe}_2\text{O}_3(\text{s})$ {corrosion}

Increased by high humidity, high temp, and particulates

Heavy metals leach into water, e.g. Hg, Cd, Pb

- 6) *Vegetation*: **Acute injury**: short term exposure to high [acid]-----dead and bleached leaves

Chronic injury: long term-----disrupt chlorophyll synthesis, yellow leaves, suppressed growth

- 7) *Visibility*: sulphuric acid and sulfate aerosols create mist

Solution (see Air Pollution)

Primary Air Pollutant: directly to air e.g. CO₂

Secondary Air Pollutant: formed in atmosphere e.g. ozone

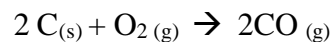
5 air pollutants: *CO, NO_x, SO_x, HCs, particulates*

Carbon Monoxide

- polar covalent
- not soluble in water
- colourless, odourless, tasteless

Source

incomplete combustion of carbon and carbon-containing compounds



with more O₂ present $2\text{CO} + \text{O}_2 \rightarrow \text{CO}_2$ or $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$
therefore, CO is due to insufficient O₂, e.g. forest fire, internal combustion engine

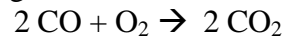
90% natural sources: oxidation of CH₄

10% human sources (anthropogenic): fossil fuels, internal combustion engine, forest fire

problem with human sources: 1) **localization**: small area

2) **high emission rates**: high []

3) fungi in soil convert CO to CO₂



but cities don't have much soil

Harm

Human blood

CO interferes with oxygen transport, causing asphyxiation, shortness of breath, etc.



If more O₂ react with Hb, COHb production is not favoured according to Le Chatelier

Solution

- 1) Thermal Exhaust Reactor: - oxidize CO to CO₂ $2 \text{CO} + \text{O}_2 \rightarrow 2 \text{CO}_2$
 - convert HC to CO₂ + H₂O
 - low air to fuel ratio = more CO & HC and less NO_x
 - CO and HC oxidize in exhaust reactor
 - expensive engines

- 2) Catalytic converter: $2 \text{CO} + 2 \text{NO} \xrightarrow{\text{Pt catalyst and moderate } ^\circ\text{C}} 2 \text{CO}_2 + \text{N}_2$
must use high octane, non-leaded fuel, free of sulfur impurities

Ozone Depletion

Evidence for ozone depletion

- satellite data from 1979 to 1995 shows decline in ozone concentration by 6%
- from 1956 to 1992, data shows decline of 50% over South Pole
- Environment Canada concludes Antarctic has 70% and Arctic has 45% ozone [] drop
- NASA's satellites show depletion over South Pole
- ozone over Canada depleted 6% since 1980

OZONE

- in stratosphere
- bluish, acrid-odour
- oxidizing agent

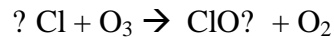
Photo-dissociation of oxygen by UV rays: $O_2(g) + UV \text{ ray} \rightarrow 2 \cdot O$ (free radical)
 $O_2(g) + \cdot O(g) \rightarrow O_3(g)$
Reversible when O_3 absorbs UV rays
99% UV rays absorbed

Decrease in O_3 = skin cancer, sunburn, genetic mutations, world climate change...
 O_3 cause smog (merely 0.2 ppm), which attacks rubber products, crops....

CFCs— aka freons, propellant, air conditioner, solvents.....etc

In the upper atmosphere: $CCl_2F_2 + UV \text{ light} \rightarrow \cdot CClF_2 + \cdot Cl$

C-F = 484 kJ
C-H = 412 kJ
C-Cl = 338 kJ



NO also depletes ozone: $NO + O_3 \rightarrow NO_2 + O_2$

CFC alternatives

- 1) propane and 2-methylpropane HCs as refrigerant coolants. But they are flammable and are greenhouse gases
- 2) Fluorocarbons: strong C-F bonds means stability, and won't react with ozone
- 3) Hydrochlorofluorocarbons (HCFCs): C-H stronger, more stable than C-Cl bond
- 4) hydrofluorocarbons (HFCs): best alternative, e.g. CF_3CH_2F (1,1,1,2-tetrafluoroethane)

Toxic Substances in Water

Discuss the different approaches in expressing toxicity.

Advantages and disadvantages of LD₅₀ (lethal dose in 50% of the population) and maximum daily tolerance

Toxicity

- short term: causes acute effects occur shortly after intake
- long term: chronic effects – causes damage over a long time of exposure

2 ways to express toxicity:

=LD₅₀

- mg per kg mass that kills 50% of lab animals
- smaller LD₅₀ means more toxic

=Disadvantages:

- Different species react differently to various poisons
- To make any extrapolation, studies are carried out with different animals
- Human is different from animals
- Children and adult have different body mass (may accumulate in body)
- Adult may have mechanisms for protection against some poisons

-Toxicity is also expressed as the mass of substance required for a lethal dose

LD ₅₀ < 1mg/Kg :	extremely toxic
1-50 mg/Kg:	highly toxic
50 –500 mg/Kg:	toxic
500 – 5000 mg/Kg:	moderately toxic
5000-15000 mg/Kg:	slightly toxic

The maximum daily tolerance to a substance

=The mass of the substance that can be safely eaten on a daily basis without adverse effects. Calculated based on body mass

-Carry studies on several species of animals and divide the tolerance quantity observed by 100.

→ not always possible to divide by 100 because naturally occur levels may exceed that

State the principal toxic type of chemicals that may be found in polluted water. Include heavy metals, pesticides, dioxins, PCBs

- Pesticides, dioxins, PCBs (polychlorobiphenyls)
 - Pesticides such as DDT (now banned because of biological magnification)
 - Dioxin: impurity in herbicides
 - PCB: highly stable compounds used in electrical transformer
- Heavy metals:
 - cadmium, copper, lead, mercury
 - Mercury converted to methyl mercury by anaerobic bacteria
 - fish consume those and pass on to the food chain

Smog = smoke + fog

Discuss reducing and photochemical smogs. A comparison between reducing and photochemical smogs should be made

Two types:

- Industrial smog (reducing smog, London smog)
 - =pollution from burning sulfur containing coal and oil
 - contains SO_x , particulates, sulfuric acid
 - Happens in cold/wet wintry weather. Thermal inversion worsens it.
 - Acid rain effects (SO_x)
 - <breathing difficulties, corrosion, marble, aquatic life>
 - Prevented by:
 - Alkaline scrubber (kill SO_x and particulates)
 - Electrostatic precipitators (kill particulates)

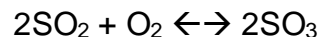
- Photochemical smog (oxidizing smog) (**Do not contain SO_x**)
 - =pollution from automobile exhaust
 - NO_x , ozone, alkanals, unburnt hydrocarbons, PANs (peroxyacyl nitrates)
 - Needs sunlight, warm sunny weather. Thermal inversion worsens it.
 - Acid rain effects (NO_x) + irritate eyes by lachrymator (PANs and O_3)
 - (lachrymator = things that cause eye to water)
 - Prevented by
 - Catalytic converter, and thermal exhaust reactor
 - Lean burning engine
 - (low air to fuel ratio lower NO_x but more HC)
 - (high air to fuel ratio lower HC but more NO_x)

Describe the catalytic effect of particulates and nitrogen oxides on the oxidation of sulfur dioxide. Particulates and SO_2 : hemolytic catalysis to form SO_3 ; NO_x + SO_2 : free radical catalysis to form SO_3

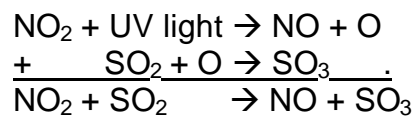
= SO_2 is combusted from coal and is used for heating, manufacturing industry and generation of electricity

-converted to H_2SO_4 by oxygen, particulates, sunlight and water vapor

Process:



- Catalyzed by heterogeneous catalyst: particulates (especially metallic particles)
 - Oxygen molecules are adsorbed onto metal surface, weakening the bond between the oxygen atoms, allow them to react with SO_2



- SO_3 (anhydride of sulfuric acid) + $\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$

Oxygen Demanding Wastes

=Water pollution is measured by amount of:

- oxygen demanding waste
- disease-causing pathogens or microorganisms
- nutrition (that could lead to growth of oxygen-depleting plants)
- particulates
- benzene, chromium, mercury, dissolved minerals
- heat (thermal pollution)

-Explain the importance of dissolved oxygen (DO) in water

- amount of DO is indicator of water quality
- measured in parts per million
(i.e. good quality water contains 9 ppm DO – it means 9 mg of oxygen in a million mg of water, < 4.5ppm is bad quality)
- aquatic plants and animals rely on the dissolved oxygen to survive

Describe aerobic and anaerobic decomposition of organic material in water. Include the influence of nutrients such as nitrates and phosphates on the growth of aquatic plants (eutrophication) and the effect of their subsequent on oxygen concentration

Discuss the effects of oxygen demanding wastes on water quality

Eutrophication = the excessive growth of plants (e.g. red tides)

- caused by:
 - plant nutrients (nitrates and phosphates from detergents and fertilizers)
 - dead body of animal, and animal wastes
 - bacterial activity
- ran out of oxygen. Aerobic bacteria and fish die of asphyxiation

=Aerobic bacteria oxidize carbon to become carbon oxides

=Anaerobic bacteria reduce elements:

- carbon into methane
- nitrogen into ammonia and amine (strong fishy smell)
- sulfur into H₂S (foul smelling) <used as an indication of the presence of anaerobic activities>

-Define Biological Oxygen Demand and describe how it is a measure for oxygen demanding wastes

BOD = a measure of the amount of oxygen needed to decompose all the biodegradable organic wastes and ammonia in a given amount of water usually over 5 days at 20°C.

- An effluent sample is diluted in oxygen saturated water and enclosed without air space in a BOD sample bottle. The decrease in dissolved oxygen is then measured using an oxygen electrode after 5 days

-The greater the amount of oxygen-demanding wastes, the higher is the BOD

=Sources of BOD:

- organic substances from eutrophication
- animal and human wastes
- industrial processes: meat-packing and food processing, plant and paper mills

Discuss ways to obtain fresh water from sea water using distillation, reverse osmosis or ion exchange

Desalination = remove salt from sea or brackish water to produce fresh water

-sea water is not fit for drinking, and it erode equipments

Distillation = separation of volatile liquid from non-volatile material (very expensive!!)

-Heat it, collect the vapor as fresh water

-Can be made more efficient by using a multistage process

-maximize the use of heat (recycle the heat when vapor is condensed)

Reverse Osmosis: (expensive)

-Pushing sea water through a semi-permeable membrane that allows water to pass through

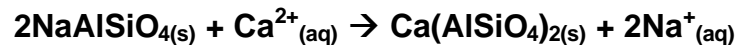
-When the "pushing" is greater than natural osmotic pressure of water

→ reverse osmosis

-Salty solution (brine) remain in the original side, and is later disposed

Ion exchange : See tertiary treatment

-Ca²⁺, Fe²⁺ and Mg²⁺ exchanged by Na⁺ because Ca bounds to AlSiO₄ more tightly:



-Hard water ions (scum forming) are replaced by soft water ions (Na⁺)

Bondings

Multiple Bonds

-Multiple bonds can form between two atoms, but the bonds are not identical

= **First bond:** (sigma bond)

- Maximum electron density is on a line joining the two nuclei
- Can be s-orbitals, one of the p-orbitals or a hybrid orbital
- A bond symmetrical about the internuclear axis is formed

=**Second bond:** (pi bond)

- Interactions of the electrons in p-orbitals that are at right angles to the internuclear axis
- The pi bond has a low electron density at where the sigma bond is (the internuclear axis)

=**Third bond:** (pi bond)

- also a pi bond, 90° to the second pi bond

=Single bond are always sigma bonds, double bonds (**the area is flat**) are 1 sigma plus 1 pi, and triple bonds (**the area is flat**) are 1 sigma and 2 pi's.

=When more electrons are shared, the two atoms are closer together
→ stronger bonding

=When number of bonds increases, bond energy increases, and the bond length decreases

For example:

	Bond energy (kJ)	Bond Length (pica meter)
C-C	348	154
C=C	612	134
C≡	837	120

-This is also true for bonds other than the ones between carbons:

N≡N : 994

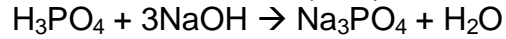
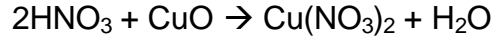
O=O: 496

F-F: 158

CH₃COOJH contains 2 CO bonds, one single and one double bond. The double bond is shorter than the single.

Acid and Base

-The types of reaction that can occur between acid and base:



Difference between strong and weak acids

- conductivity
- pH
- reaction rate

All acid and base reaction are **dative covalent bond**, and are **redox reactions**

Lewis Acids / Base

- Acid = electron acceptor**
- Base = electron donor**

Lewis can be used to explain acid/base that do not involve H^+ in them. An acid is Lewis only when it is not a Lowry-Bronsted.

e.g.

=Other common Lewis acids are in the same family as group III

=All interactions to form a complex ion are also Lewis acid/base reaction

Know about: K_a , K_b , $\text{p}K_a$, $\text{p}K_b$, pH, pOH

Calculating the pH of the buffers:

$$\text{pH} = \text{p}K_a - \log \left(\frac{[\text{HA}^-]}{[\text{A}^-]} \right)$$

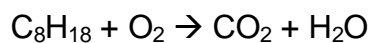
Salts

Stronger the conjugate acid / base, then its conjugate partner would be weaker

Organics

Reactions of the alkanes

Clean burning:



=The number of **carbons** determines the number of CO₂ produced.

=The number of **hydrogen** determines the number of water produced.

The number of oxygen can then be balanced: