# 11 - Further kinetics

## Rate of reactions

Rate of reaction - Rate of change of concentration of reactants. Unit: mol dm-3 s-1

Order of reaction - Power of concentration of reactants in rate equation

Overall order of reaction - The sum of the powers of all concentration of reactants in rate equation

Rate = k[A]x[B]y

[A][B]: Concentrations of the respective reactants

k: Constant in rate equations. Proportional to rate

X, Y: The order of reaction with respect to [A][B]

X \* Y: The overall order of reaction

E.g. when rate=k[A]2, concentration of A multiplies by 2, rate multiplies by 4.

**The units of k varies and must be derived via rate equation**

### Determining orders of reactions

Half-life - Time for concentration to halve from last half-life / 0s

Concentration-time graph’s slope is the instantaneous rate of reaction (by definition)

|  |  |  |
| --- | --- | --- |
|  | **Concentration-time graphs ([A]-t)** | **Rate-concentration graphs (1/t-[A])** |
| **0 order** | Straight line | Flat line |
| **1st order** | Half-life unchanged | Straight line through origin |
| **2nd order** | Half-life x2 | 1/t-[A] | 1/t-[A]2 |

### The rate determining step

Rate determining step - The slowest step in a multi-step reaction

1. in the rate determining step = [R] in rate equation

#### Determining the rate equation from steps

1. Remove intermediates from list of steps
2. Find RDS (slowest step)
3. Check for **equilibrium** – they can substitute for intermediates and appear in the rate equation
4. Deduce rate equation by mol ratio in RDS

### Initial rate and average rate

*Initial rate* ≈*Average* rate t-1 ∵ assuming rate constant

Rate Δ (over time) ↑ → error ↑

## Arrhenius Equation (Given in exam)

A = Arrhenius constant

k = Rate constant

T = Temperature **(K)**

Ea = Activation Energy (J mol-1)

R = 8.31

m = (unit K)

m =

c =

//

Standard // Arrhenius Plot ( - graph)

Remember to give units in axis

## Catalyst types

### Homogeneous

* Phase: Same phase as [R]
* Mechanism: React with [R] to form **intermediates → products** + **re-form** catalyst
* Reformation: Yes

Note that the Ea of forming intermediate + products is lower than the uncatalysted reaction

### Heterogeneous

* Phase: Different phase as [R]
* Mechanism:

1. R A**d**sorb onto surface
2. Weakens bond in R
3. Products then desorb

∴Surface area ↑Rate ↑

**Support mediums** are used to ↑area → ↓cost

* Reformation: Not used up

Advantage over homo: Does **not need separation from products**

### Autocatalysis

**Product of reaction acts as catalyst**: [P] ↑→ rate ↑

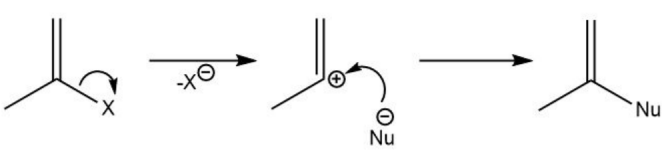
* Phase: Same phase as [R]
* Mechanism:

1. Reaction is slow at start
2. Catalyst [P] is formed → reaction speeds up (rate↑)
3. [R] ↓→ reactions slows down (rate↓)

* Reformation: None after reaction

## Mechanisms of nucleophilic reactions and rate of reactions

|  |  |
| --- | --- |
| **Question** | **Answer** |
| What does the rate equation give about mechanism of reaction? | * Mechanism is SN1 * Since there are *n* steps, the RDS only involves [*X*] |



### RX SN1 [3]

* Mechanism: X leaves → Nu: attacks C+
* Steps: 2
* Rate equation: rate = k[RX] (∵ **Step 1 is the rate determining step** (slow))
* Speed depends on: Stability of the C+ (∵ X leaves)
* ∴fastest reaction: **Tertiary RX** (∵ most stable RX)

### RX SN2 [1]

* Mechanism: Nu: attacks C+ + X leaves (simultaneous)
* Steps: 1
* Rate equation: rate = k[RX][Nu:] (∵ **Only one step**)
* Speed depends on: Ease of access of Cattached to X by Nu: (∵ Nu: attacks)
* ∴fastest reaction: **Primary RX** (∵ smaller groups attached to X)

[More about SN1 and SN2 reactions](#_NS_Mechanisms)

## Following rate of reactions

Record different varied quantities at **regular time intervals**

### Titration

1. **Remove small samples** with pipette from reaction where rate is measured
2. **Quench** (temp pause) the reaction by removing catalyst (or icing)
3. **Titrate** with solution depending on product.

Example: Hydrolysis (RX + H2O → ROH + HX)

1. Remove small samples
2. Quench with nitric acid (HNO3) ∵ Remove OH- *(stop reaction)*
3. Titrate with silver nitrate solution (AgNO3(aq))

### Color change

Only works for aq solutions (not gas)

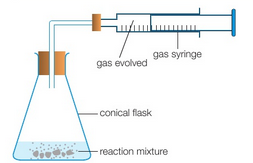
E.g. CH3COCH3(aq) + I2(aq) → CH3COCH2I(aq) + H+(aq) + I-(aq)

I2 brown →Absorbance of solution ↓

### Change of volume of gas

Reactions with [P](g)

1. Collection of gas over water

* *Not applicable: NH3 CO2 dissolves in water*

1. Collection of gas with gas syringe

* *Higher precision*

### Change of mass of gas

Reactions with high density [P](g)

* *Not applicable: H2 (∵ low density)*

### Electrical conductivity

Reactions with Δn of ions

Number of ions ↑Conductivity ↑

## Iodine clock reaction

For acid-conditioned decomposition of H2O2:

*H2O2 + 2I- + 2H+ → I2 + 2H2O*

Starch and Thiosulfate is added

* Blue-black color is formed ∵I2 reacts with Starch
* 2I- is reproduced *(I2 + 2S2O32- → 2I- + S4O62-)* ∵I2 reacts with thiosulfate
* When all thiosulfate reacted, color shows ∴Time to show color is delayed

★ S2O32- does not oxidize due to the reaction being slow.

### Titration to follow rate

1. **Remove small samples** with pipette from reaction
2. **Quench** the reaction

* H+ is neutralized by **NaCO3 (carbonates)** ∵ Remove acid catalyst *(stop reaction)*
* Alkali are **not used** to quench ∵ They would **react with I2**

1. **Titrate** with Na2S2O3(2-)(aq) Sodium **thiosulfate** (reacts with I2) and use starch indicator.

# 12 - Thermodynamics

## Entropy and reaction feasibility

Entropy (S) - Degree of disorder

Spontaneous reactions - Reactions that take place without continuous intervention (e.g. heat supply)

### General entropy formulas

Entropy change: ΔS (J K-1 mol-1)

ΔST =

ΔSsys = *Sometimes referred to as the entropy change of reaction*

ΔSsur = *Remember ΔH in ­­J, so kJ requires multiplying by 1000*

n of molecules ↑ → n of possible arrangements ↑ *Remember to state change of num of moles*

State *(g > l > s)* ↑ → disorder ↑ → ΔSsys ↑ → ΔST ↑

T ↑ → ΔSsur ↓ → ΔST ↑

n of e- ↑ → disorder ↑

Use entropy to see how equilibrium changes:

### Feasibility of reactions

Free energy change: ΔG (J mol-1)

ΔG = ΔH – TΔS

ΔG ≤ 0 || ΔST ≥ 0 🡪 reaction will be **spontaneous** and hence **feasible**.

The solubility of an ionic solid can be deduced with ΔST of the dissolving reaction. ΔST ≥ 0 → soluble *else* insoluble

#### Explaining changes

1. Explain using ΔSsur: State ΔH and ΔS signs
2. doesn’t change significantly with temperature

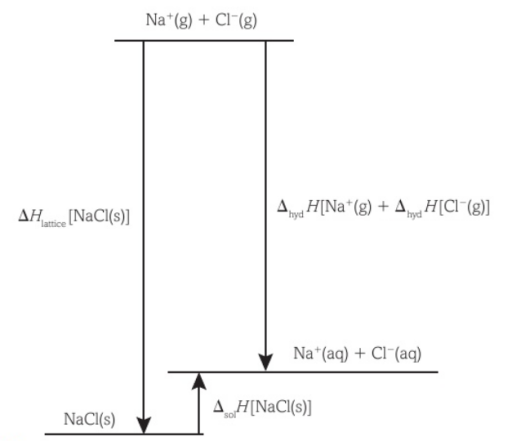
#### Justifying use of temperature

1. Calculate
2. Comment on feasibility

### Old stuff

Q = mcΔt *Q* heat energy | *m* mass of liquid in cm3, 1g = 1cm3 | *c* s.h.c. of water, if *m* in g, *c* = 4.18 J g-1 K -1

ΔH = *n* number of moles of reactants | Unit: kJ mol-1

**The ΔH measured at 100kPa and 298K, (In standard conditions, )**

Standard ΔH of Rx equation quantities of materials react

Standard ΔH of Form 1 mol of substance formed its element in standard states

### New stuff

**Definitions:** *1 mol of [X] formed from 1 mol [Y]*

Atomisation grd → g

Electron affinity g → gi-

Ionisation energy g → gi+

Solution si → aqi by dissolve H2O form solution of infinite dilution

Hydration gi → aqi by dissolve H2O form solution of infinite dilution

Lattice Energy (frm) gi → s

Lattice Energy (dis) [frm rvse] by complete dissociation

**Formulas**

Atomisation - ½X2(ground) → X(g)

Solution - NaCl(s) → Na+(aq) + Cl-(aq)

Hydration - Na+(g) → Na+(aq)

L.E. formation - Na+(g) + Cl-(g) → NaCl(s)

L.E. dissociation - NaCl(s) → Na+(g) + Cl-(g)

### Lattice energies of formation and dissociation

Same values Measures of ionic bonding strength

Opposite signs Represent opposite processes

Formation exothermic, E given out when bonds made to form lattice

Dissociation endothermic, E required to break bonds from lattice

### LE & ΔHhyd

Charge of ions ↑*or* Radius of ions ↓→ Stronger forces of attraction between ions → More exothermic

### % Difference of theoretical and actual LE

Experimental Calculated from Born-Haber cycles

Theoretical Calculated from ionic models

Experimental > theoretical due to additional covalent (and ionic) bonding

**Theoretical LEs assumptions:**

1. Ions touching each other
2. Ions are perfectly spherical
3. Charge is evenly distributed around the center

**Reasons for higher difference**

Charge density difference ↑ → Polarization ↑ → Covalency ↑→ %diff ↑→ Solubility in H2O ↑

**To explain difference for a molecule**

*Reverse applies for anion & 100% ionic bonds*

1. Cation size, charge → high charge density
2. Cation polarizes anion
3. There is some covalency in bonding

#### To explain LE difference between molecules

1. Compare size / charge / charge density
2. Compare polarizing power / polarizability
3. Compare covalency in bonding (e.g. NaCl almost 100% ionic bonding, MgI2 some covalency in bonding)
4. Compare ionic bond strength and link to LEs

★ **Ag** has outermost shell 4d10 which offers less shielding than most cations → **Covalency ↑**

### Electron affinity

ΔHea1 is always **-ve** (∵new e- and protons in nucleus attracted to each other, releasing E)

ΔHea1 is always **+ve** for group 0 (∵ full outermost shell, so new e- would be in new shell)

ΔHea2 is always **+ve** (∵ E required to overcome repulsion between ion-1 and e-)

# 13 – Chemical equilibria

## The Equilibrium constant

For reaction wA(s) + H2O + xB(g) ⇌ yC(g) + zD(g)

|  |  |
| --- | --- |
|  | Kc is a value  1. At a given temperature  2. Concentrations at equilibrium   * Conc. of H2O is always 1 so omit in equation * If reaction is homogenous (R & P same phase) then all solutions include in Kc |
|  | Kp is a value  1. At a given temperature  2. Pressures at equilibrium |

### Kp calculations

1. Find equilibrium moles by equation (moleq = original – used, w/ respect to mol ratio of equation)
2. Find total mole in equilibrium
3. Find partial pressures
4. Substitute to Kp equation

## Factors affecting the equilibrium constant

**Only Temperature** affects K. Temperature shifts equilibrium, and hence changes the ratio of K.

Pressure and concentration **do not** affect K as at equilibrium the effect balances out, since the partial pressure of all things changed.

## Deducing direction of equilibrium shift with Kc and Qc

|  |  |
| --- | --- |
|  | Qc is a value  1. At a given temperature  2. Concentrations defined at instance / not necessarily at Eq |

The units for K & Q are derived via calculation

Pressure and concentration **do** affect Qc since they change the initial conditions

Kc > Qc: Eq → Products

Pressure → Qp Δ according to equation → Kp Δ in opposite directions to remain constant → more R / P needed so Eq shift

To find equilibrium constant with entropy change:

### Other methods of increasing yield

1. Remove the product as they are formed; or
2. Reuse **unreacted** reactants

# 14 – Acid base equilibria

## Brønsted–Lowry acid–base theory

*Proton refers to 1 mol of H+(aq)*

Acid - proton donor

Base - proton acceptor

Strong X - dissociates completely to ions

Weak X - dissociates to a small extent to ions

Conjugate acid - species formed when base accepts a proton

Conjugate base - species formed when acid donates a proton

Acidic solution - [H+] > [OH-]

Alkaline solution - [H+] < [OH-]

Amphoteric - solution which can act as both base and acid

## **pH values**

HCl + H2O → Cl- + H3O+

Conjugate pair

H+

Acid

Conjugate base of HCl

### Weak acids and bases

Weak acids and bases slightly dissociate in solution, forming equilibrium mixture. Reaction has acid dissociation constant Ka

For weak acids, [H+] can be deduced with the value of Ka:

Ka ↑ acid strength ↑

### Strong bases

Since strong bases complete dissociate in water: (If Group 2 metal M(OH)2: )

The value for [H+] can be found with the value of Kw:

Expression for dissociation of water. For water, **[H+] = [OH-]**

From the sign of enthalpy change temperature ↑ [H+] ↑, but since water **[H+] = [OH-]**, it’s still neutral

|  |  |  |  |
| --- | --- | --- | --- |
| Neutral | | | |
| Acid < | 7 | > Alkaline |

### Deducing salt relative pH

* If salt’s acid component is stronger than the base, the salt is acidic in aqueous solutions. If strength same, then neutral.
* An acid reacts with a base to form a salt. Doing so removes the proton from the reaction.
* Write the dissociation equation to determine the components of a salt:

### Calculation assumptions

When calculating pH, the following should be assumed:

* Water does not dissociate to change [H+]
* Acid does not dissociate to change [H+]

### Diluting solutions

* Equilibrium shifts to the left as fewer moles in reactant side
* [HA] ↑ [H+] ↓ pH ↑
* Ka unchanged since Eq constants are only affected by temperature

## Strengths of acids and bases

Strong acids: Halides HX (except HF), Sulfuric acid H2SO4,, Nitric acid HNO3

Strong bases: Metal hydroxides MOH

All other acids / bases are weak.

### Ammonia

NH3 is a common weak base:

NH3 is amphoteric (donates proton NH2 accept proton NH4)

## Titration curves

### Curve properties

#### Equivalence points

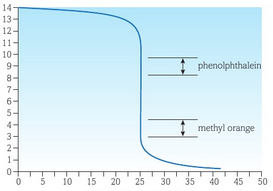
* The vertical region of the titration curve is the eqv point.
* Eqv volume = volume of starting solution reacted
* Equivalence vertical sections depends on the composition of reaction:
  + SA + SB = middle
  + SA + WB = bottom
  + SB + WA = top
* At half equivalence volume, pH = pKa

#### Graph shape & points

* Initial increase in pH is due to [HA] >> [A-] which the ratio changes
* If acid added to base in titration, volume added↑[H+]↑pH↓(RHS curve: base to acid)
* Initial pH = pH of starting solution

### Choosing a suitable indicator

Select an indicator with pH range (y) closest to equivalence point

The end point for a weak acid can’t be identified with indicator.

## Buffer solutions

* Buffer solutions is a solution which is able to resist changes in pH when small volumes of acid or base are added.
* They are formed from weak AB + conjugate BA / salt (HA & A­- or HA & AX)
* Volume of AB determines if the AB is used up completely. This affects the presence of both weak AB + conjugate BA.

#### **Explain how solution acts as buffer when small amounts added**

Key: HA: Acid, A- conjugate base

1. There are excess amounts of HA & A-
2. Added acid reacts with A- / Added base reacts with HA
3. Equation: / (must be eq rx)
4. Ratio of HA to A- remains unchanged

#### Explain how solution acts as buffer with given equilibriums

1. Added AB reacts with BA
2. Eq1 and Eq2 products and moves to keep [H+] constant

#### Buffer solution has x conc. R, find pH

#### Buffer solution created by x vol of R with conc. of y, find pH

1. Find mols of reactants.
2. Find n(reactants in buffer):  
   If buffer solution created by A + conj. B, the mol is exactly as in buffer.  
   If buffer solution created by ­A + B, find mol of conj. B by
3. Find total volume & conc. in buffer

# 15 – Organic chemistry: The second coming

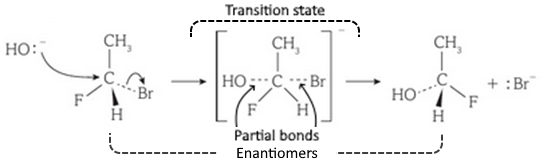
## New organic stuff

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| R = CnH2n+1 *n = chain name - 1* | | | |  |
| Alcohol  Aldehydes  Carboxylic acid  Ketone  Esters  Nitriles  Amines  Amides | | R-OH  R-CHO  R-COOH  R-CO-R’  R-COO-R’  R-C≡N  R-NH2  R-ONH-R’ | -ol  -al  -oic acid  -one  R’-yl R-oate  -nitrile  -amine  N-R’-yl R-amide |
| Aldehydes  **RCHO**  Ketones  **RCOR’** | Carbonyl compounds properties **Aldehydes**  Name of the nitrile: R + 1  Can be oxidized with O2 in air to form acids  Hydroxyl-nitriles to acids:  **Nucleophilic addition {NA}**  Racemic mixture is formed: Molecular is planar around Carbonyl C atom, Nu can attack from both sides    **HCN [KCN Alkaline aq. sol]**  KCN provides sufficient CN- for reaction  pH↓ CN-↓ pH↑ H+↓ 🡪 reaction won’t occur if extreme  **Properties of carbonyl compounds**   * H-bond does not form. * Soluble, Solubility ↓ with chain length ↑ as increasing significant of hydrocarbon part  Testing for carbonyl compounds **Testing for C=O (Ketone / Aldehydes only) group**   * 2,4 DNPH 🡪 Bright orange solid * The derivative purified with recrystallization * Measure reaction derivatives’ m.p. and compare with databook values to identify compounds   **CH3C=O** **group**   * Warm alkaline sol. I2 🡪 yellow p.p. (CHI3)   **Distinguishing between aldehydes and ketones**   |  |  |  | | --- | --- | --- | | *Reagent* | *Positive reaction for aldehydes* | *Reason* | | Acidified K2Cr2O7 | Orange 🡪 Green | Cr+6 → Cr+3 | | Fehling’s solution or  Benedict’s solution | Deep blue 🡪 Red | Cu2+ → Cu2O | | Tollens’ solution | Colorless 🡪 Silver mirror | Ag+ → Ag(s) | | | | |

|  |  |
| --- | --- |
| Carboxylic acids  **RCOOH** | Carboxylic acid properties  * Possible 2 H-bonds between modules * Soluble, Solubility ↓ with chain length ↑ as increasing significant of hydrocarbon part   **Speeding up esterification**   * Use an acid catalyst * Increase temperature   **Testing for acids**  Reaction with Na2CO3 🡪 Sodium alkenoate + H2O + CO2 |
| Acyl chlorides  **RCOCl** | All reactions nucleophilic and fast ROOR’ productionRCOCl tests Procedure: Add water drop by drop  Observation: Vigorous  Procedure: Mix with water  Observation: highest pH (organic)  **Advantages of producing esters with acyl chlorides over carboxylic acids**  This is due to  1. C-Cl bond being weaker than C-O  2. C in C=O is partially more positive  1. No catalyst needed  2. No heat required  3. Goes to completion  **Disadvantages**  1. Produces HCl, requires use of fume cupboard  2. Acyl chlorides are expensive Ester properties 1. Colorless  2. Fruity smell |
| Esters  **RCOOR’** | RCOOH production **Advantages of reaction under alkaline** **solution**  1. Goes to completion **Disadvantages**  1. Produces carboxylic salt instead of acids  **Differences**  1. Na+ as electrophile |

### NS Mechanisms

**RX SN1 [3° 2°]**

* ****Optical activity: No, racemic mixture

**RX SN2 [1° 2°]**

* Optical activity: Yes

[Relationship with rate of reaction](#_Mechanisms_of_nucleophilic)

### Condensation Polymerization

The formation of a polymer, by a reaction of 2 different monomers, each with 2 reaction groups at each end, when another small molecule is also formed.

Breakdown of condensation polymers is a process of **hydrolysis**

**Examples**

Acids & Alcohols: n[ HOOC-R-COOH ] + n[ HO-R’-OH ] **→** n[ -OOC-R-COO-R’- ] + 2nH2O

Acids: n[ HC-R-COOH ] **→** n[ -O-C-R-CO- ] + nH2

### Solubility & boiling point

Due to C=O and O-H in acid, they can form 2 h-bonds with H2O and themselves.

Esters and carbonyl compounds can only form 1 h-bond with H2O and none with themselves (as no small atom bonded to H)

## Optical isomerism

Presence of a chiral center 🡪 has optical isomers

Enantiomers have equal angles of rotation of plane of polarization in opposite signs.

Racemic mixture - A mixture containing equal amounts of enantiomers.

Distinguish between 2 optical isomers: They rotate PPL (plane-polarized light) in opposite directions.

## Chromatography

### Mobile and Stationary Phases

Species that are more attracted to the mobile phase move further and faster within the mobile phase

Species that has greater affinity to the stationary phase move shorter and slower within the mobile phase

|  |  |
| --- | --- |
| Classical chromatography | Column Chromatography |
| **Measurement: Rf** | **Measurement: Retention time**  The time taken for solvent to drain out  Variation of retention time can be explained by  Separation: Diff interactions with **mobile & stationary** phase of the species  (e.g., intermolecular forces with solvent & stationary phase) |
| Gas Chromatography (GC) |
| Separation: Diff interactions with **stationary** phase of the species |

## High resolution mass spectrum

#### Solving questions

Deduct m/z value with sum of CA, then try deducting with xN OA and finally divide with HA and see if it’s a whole number.

## NMR Spectroscopy

### Answering NMR questions

State the following:

1. n of ChemEnv

2. n of Split

3. Reason for split

4. Ratio of areas

5. Position of peaks

* Radio wave is used
* Bond peaks are measured against TMS Si(CH3)4. 
  + TMS has strong signal since 12 H+ in same ChemEnv
* Position of peaks are the chemical shifts of corresponding atoms
* n of peaks n of X in diff ChemEnv
* Ratio of (area of) peaks Ratio of amounts of ChemEnv
* Protons’ spin property flips when the radiation is absorbed

### Chemical environments

For atom X: Z1-X-Z2 *Z includes its adjacent atoms*

If Z1 and Z2 is not the same for atoms of X, they are in a different chemical environment.

🡪 Different chemical environments **do** **not** imply different chemical shift ranges!

### 1H High resolution split peaks

For specific H0 atom: H0-C-CHN Splitting of H0’s peak: (N+1)

*To explain why there are splits, state how many adjacent protons are there.*

# References

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