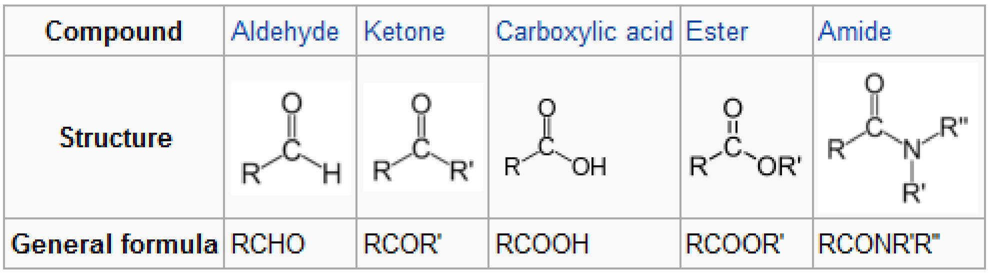
Chemistry Reactions and Synthesis

Organic Chemistry

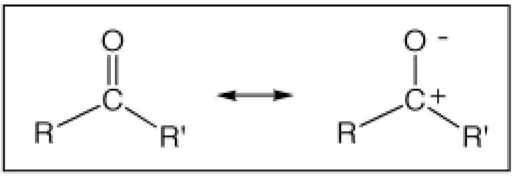
The Carbonyl Group

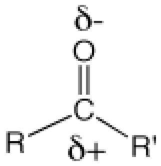
A carbonyl group is a functional group composed of a carbon atom double-bonded to an oxygen atom: C=O. It is common to several classes of organic compounds, as part of many larger functional groups.



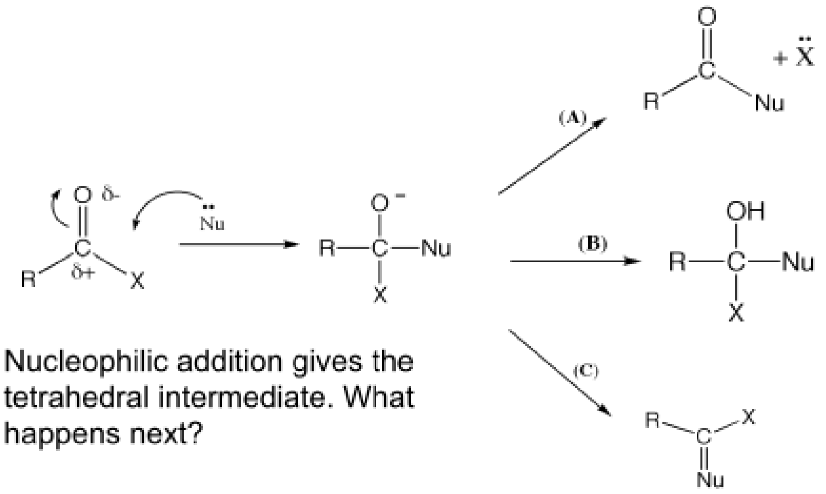
Compound	Aldehyde	Ketone	Carboxylic acid	Ester	Amide
Structure					
General formula	RCHO	RCOR'	RCOOH	RCOOR'	RCONR'R"

The C=O pi bond is highly polarised.





Because of this polarisation, several types of reaction involving the carbonyl group are possible.



Nucleophilic addition gives the tetrahedral intermediate. What happens next?

(A): X = good leaving group (e.g Cl or Oxygen) - Nucleophilic Acyl Substitution.

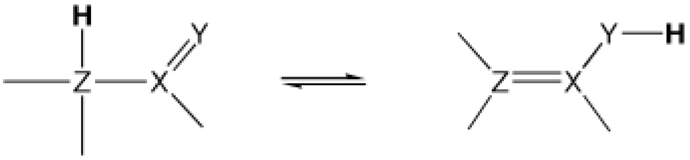
(B): X = poor leaving group (e.g alkyl, or H) - Nucleophilic addition.

(C): X = poor leaving group, Nu = NH_3 or RNH_2 Nucleophilic addition followed by dehydration

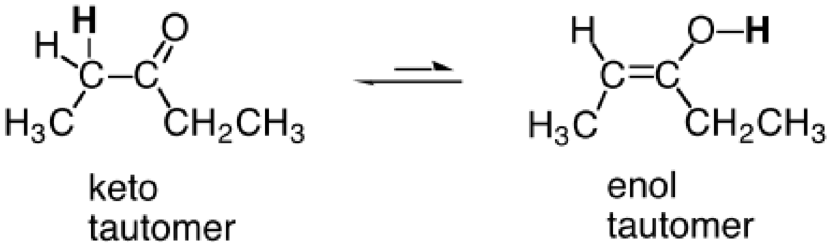
Keto-Enol Tautomerism

Tautomers

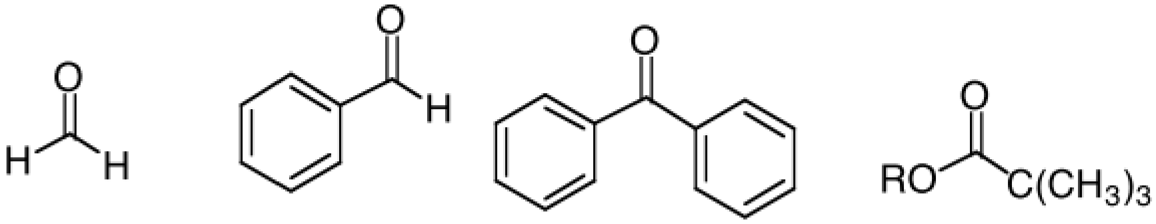
Tautomers are structural isomers which exist in rapid equilibrium with each other. Tautomerism involves a hydrogen atom moving from an atom (Z) in one structure onto an atom (Y) in its tautomer.



Carbonyl compounds exhibit what is called keto-enol tautomerism provided that one of the alpha-carbons possess at least one hydrogen atom.



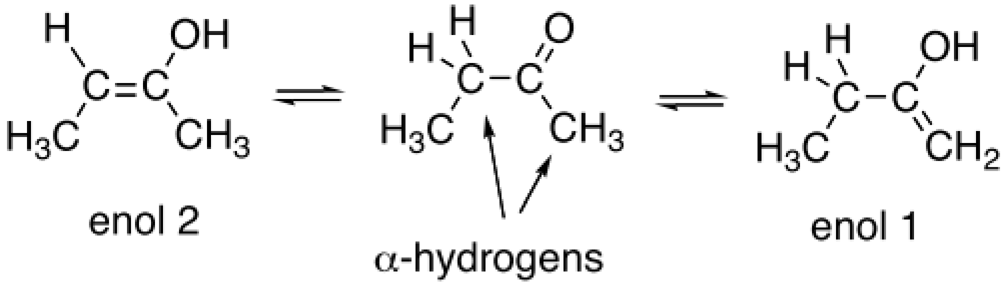
Aldehydes, ketones and esters without α-H's have no ENOL forms. Examples include:



Unsymmetrical Ketones

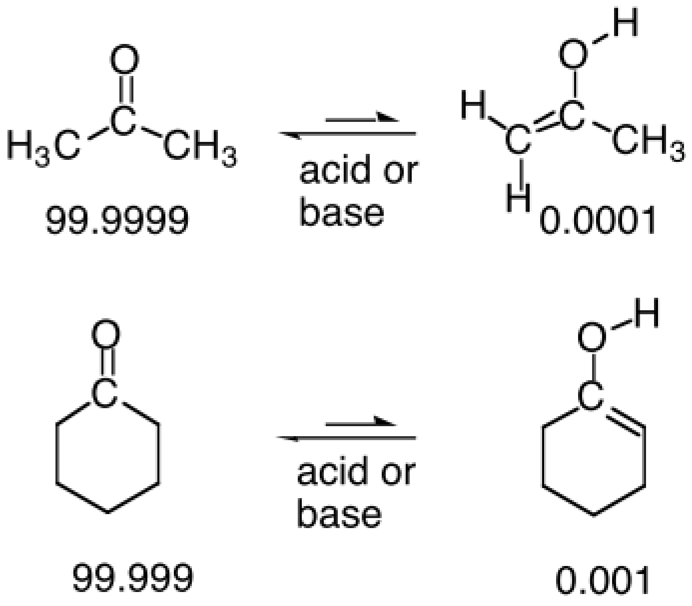
Whereas symmetrical ketones have only one enol tautomer, unsymmetrical ketones can have two, as they can enolise on both sides (provided α-H is present). Esters and aldehydes cannot have α-hydrogen on both sides of the carbonyl, and so never have two enol forms.

2-Butanone



Equilibrium

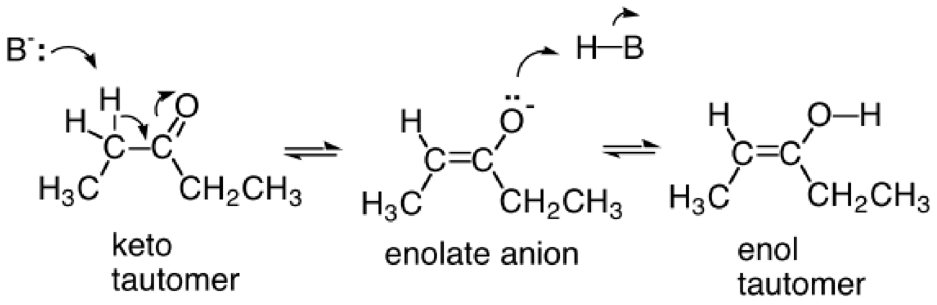
For simple carbonyl-containing molecules, the contribution that the enol-form makes to equilibrium is very small (generally ca. 0.01%).



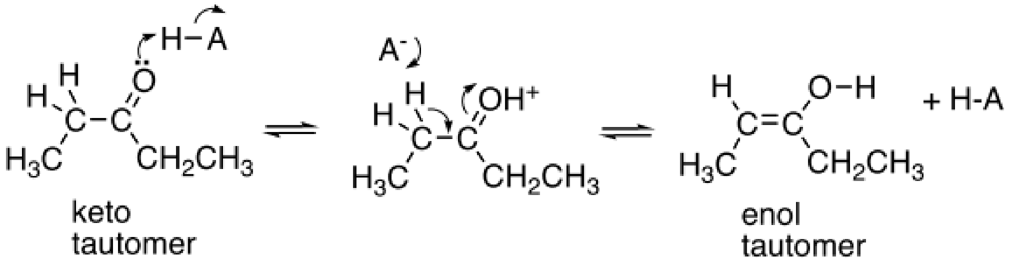
Mechanisms for Interconversion

The conversion of the keto-form into the enol-form is usually be catalysed by either an acid or a base, however it can also occur in the absence of acid or base.

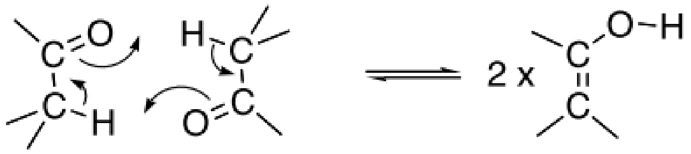
Base-Catalysed Enolisation



Acid-Catalysed Enolisation

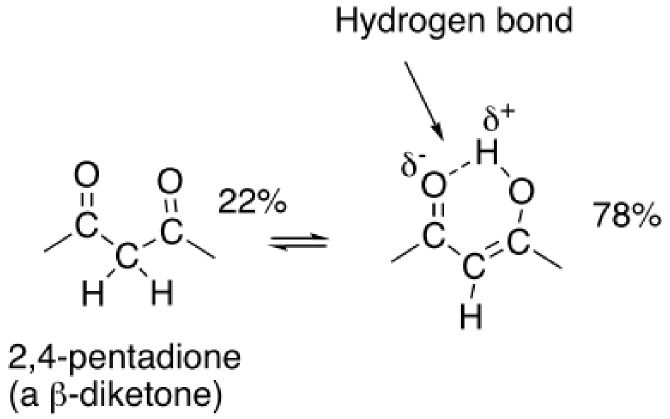


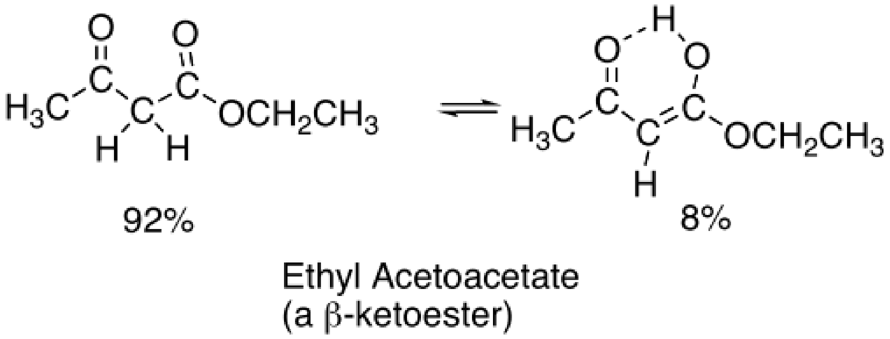
Tautomerisation in the absence of acid or base catalysts



Stable Enol Tautomers

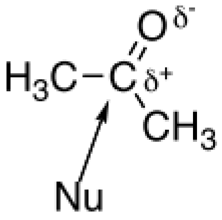
In contrast to simple ketones, some molecules have enol tautomers that make a significant contribution at equilibrium. The most notable of these are β-dicarbonyl compounds and also β-keto esters, which are stabalised by an intramolecular hydrogen bond, and conjugated C-C double bond.



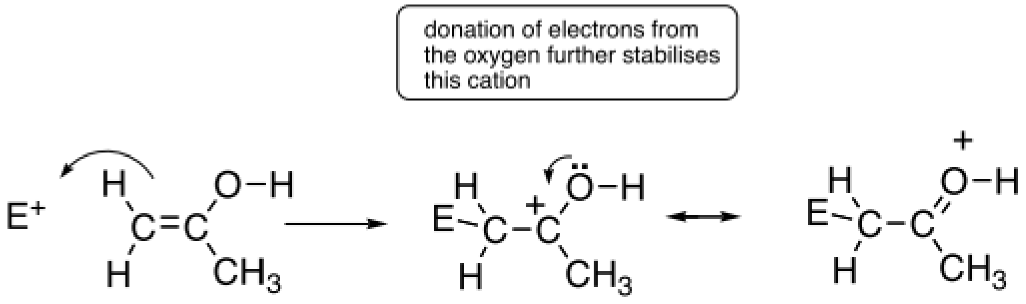


Properties of the Enol Form

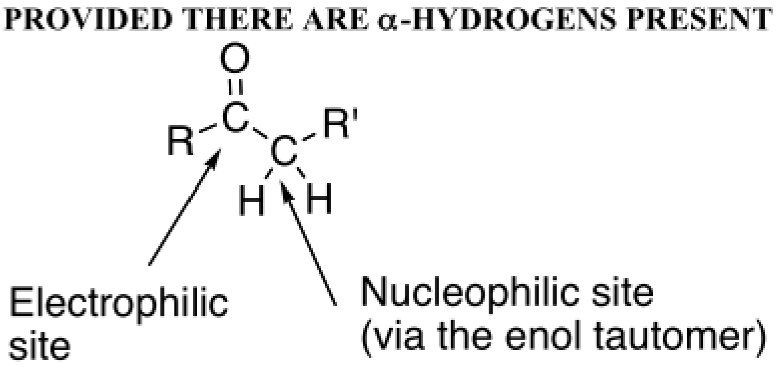
The keto tautomer is generally electrophilic, and so reacts with nucleophiles:



In contrast, the enol tautomer is generally nucleophilic (since they are essentially substituted alkenes), and so reacts with electrophiles:



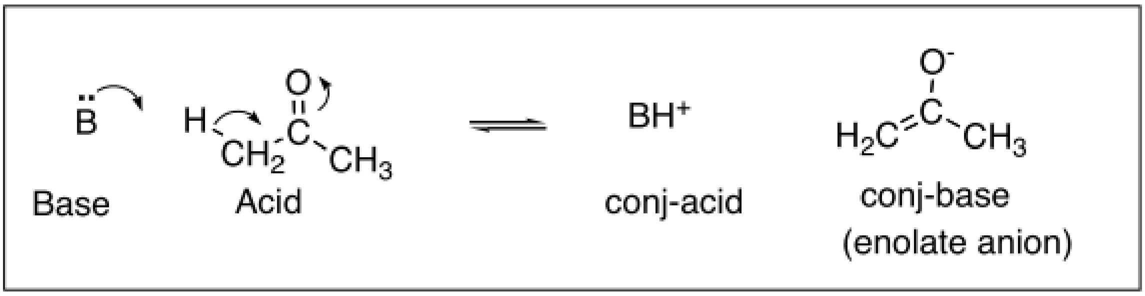
This means that carbonyl compounds can display two different modes of reactivity:



Enolate Ions

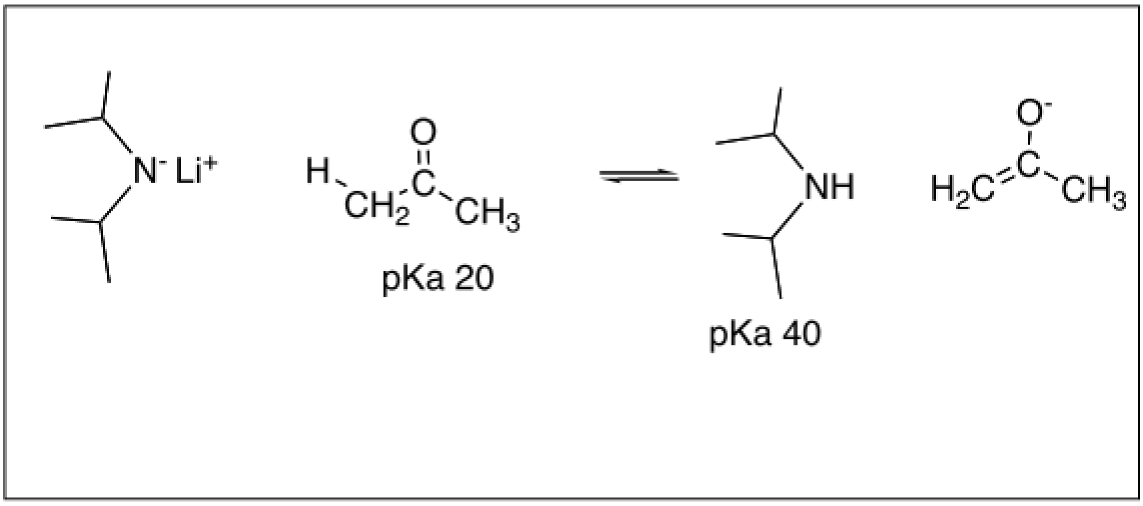
Forming an Enolate Ion

For simple carbonyl systems the enol tautomer is present at a very low concentration, therefore reactions involving the enol will be slow. To circumvent this difficulty, we can instead use the enolate anion form.



The enolate anion is formed in a simple acid-base equilibrium, and the position of this equilibrium depends on the strengths of the acids and bases involved. Therefore it is controllable by selecting a conjugate acid which is a weaker acid than the carbonyl compound we are trying to deprotonate (as the equilibrium will always lie to the side where the strongest acid is replaced by the weakest acid).

It turns out that most carbonyl acids useful for synthesis are only very weak acids, which means that we need to use a very strong base in order to produce a yet weaker conjugate acid. One possible base is NH_2^-, with a pKa of 35, however the most useful is LDA, with a pKA of 40.

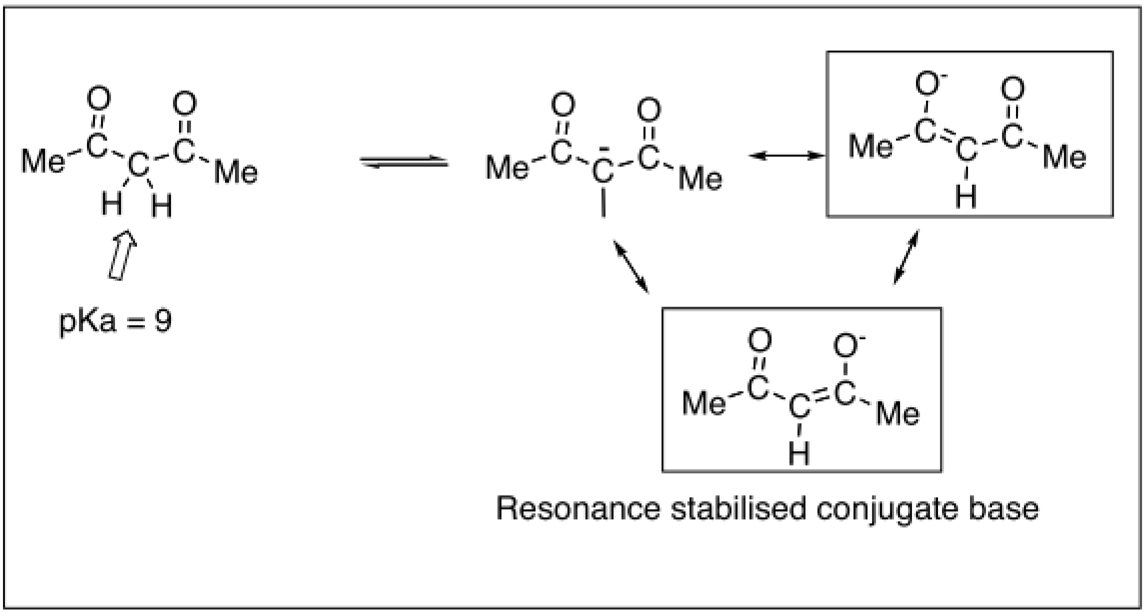


Advantages of LDA

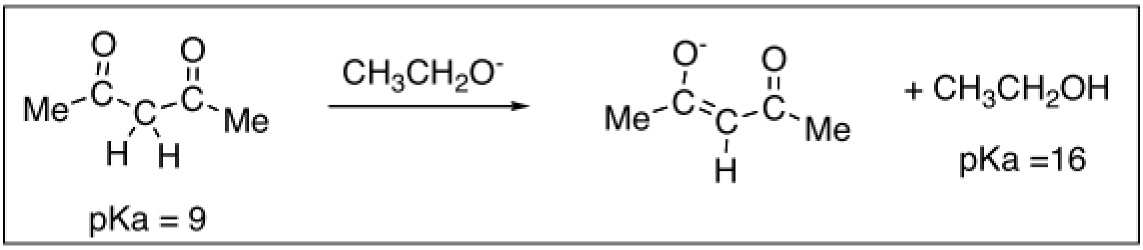
- It is a very strong base so it will completely deprotonate the carbonyl compound
- It is soluble in organic solvents
- It is sterically hindered by the presence of the two bulky isopropyl groups, meaning that side reactions where it attacks at the electrophilic carbonyl carbon are suppressed

β-Dicarbonyl Compounds

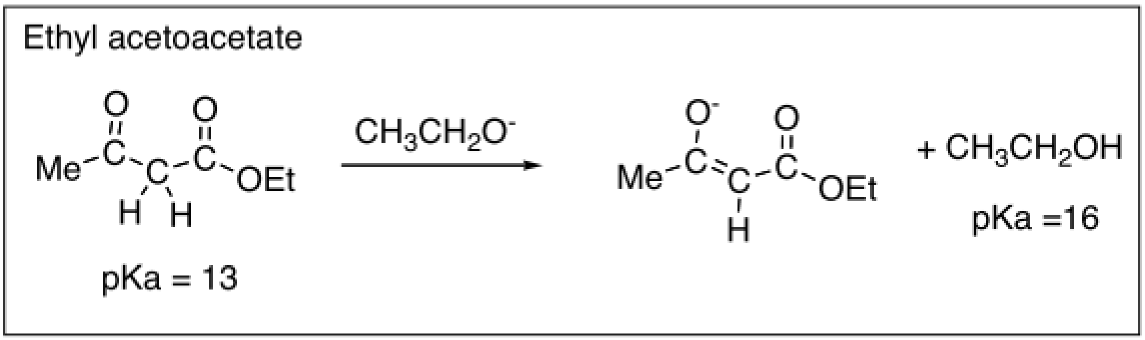
These compounds are much stronger acids than most carbonyl compounds, owing to the fact that their conjugate bases are stabilised by resonance.



This means that β-diketones can be deprotonated completely using simple alkoxide bases.



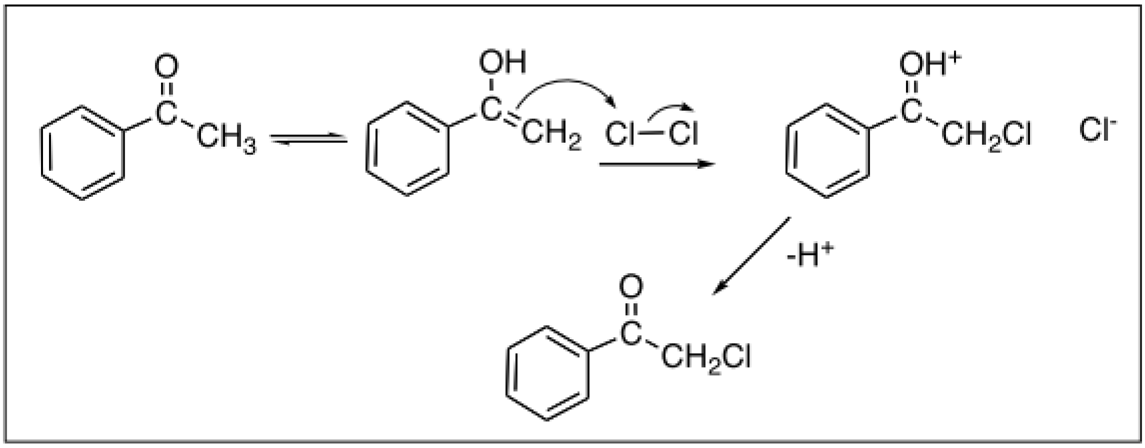
Likewise for β-ketoesters



Halogenation

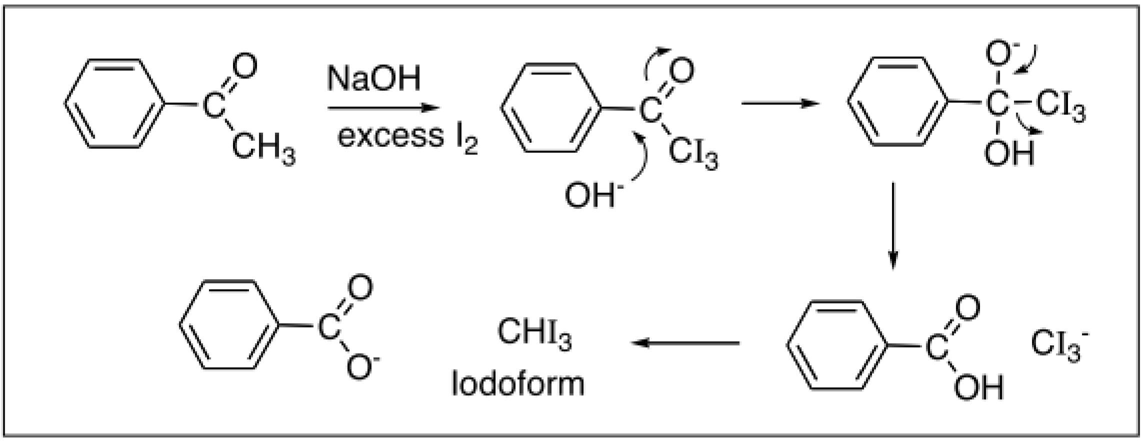
Reaction of Enols with Halogens

Halogens are very reactive electrophiles, and so react effectively even with the low concentrations of the enol. Polyhalogenation is also possible if more than one alpha-hydrogen is present.



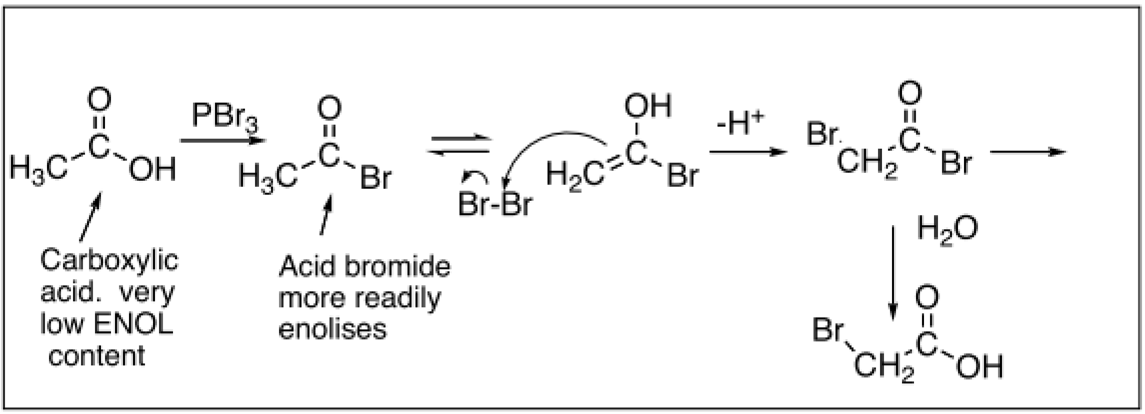
Iodoform Reaction

A polyhalogenation reaction used to substitute three alpha-hydrogens for three iodines in order to test for the presence of methyl ketones.

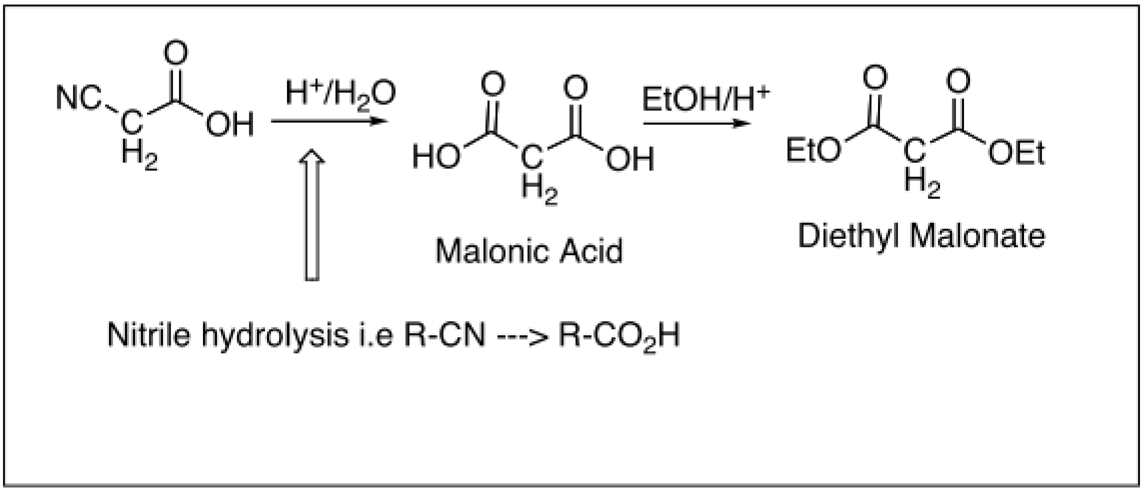


Halogenation of Carboxylic Acids

This is also called the Hell-Volhard-Zelinsky Reaction, and involves converting a carboxylic acid into an alpha-bromocarboxylic acid, which is very useful for further synthesis because the bromine can easily be displaced by a variety of nucleophiles.



Diethylmalonate, for instance, can be formed using this reaction.



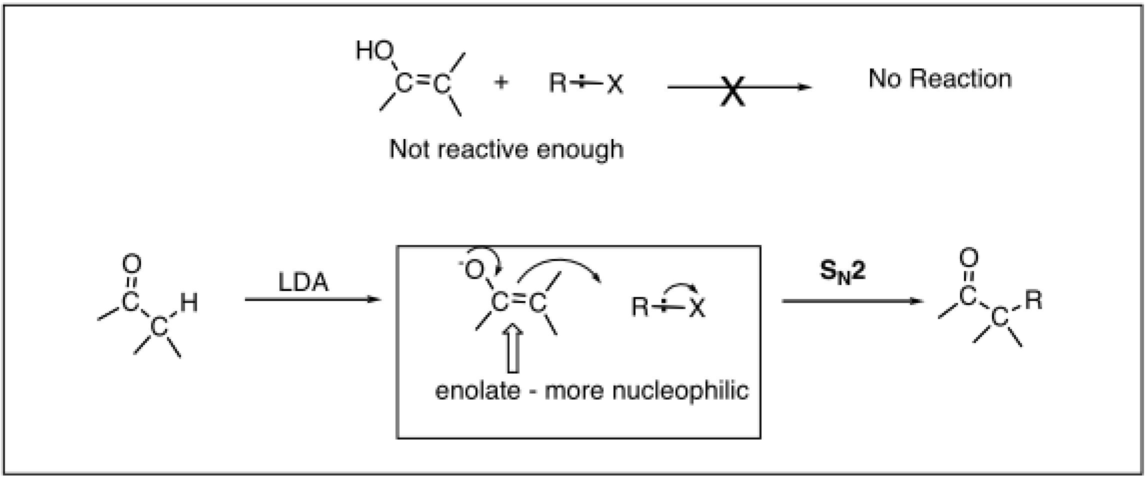
α-Alkylation

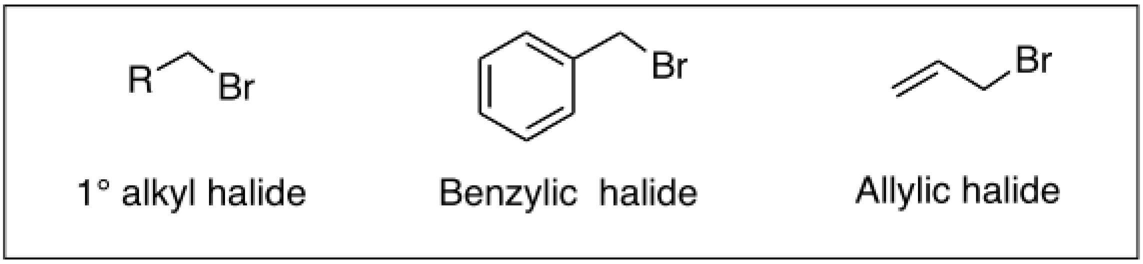
Overview

An alkyl halide is reacts with the C=C bond of an enolate anion in a substitution reaction. Alkyl halides are significantly less electrophilic than halogens and as a result are essentially non-reactive towards the enol form. Instead, the enolate anion must be used.

Mechanism

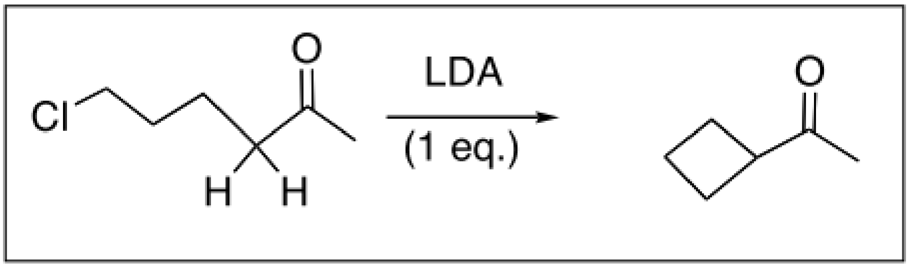
This reaction proceeds by an SN2 mechanism, and hence requires a good enough leaving group. It is also necessary that the alkyl group should be primary (1°), benzylic, or allylic.





Intramolecular Alkylation

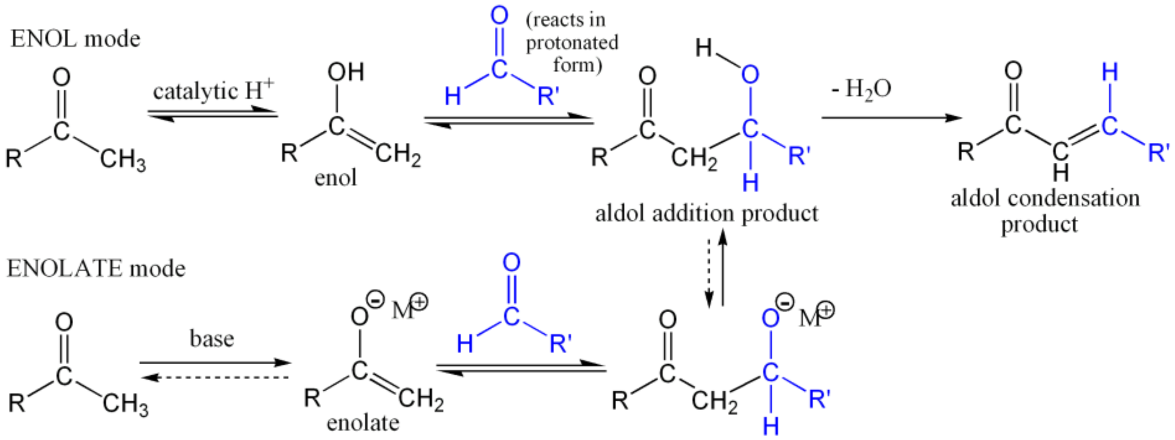
If the enolisable carbonyl and the leaving group are contained within the same molecule, then, intramolecular nucleophilic displacement of the leaving group results in the formation of a ring structure.



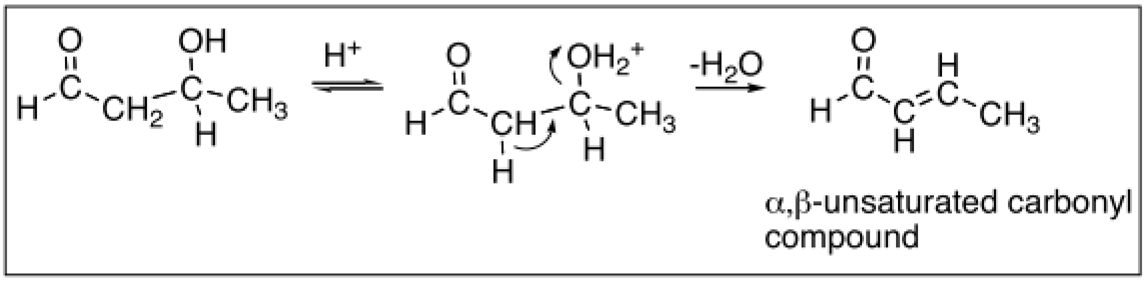
Aldol Condensation

Overview

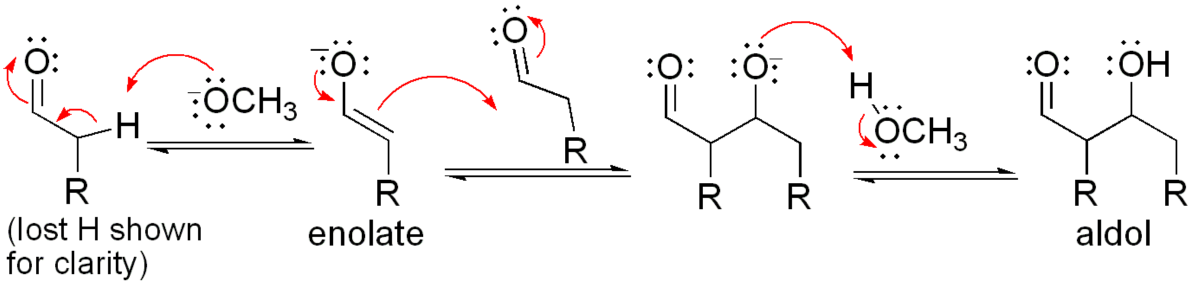
In this reaction the enol or more usually the enolate form of one carbonyl compound reacts as a nucleophile with the carbonyl carbon of the keto form of a second carbonyl compound. It is a very important reaction for forming C-C bonds.

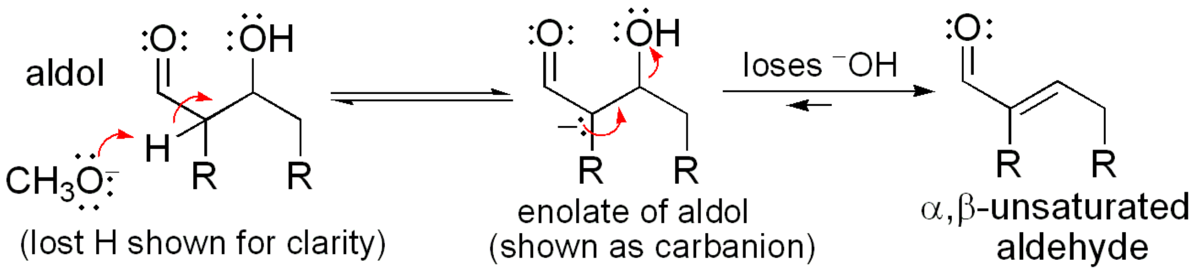


Aldols are not very stable and readily eliminate water, a process which is often carried out deliberately by treating them with acid. The product is an α,β-unsaturated carbonyl, which is stabilised by resonance.



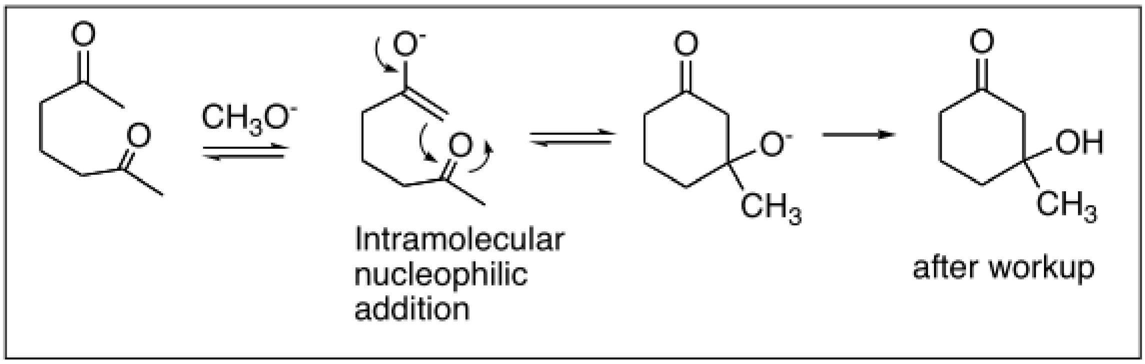
Mechanism





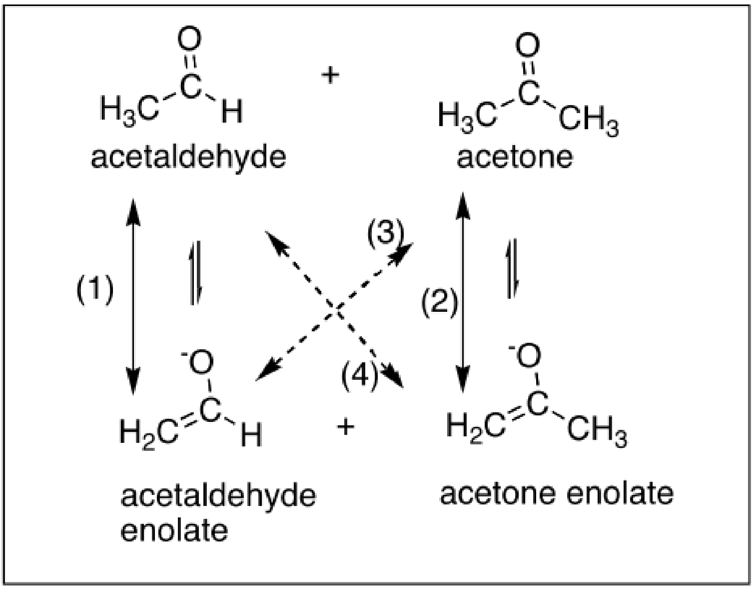
Intramolecular Reactions

When certain dicarbonyl compounds are treated with base, then intramolecular aldol reactions can occur, leading to cyclic products. The mechanism is the same as before, only as applied to a different substrate. Conversion of one of the carbonyl groups into its nucleophilic enolate anion is followed by intramolecular nucleophilic addition to the electrophilic keto-form of the second carbonyl.



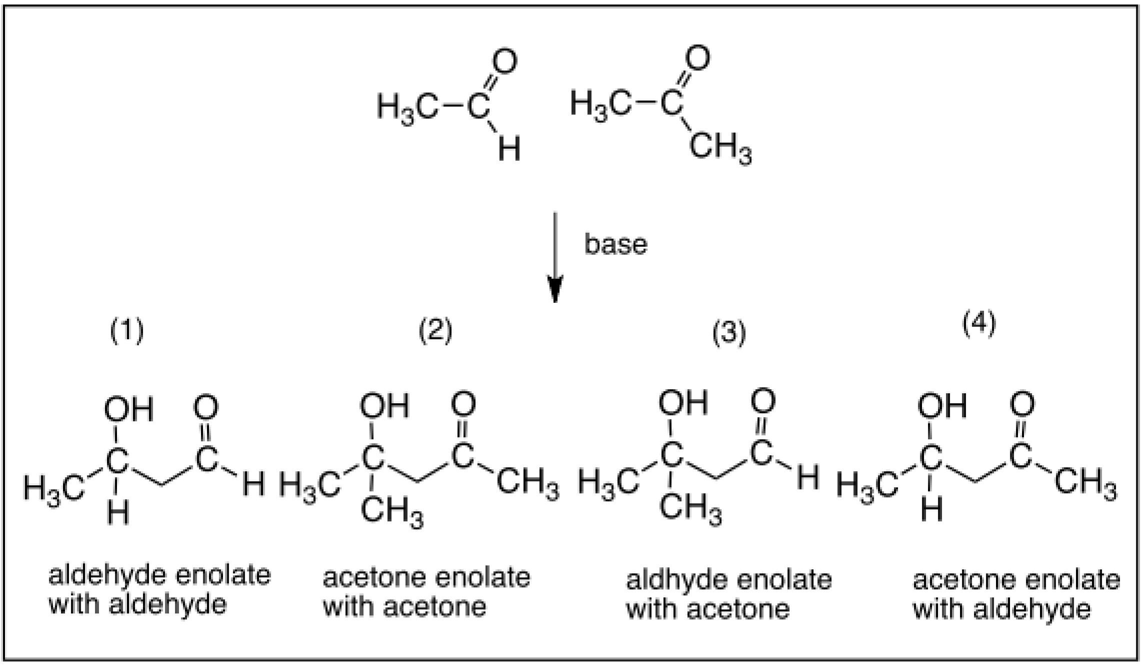
Mixed Aldol Reaction

An Aldol reaction between two different carbonyl compounds is not generally useful since a mixture of products often results. For example consider a mixed aldol reaction between acetaldehyde and acetone. A mixture of four components will be involved: the keto forms of acetone and acetaldehyde and their corresponding enolate anions.

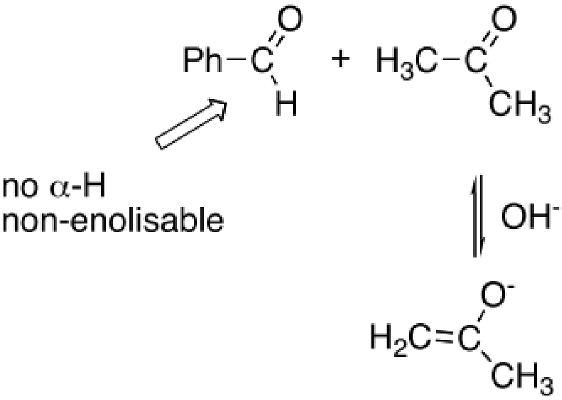


This means that there will be four possible reactions:

- The enolate of acetaldehyde reacts with its own keto form (self Aldol reaction of acetaldehyde)
- The enolate of acetone reacting with its own keto form (self Aldol reaction of acetone)
- The enolate of acetaldehyde reacting with the keto form of acetone (mixed Aldol reaction)
- The enolate of acetone reacting with its the keto-form of acetaldehyde (mixed Aldol reaction)

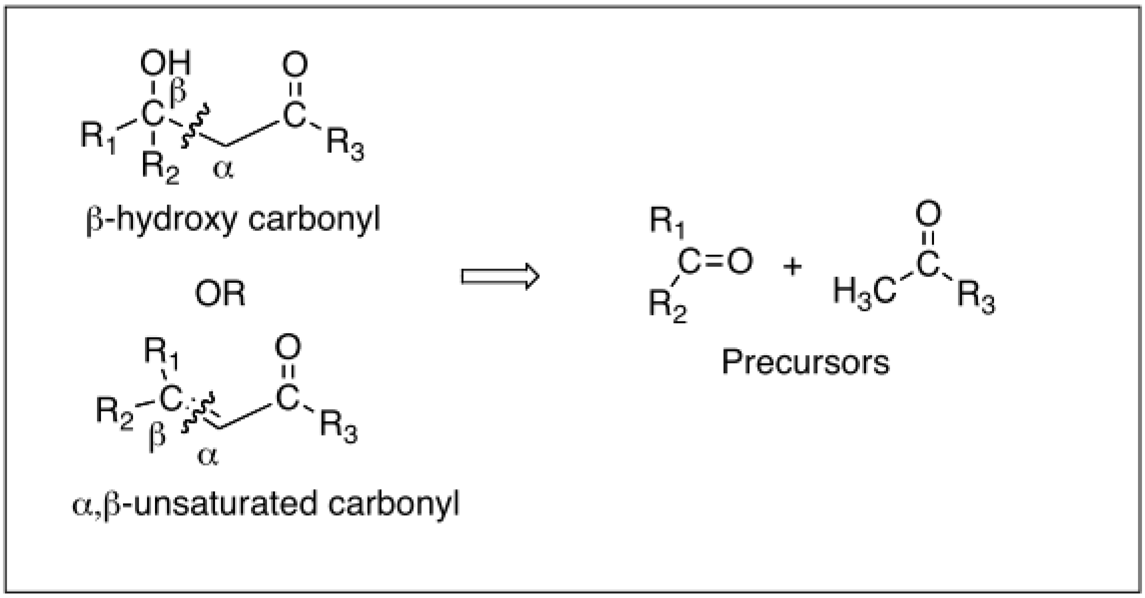


We can make mixed aldols useful by using a non-enolisable aldehyde with an enolisable ketone. The ketone enolate ion usually reacts preferentially with the aldehyde carbonyl (rather than with its own keto form) because aldehydes are more electrophilic and reactive than ketones. Hence we only get one reaction rather than four.



Retrosynthesis

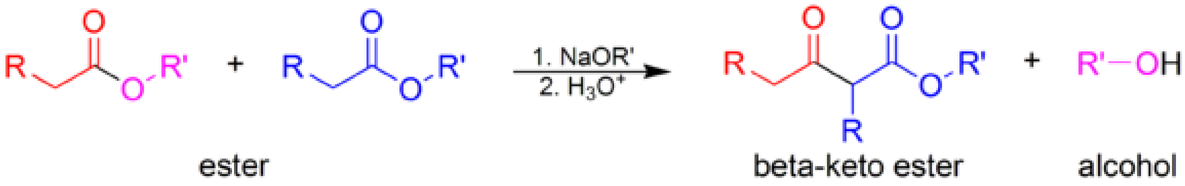
Any β-hydroxy carbonyl or α,β–unsaturated carbonyl compound is potentially obtainable from simpler carbonyl-containing starting materials using Aldol Chemistry. In the retrosynthesis, first disconnect the α and β carbons. At the α-carbon replace the C-C bond (or C=C bonds) with the required number of hydrogens, while the β-carbon carbon becomes a carbonyl.



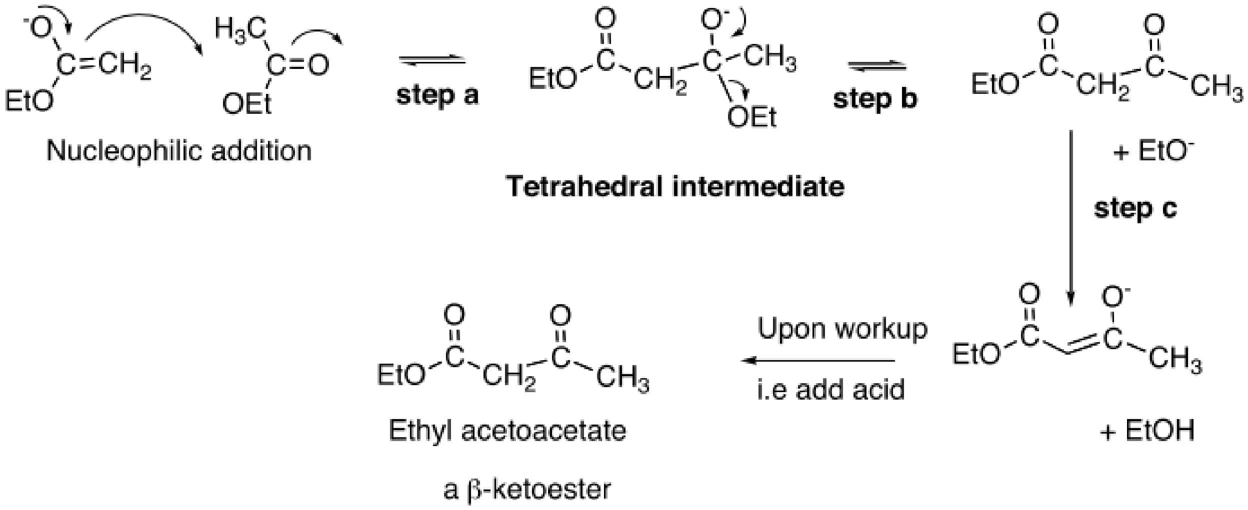
Claisen Chemistry

Overview

A carbon-carbon bond forming reaction that occurs between two esters or one ester and another carbonyl compound in the presence of a strong base, resulting in a β-keto ester or a β-diketone. At least one of the reagents must be enolizable for the reaction to be possible.

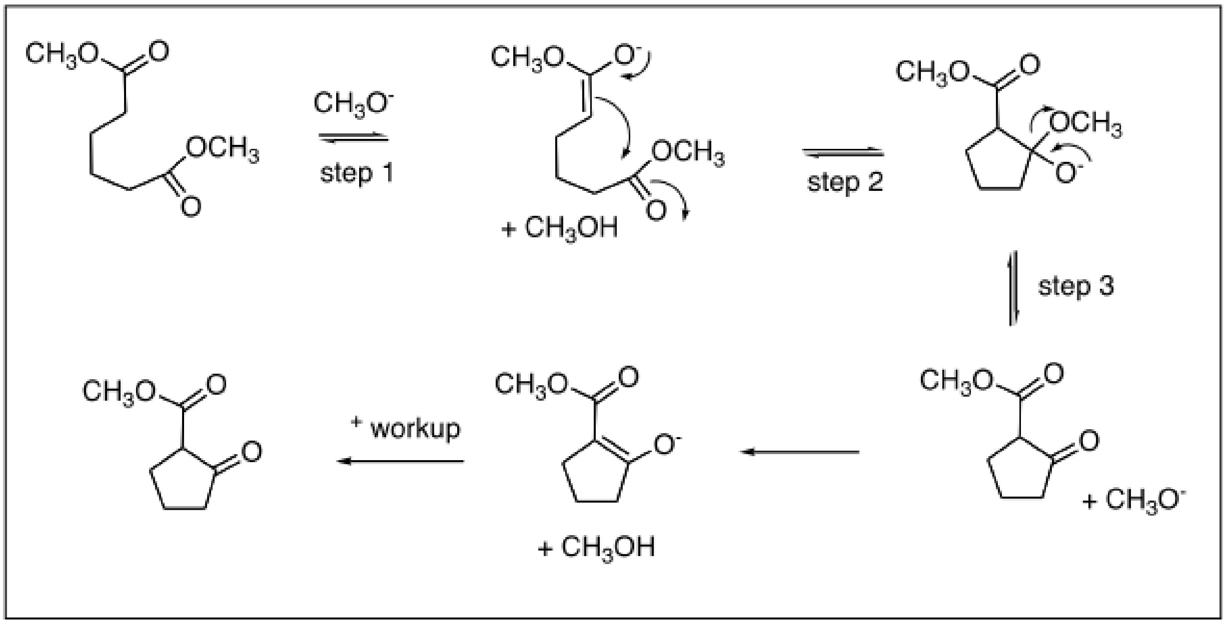


Mechanism



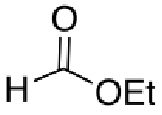
Intramolecular Reactions

An internal Claisen reaction can occur for certain diesters to form a cyclic β-keto ester. Dieckman cyclisation only works well for the formation of 5- and 6-membered rings.

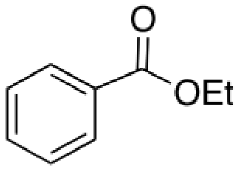


Mixed Claisen Reaction

A claisen reaction between two different esters is called a mixed Claisen reaction. This reaction is subject to the same restrictions as the mixed Aldol reaction, meaning that it works best if one of the components is a non-enolisable ester (i.e it has no α-H's). Common non-enolisable esters include:

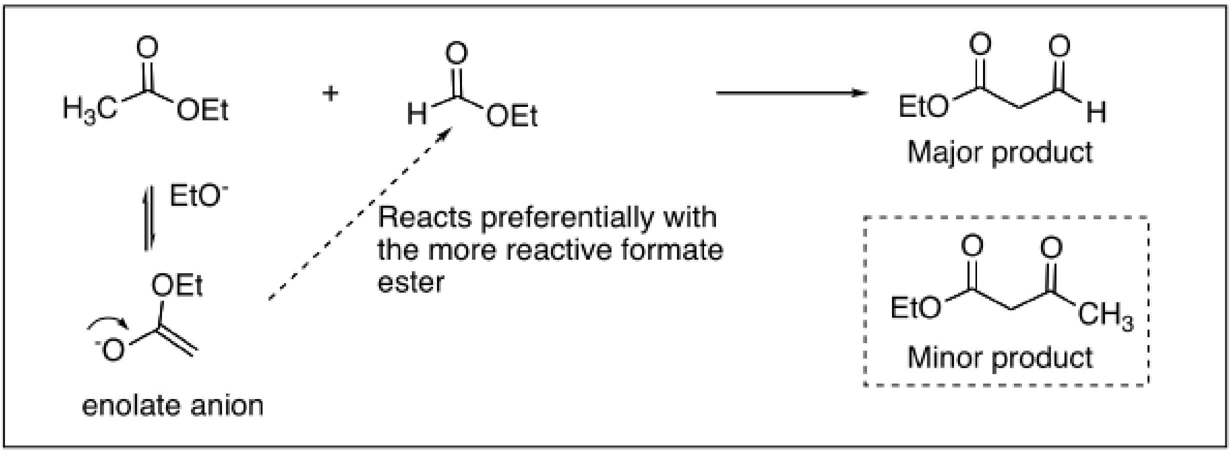


Ethyl formate



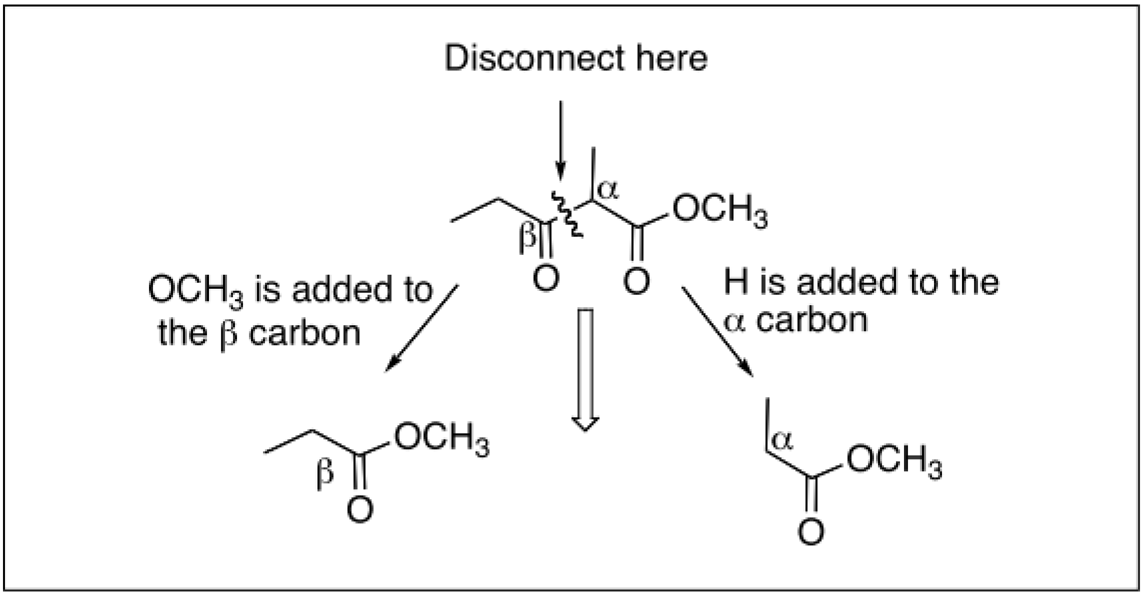
Ethyl benzoate

Often in these reactions two products are formed: one resulting from a mixed claisen reaction, and one resulting from a straight claisen reaction with its own keto form.



Retrosynthesis

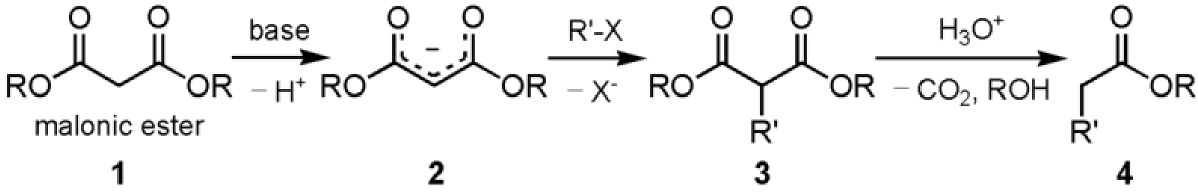
The product of a Claisen reaction is recognisable by the 1,3-dicarbonyl substitution. In the process of retrosynthesis, the α and β carbons are disconnected from each other. Once the disconnection is made, a hydrogen is added onto the α-carbon, and an alkoxide group is attached to the β-carbonyl.



Malonate Chemistry

Overview

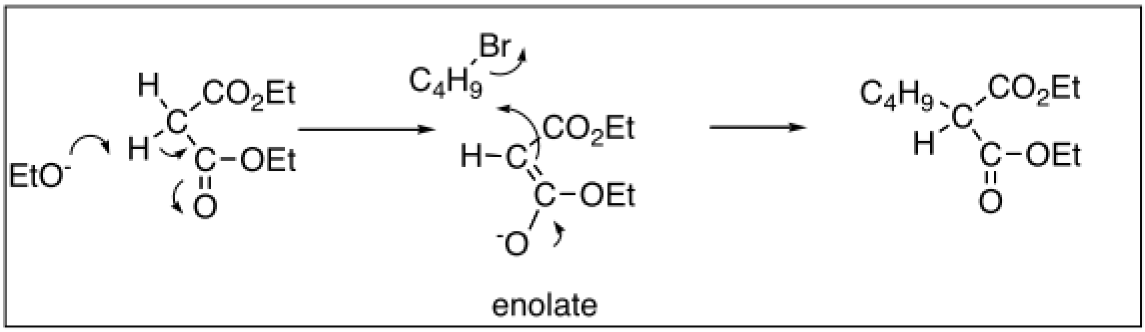
Malonic acid is a 3-carbon molecule, which, (as its diester) is a standard building block in laboratory synthesis for the introduction of a 2-carbon unit into a substrate. The malonic ester synthesis is a chemical reaction where diethyl malonate or another ester of malonic acid is alkylated at the carbon alpha (directly adjacent) to both carbonyl groups, and then converted to a substituted acetic acid. The product of this reaction is either an α- mono-substituted or an α,α-disubstituted acetic acid derivative.



Mechanism

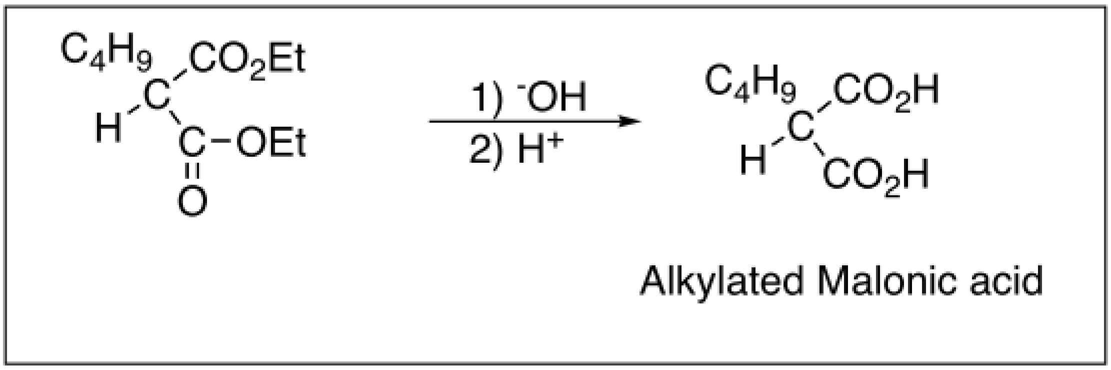
Step 1. Enolate Alkylation

Treatment of diethylmalonate with ethoxide anion results in essentially complete conversion into the nucleophilic enolate anion. This reacts by an S N 2 mechanism with C 4 H 9 -Br with displacement of the Br - leaving group and formation of the alkylated malonate diester.



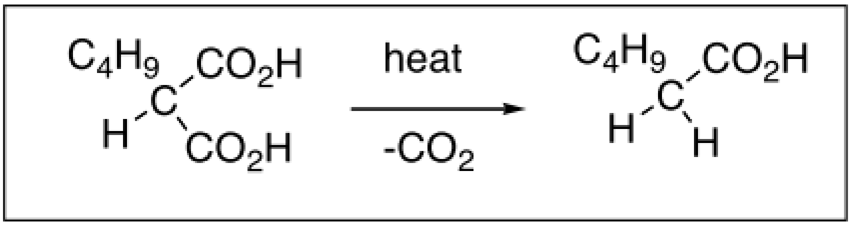
Step 2. Ester Hydroylsis

Alkaline hydrolysis of the ester groups followed by neutralisation with acid results in conversion into an alkylated derivative of malonic acid.



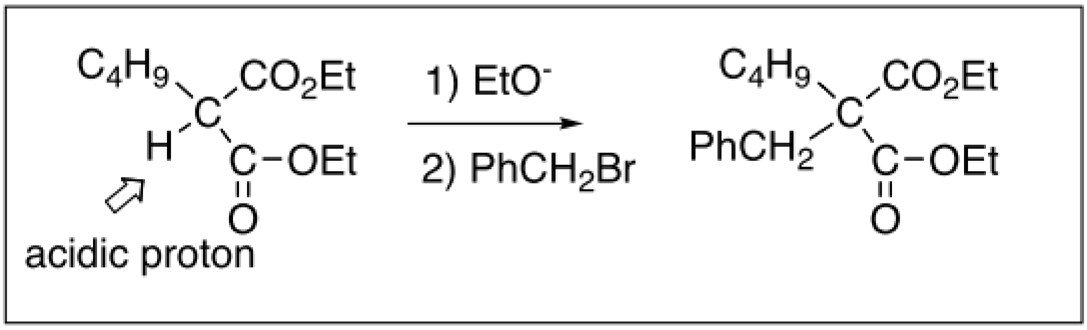
Step 3. Decarboxylation

All carboxylic acids with a carbonyl group at the β-position are prone to decarboxylation when heated. In this process one of the CO 2 H groups is lost as CO 2 and in the product it is replaced by a hydrogen atom.



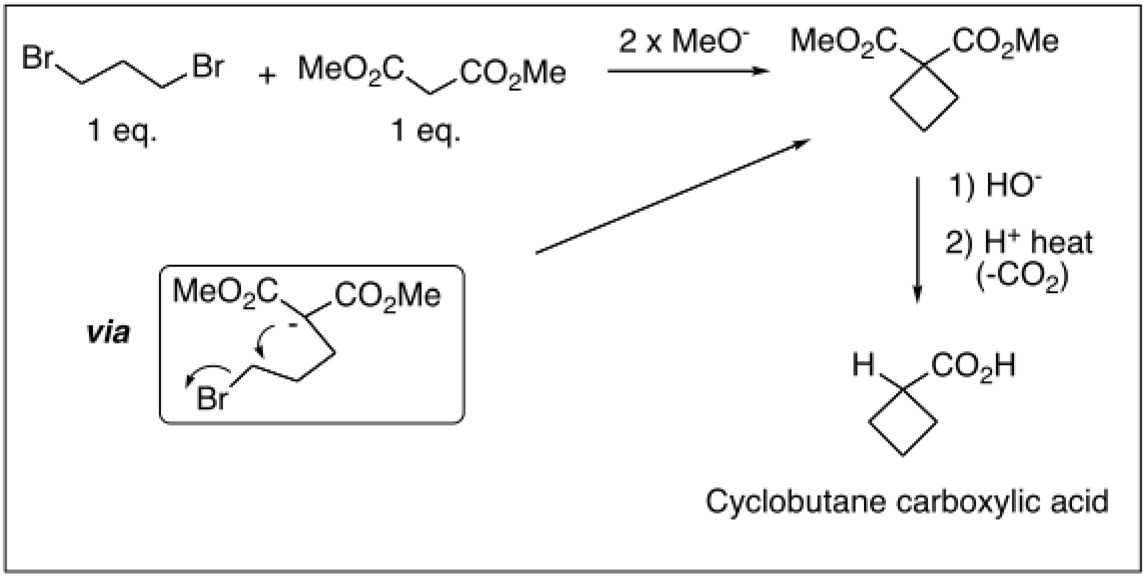
Disubstituted acetic acid derivatives

In the alkylation step above (Step 1), the initially formed mono-substituted malonate diester still retains an acidic proton, and can be converted to an ENOLATE anion by further treatment with alkoxide base. The resulting enolate anion can then be alkylated a second time e.g:



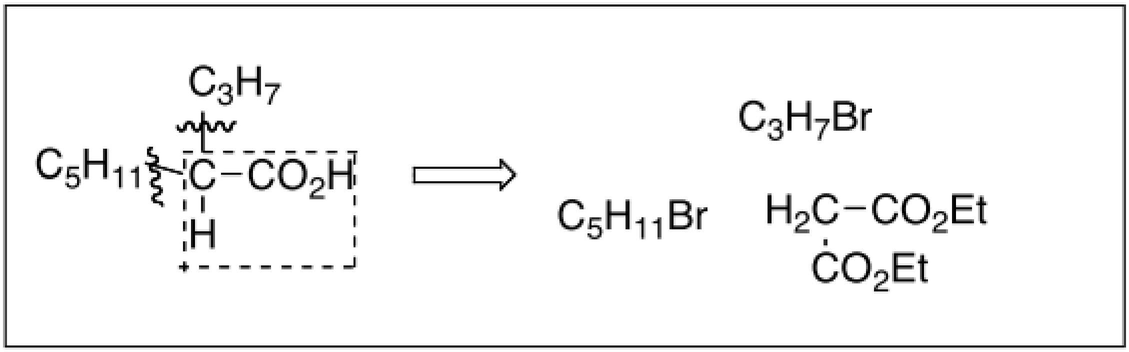
Cyclic Compounds

These can be prepared by following the same set of reaction conditions described above, but using a dihaloalkane as the substrate with malonate diester.



Retrosynthesis

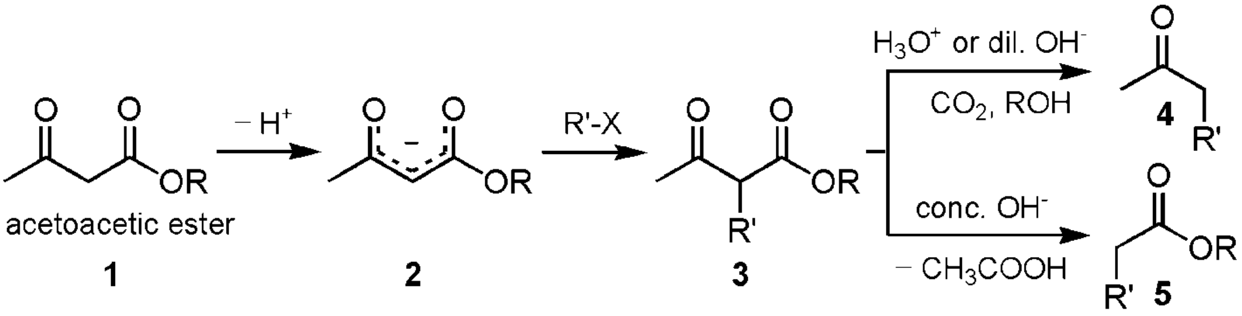
In all cases when a product contains an α-substituted acetic acid with at least one α-hydrogen then malonate diester is a possible the starting material. The retrosynthesis is given by simply reacting a malonate diester with the halogen-versions of the new desired substituents.



Acetoacetate Chemistry

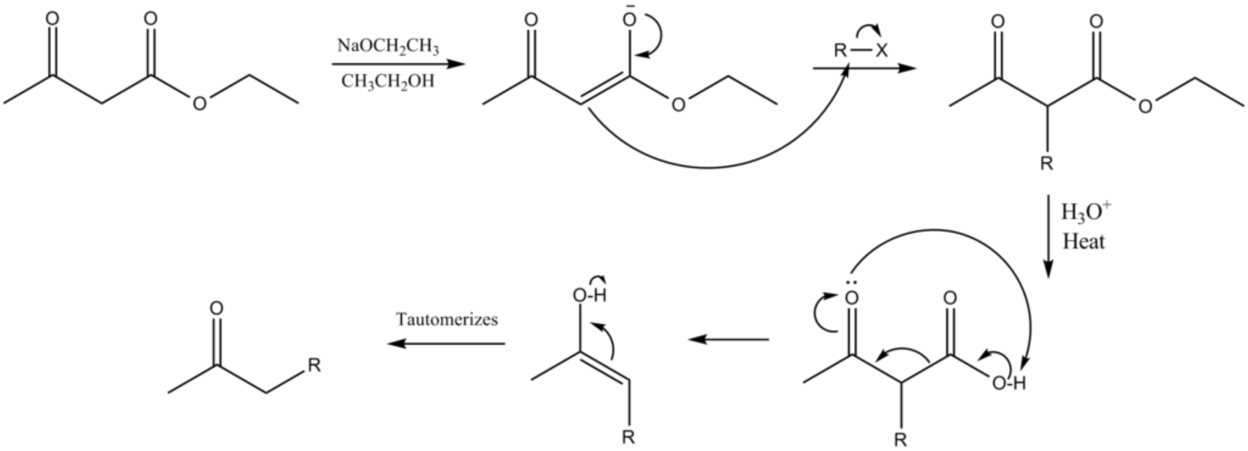
Overview

Acetoacetic ester synthesis is a chemical reaction where ethyl acetoacetate is alkylated at the α-carbon to both carbonyl groups and then converted into a ketone, specifically an α-substituted acetone. The product of this reaction is either an α- mono-substituted or an α,α-disubstituted derivative of acetone.



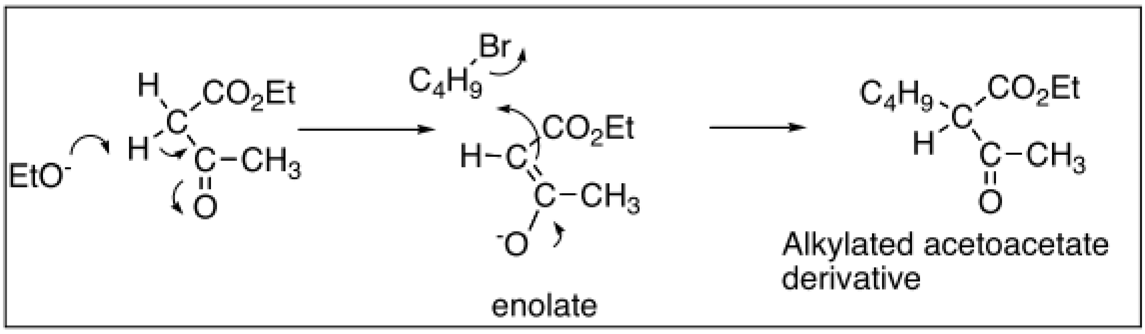
Mechanism

An overview of the reaction mechanism is given below



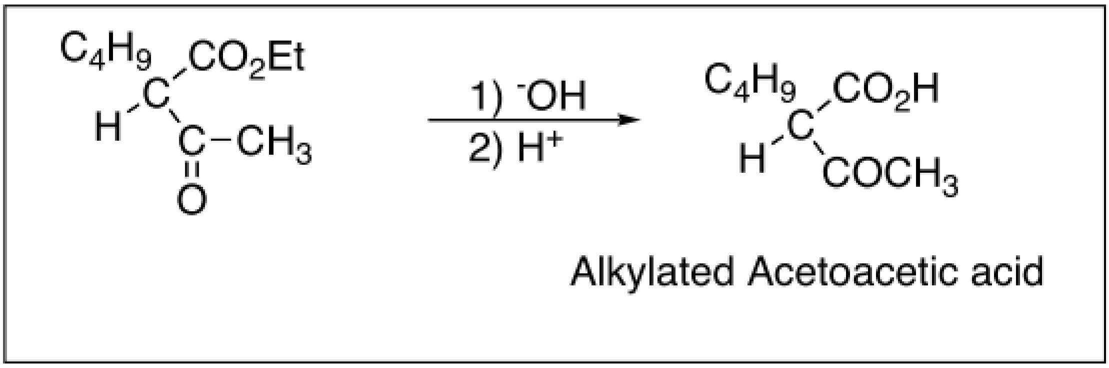
Step 1. Enolate Alkylation

After formation of the enolate ion, an alkohalide group is added via electrophilic addition to the C=C double bond.



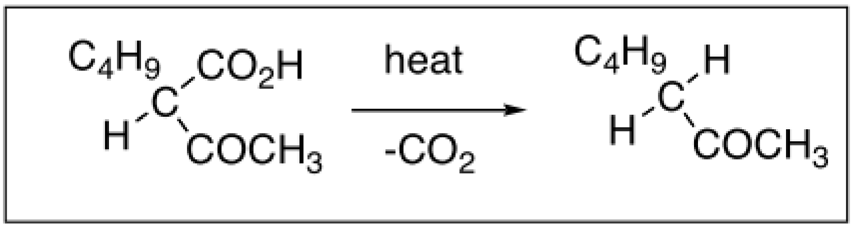
Step 2. Ester Hydrolysis

Alkaline hydrolysis of the ester groups followed by neutralisation with acid results in conversion into an alkylated derivative of acetoacetic acid.

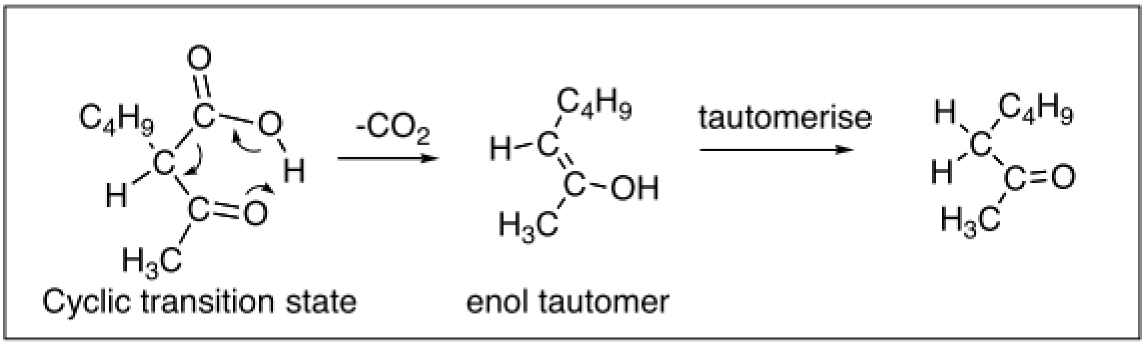


Step 3. Decarboxylation

Acetoacetic acid, which has a ketone carbonyl β-to the carboxylic acid group, is prone to decarboxylation when heated. In this process the CO_2H group is lost as CO_2 and in the product it is replaced by a hydrogen atom.

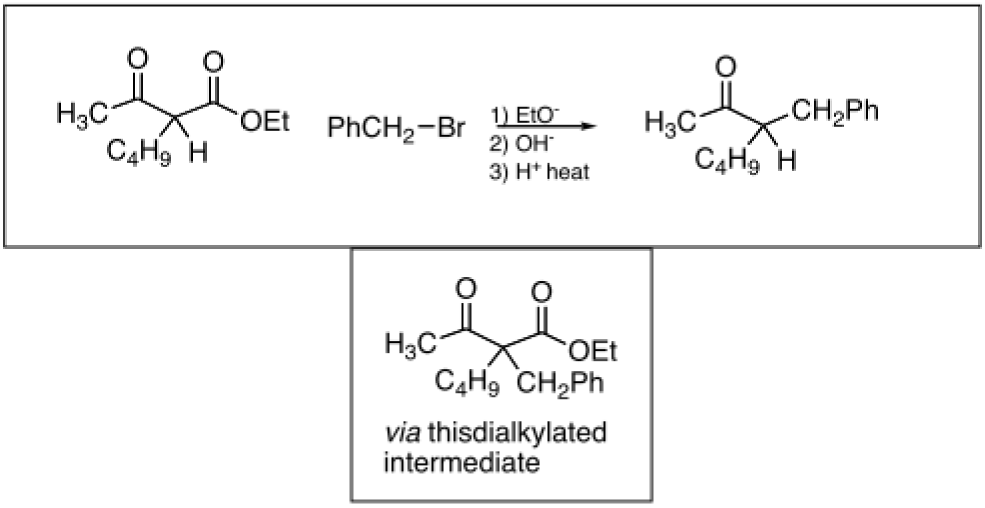


The decarbocylation occurs by a cyclic transition state, which gives initially the enol tautomer of the product. This quickly tautomerises to the more stable ketone tautomer.



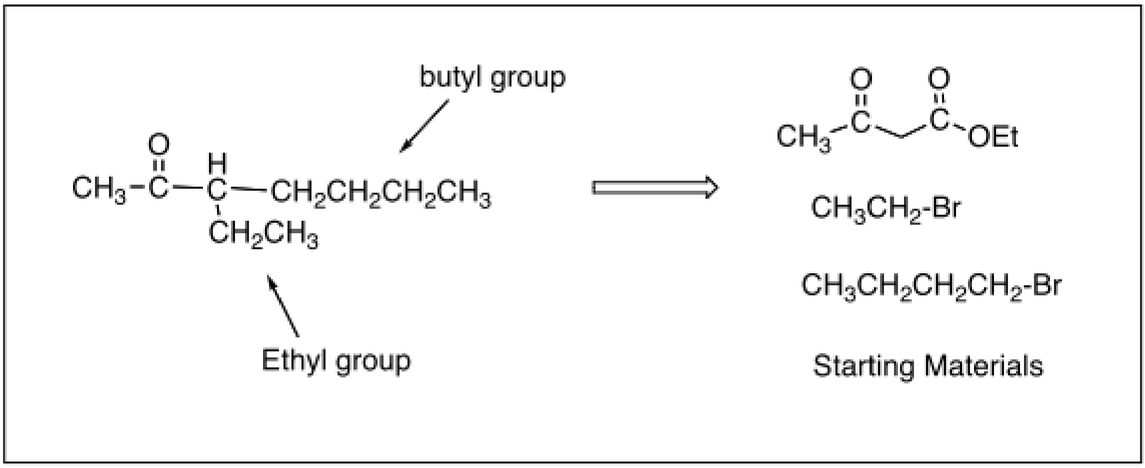
Disubstituted Reactions

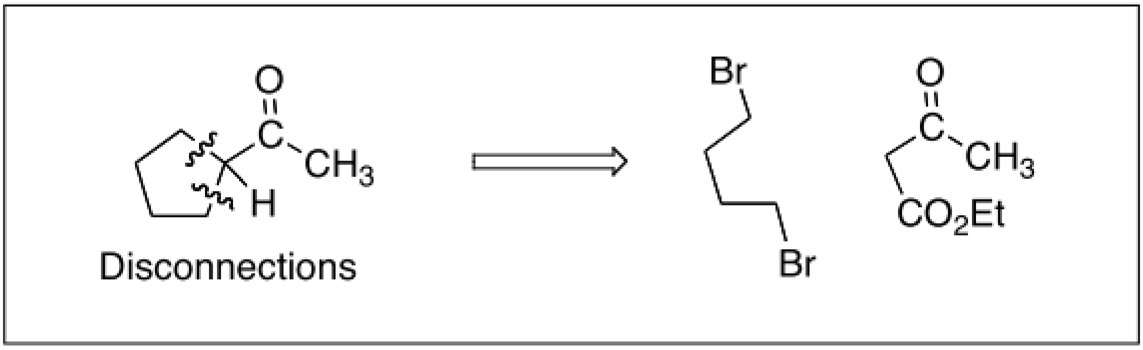
As for malonate diester chemistry, dialkylated acetone derivatives are formed by simply alkylating acetoacetic ester a second time, before the hydrolysis and decarboxylation steps.



Retrosynthesis

In all cases when the product contains an α-substituted derivative of acetone with at least one α-hydrogen then acetoacetate ester is a possible starting material. The retrosynthesis is given by simply reacting an acetoacetate ester with the halogen-versions of the new desired substituents.

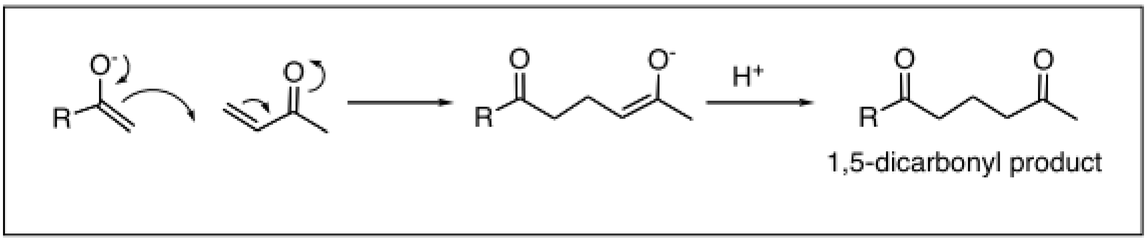




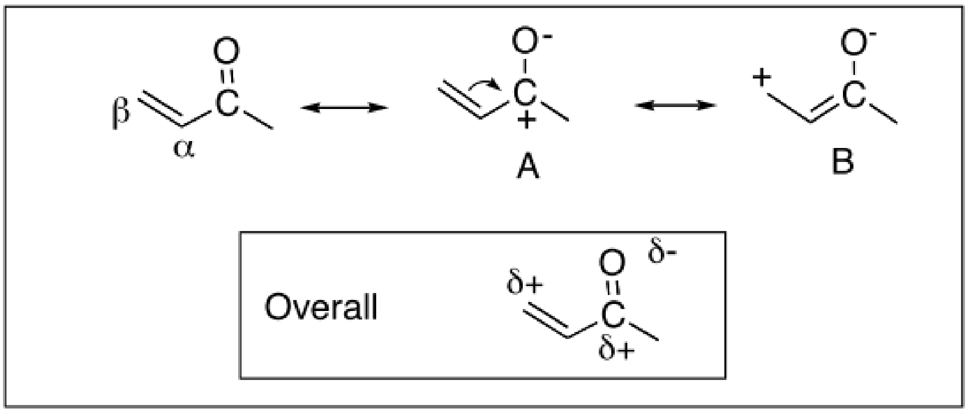
Micheal Chemistry

Overview

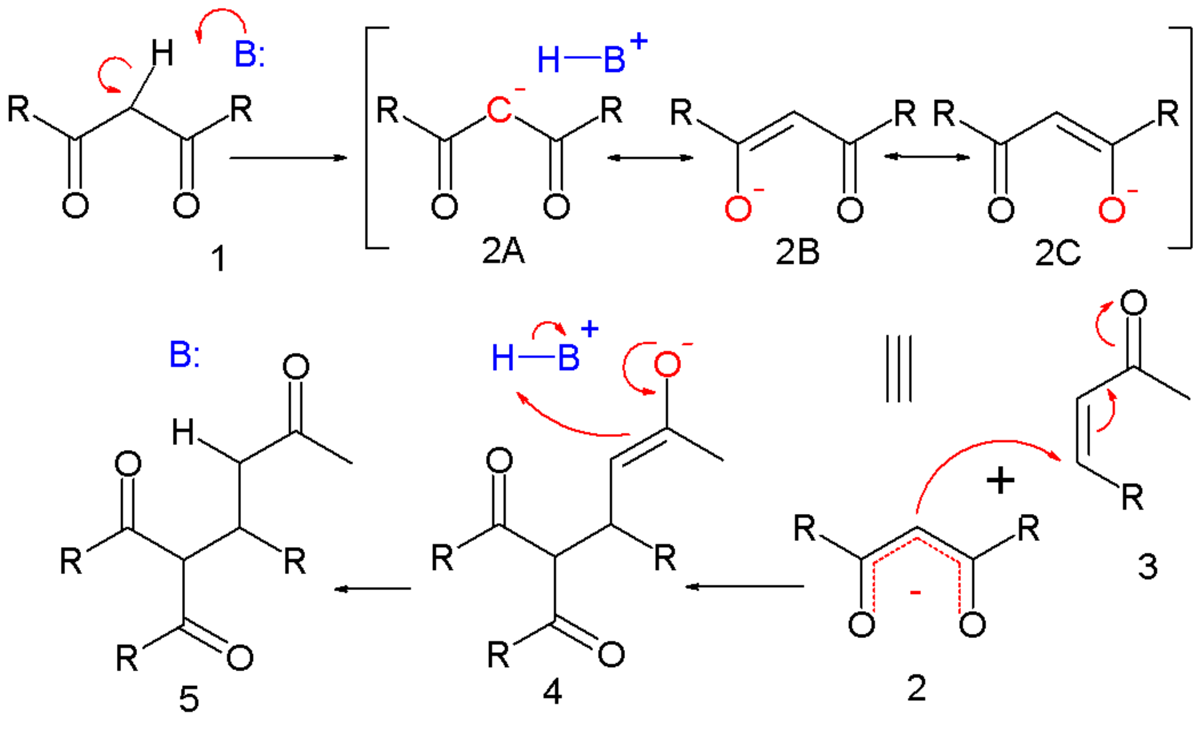
The reaction between an enolate anion and an α,β-unsaturated carbonyl compound is known as the Michael Reaction, and the α,β-unsaturated carbonyl compound is often referred to as a Michael Electrophile.



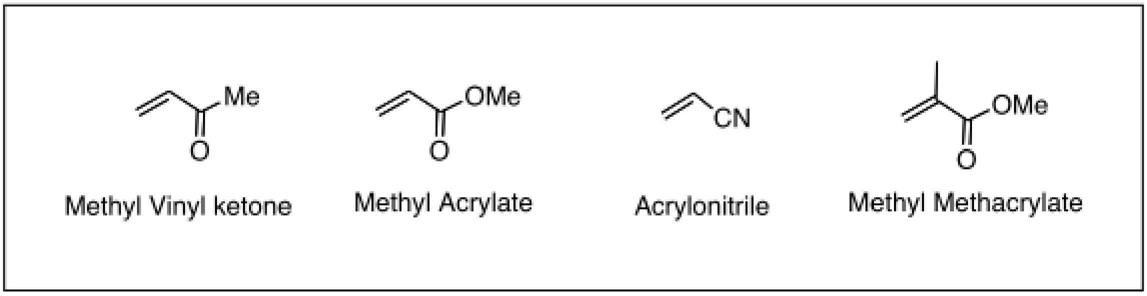
This occurs as a result of the delta-positive charge on the main and beta carbons:



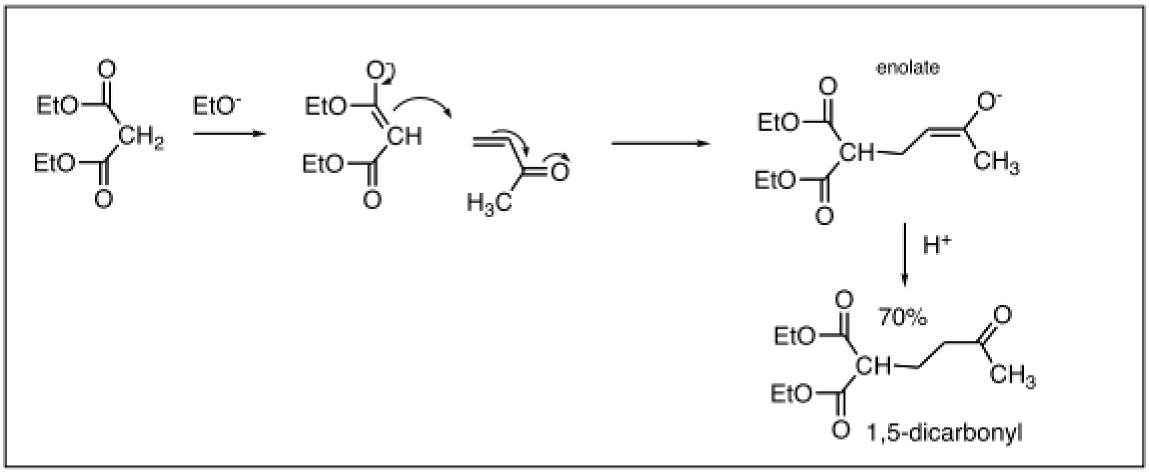
Mechanism



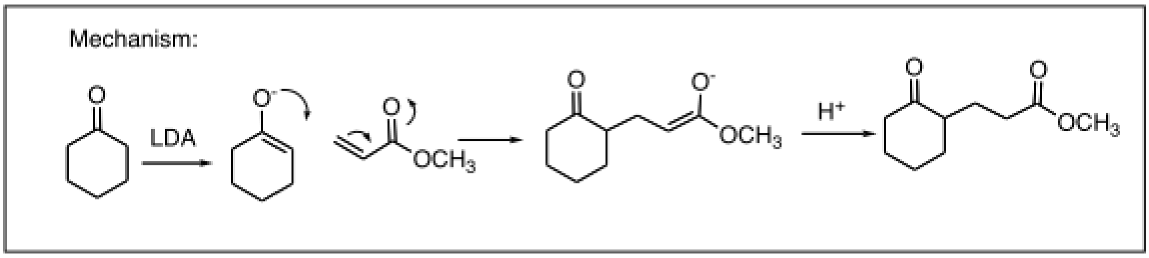
Common Michael Electrophiles



When stabalised compounds, particularly acetoacetates or malonates, are used, then weaker bases (e.g. EtO-) can be used to enolise them into enolate ions. Note that following the Michael addition, hydrolysis and decarboxylation can also be performed.

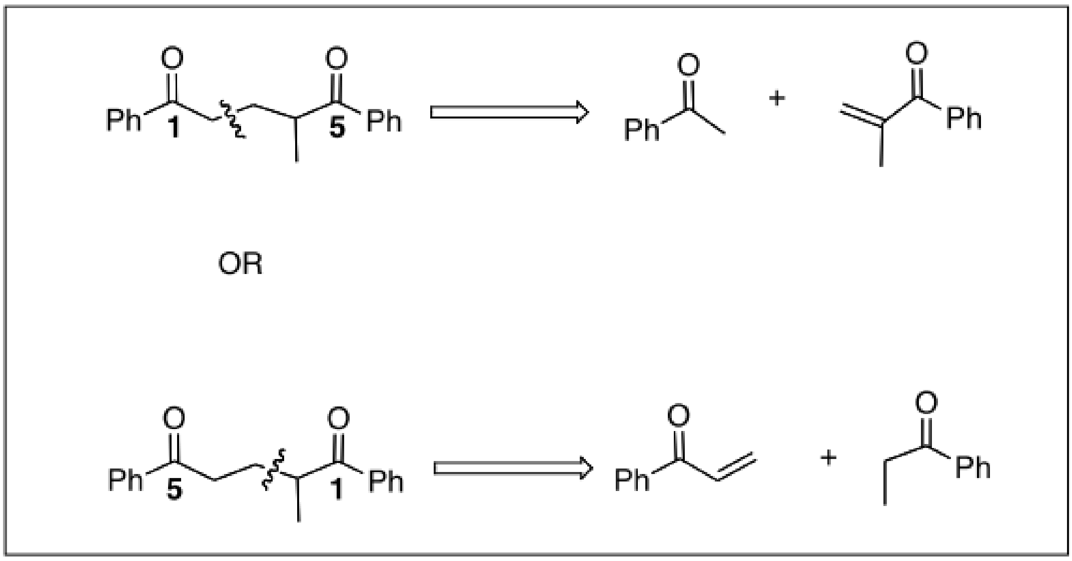


When non-stabalised enolates are used, a much stronger base (e.g. LDA) must be used



Retrosynthesis

If a compound contains two carbonyl groups, which are in a 1,5-relationship w.r.t one another, then it can potentially be prepared using Michael Chemistry. As is apparent from the example below there are two ways to make the disconnection, both of which may be suitable.


Ph
1
5
Ph
+
Ph
OR
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Ph
Ph
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Inorganic Chemistry

Basic Concepts

Common Ligands

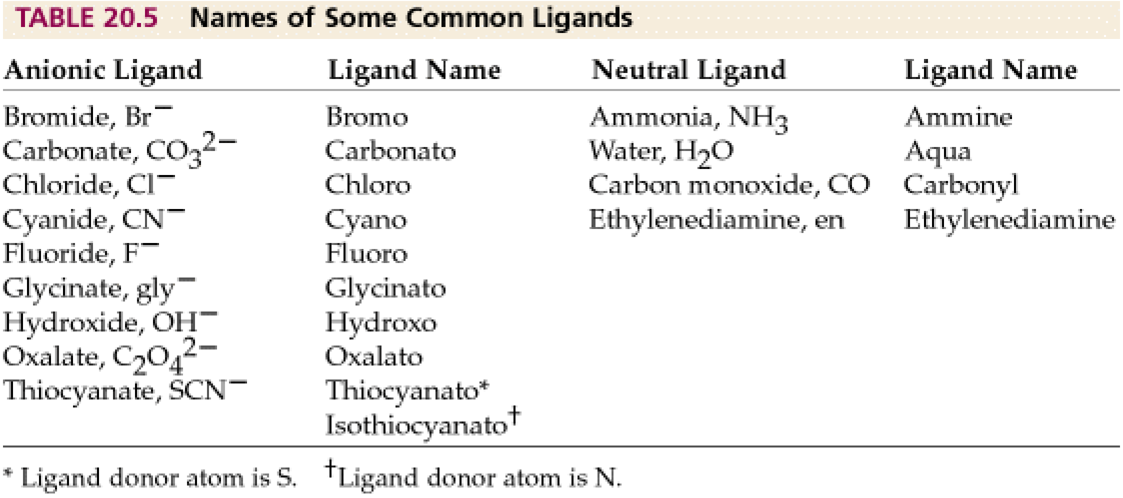


TABLE 20.5 Names of Some Common Ligands

Anionic Ligand	Ligand Name	Neutral Ligand	Ligand Name
Bromide, Br^-	Bromo	Ammonia, NH_3	Ammine
Carbonate, $CO_3{}^{2-}$	Carbonato	Water, H_2O	Aqua
Chloride, Cl^-	Chloro	Carbon monoxide, CO	Carbonyl
Cyanide, CN^-	Cyano	Ethylenediamine, en	Ethylenediamine
Fluoride, F^-	Fluoro		
Glycinate, gly^-	Glycinato		
Hydroxide, OH^-	Hydroxo		
Oxalate, $C_2O_4{}^{2-}$	Oxalato		
Thiocyanate, SCN^-	Thiocyanato* Isothiocyanato†		

* Ligand donor atom is S. †Ligand donor atom is N.

Coordination Complexes

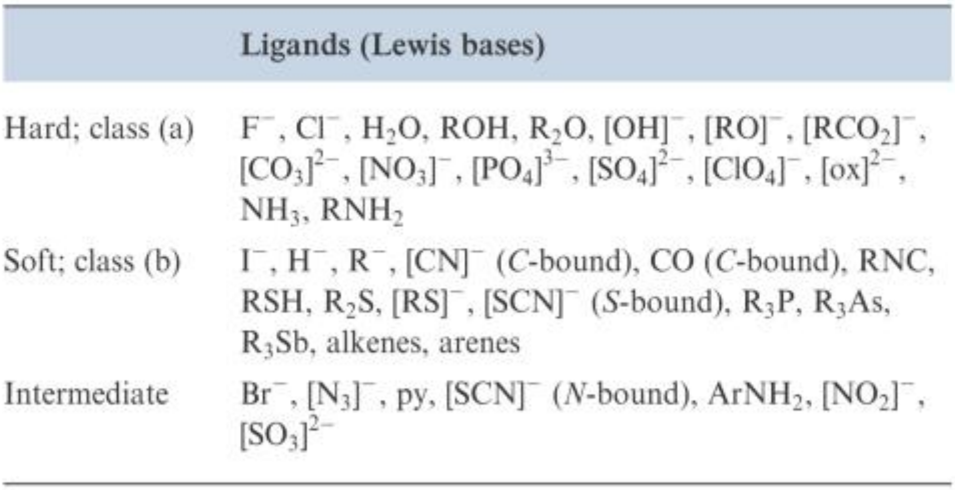
A coordination complex consists of a transition metal ion bonded to one or more ligands, with whatever counter ions are needed to ensure no net charge. The metal acts as a Lewis Acid, accepting electrons from the donor atoms of the ligands. The coordination number refers to the number of donor atoms bonded to the metal ion.

HSAB Theory

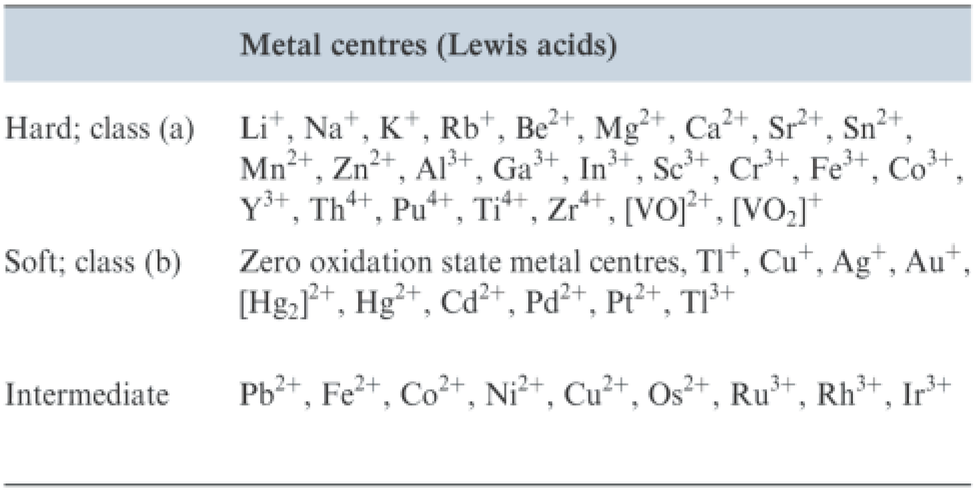
Not all metals form coordination complexes with all possible ligands. Some metals are more likely to form compounds with certain ligands. This observation has eventually led to a classification system called Hard and Soft Acids and Bases (HSAB).

Hard acids and bases are smaller, less easily polarizable, and tend to have a higher charge.

Soft acids and bases are larger, more easily polarizable, and tend to have a lower charge.



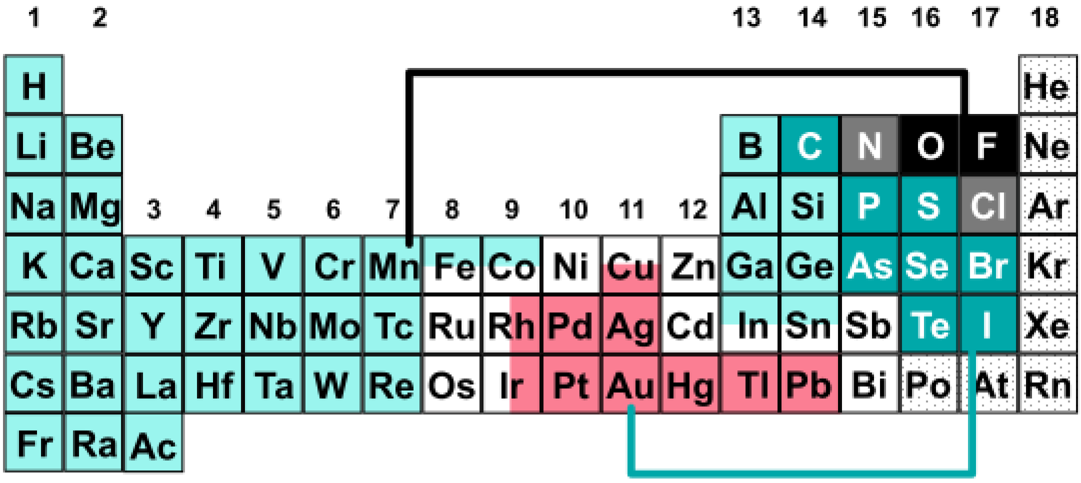
	Ligands (Lewis bases)
Hard; class (a)	F^-, Cl^-, H_2O, ROH, R_2O, $[OH]^-$, $[RO]^-$, $[RCO_2]^-$, $[CO_3]^{2-}$, $[NO_3]^-$, $[PO_4]^{3-}$, $[SO_4]^{2-}$, $[ClO_4]^-$, $[ox]^{2-}$, NH_3, RNH_2
Soft; class (b)	I^-, H^-, R^-, $[CN]^-$ (*C*-bound), CO (*C*-bound), RNC, RSH, R_2S, $[RS]^-$, $[SCN]^-$ (*S*-bound), R_3P, R_3As, R_3Sb, alkenes, arenes
Intermediate	Br^-, $[N_3]^-$, py, $[SCN]^-$ (*N*-bound), $ArNH_2$, $[NO_2]^-$, $[SO_3]^{2-}$



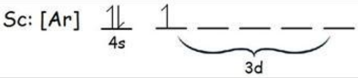
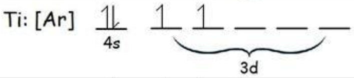
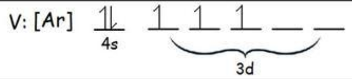
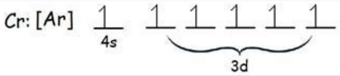
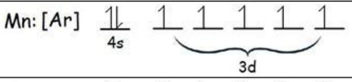
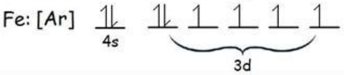
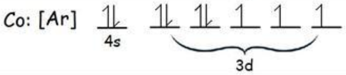
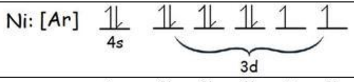
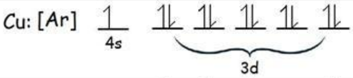
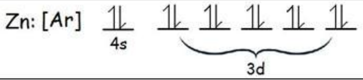
	Metal centres (Lewis acids)
Hard; class (a)	Li^+, Na^+, K^+, Rb^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Sn^{2+}, Mn^{2+}, Zn^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Sc^{3+}, Cr^{3+}, Fe^{3+}, Co^{3+}, Y^{3+}, Th^{4+}, Pu^{4+}, Ti^{4+}, Zr^{4+}, $[VO]^{2+}$, $[VO_2]^+$
Soft; class (b)	Zero oxidation state metal centres, Tl^+, Cu^+, Ag^+, Au^+, $[Hg_2]^{2+}$, Hg^{2+}, Cd^{2+}, Pd^{2+}, Pt^{2+}, Tl^{3+}
Intermediate	Pb^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Os^{2+}, Ru^{3+}, Rh^{3+}, Ir^{3+}

The key principle of HSAB theory applied to coordination complexes is that hard-hard and soft-soft ligand/metal complexes are prefered to hard-soft combinations.

Hard-soft acids-bases

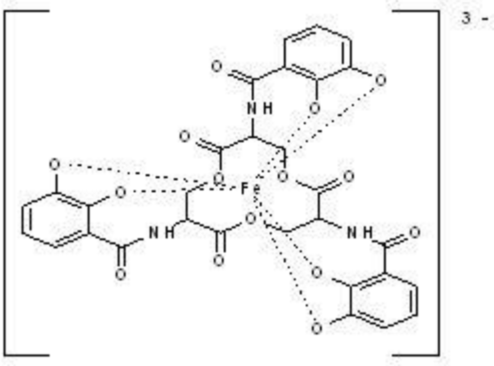


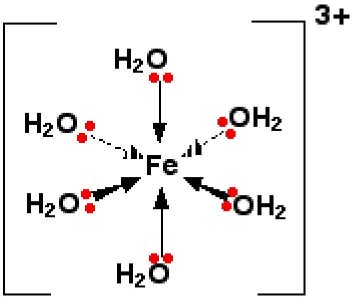
Oxidation States

Element Name and Symbol	Atomic Number	Common Oxidation States	Electron Configuration	
Scandium (Sc)	21	+3	Sc: [Ar] $4s^2 3d^1$	
Titanium (Ti)	22	+4	Ti: [Ar] $4s^2 3d^2$	
Vanadium (V)	23	+2, +3, +4, +5	V: [Ar] $4s^2 3d^3$	
Chromium (Cr)	24	+2, +3, +6	Cr: [Ar] $4s^1 3d^5$	
Manganese (Mn)	25	+2, +3, +4, +6, +7	Mn: [Ar] $4s^2 3d^5$	
Iron (Fe)	26	+2, +3	Fe: [Ar] $4s^2 3d^6$	
Cobalt (Co)	27	+2, +3	Co: [Ar] $4s^2 3d^6$	
Nickel (Ni)	28	+2	Ni: [Ar] $4s^2 3d^7$	
Copper (Cu)	29	+2	Cu: [Ar] $4s^1 3d^{10}$	
Zinc (Zn)	30	+2	Zn: [Ar] $4s^2 3d^{10}$	

To find the oxidation state of a metal ion in a given coordination complex, simply take the overall charge of the complex, and subtract the charge of each ligand attached. The result (which is generally positive but can occasionally be negative) is the oxidation number of the metal in that situation. In general higher oxidation states correlate with more ligands.

> [Oxidation state] is defined as the charge an atom might be imagined to have when electrons are counted according to an agreed-upon set of rules:
>
> 1. the oxidation state of a free element (uncombined element) is zero
> 2. for a simple (monatomic) ion, the oxidation state is equal to the net charge on the ion
> 3. hydrogen has an oxidation state of 1 and oxygen has an oxidation state of −2 when they are present in most compounds. (Exceptions to this are that hydrogen has an oxidation state of −1 in hydrides of active metals, e.g. LiH, and oxygen has an oxidation state of −1 in peroxides, e.g. H_2O_2
> 4. the algebraic sum of oxidation states of all atoms in a neutral molecule must be zero, while in ions the algebraic sum of the oxidation states of the constituent atoms must be equal to the charge on the ion.

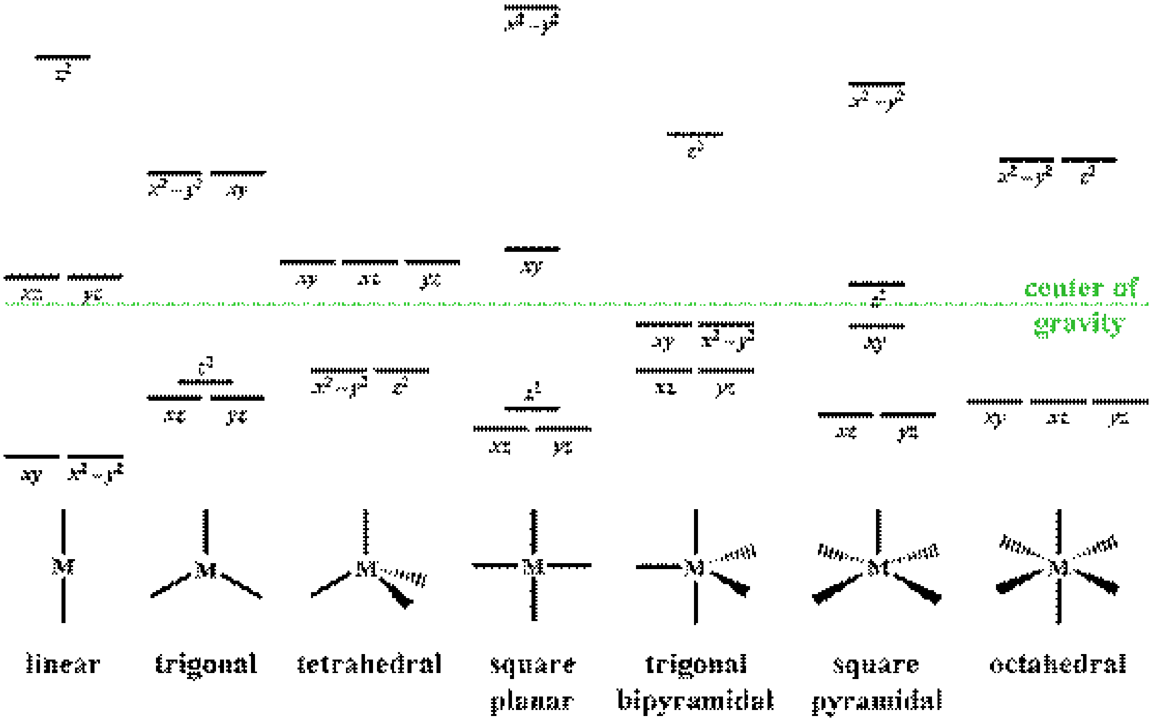




Coordination Complex Structure

Crystal Field Splitting

Crystal field effects have an important implication for reaction rates. In particular, the loss of crystal field stabalisation energy moving from one complex to another will increase the activation energy, hence slowing the reaction rate.



Strong and Weak Field Ligands

The size of the energy gap between successive orbitals is determined by both the metal ion and the ligands. Some ligands produce large energy gaps (so called strong-field ligands), and others (weak field ligands) produce smaller gaps. These are listed below:

CO □ CN^- > NO_2^- > NH_3 > $-NCS^-$ > H_2O > OH^- F^- $-SCN^-$ □ Cl^- > Br^-

strong-field ligands **weak-field ligands**

The metal ion matters two. More highly charged ions, and also ions further down a group, are both more likely to produce strong-field effects. This trends are illustrated below:

Pt^{4+} > Ir^{3+} > Rh^{3+} > Co^{3+} > Cr^{3+} > Fe^{3+} > Fe^{2+} > Co^{2+} > Ni^{2+} > Mn^{2+}

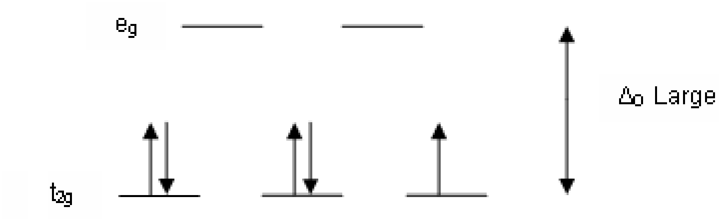
strong-field ligands **weak-field ligands**

Note that distinguishing strong-field and weak-field ligands is mainly a concern for octahedral and tetrahedral geometries. Square-planar geometries are most generally strong field.

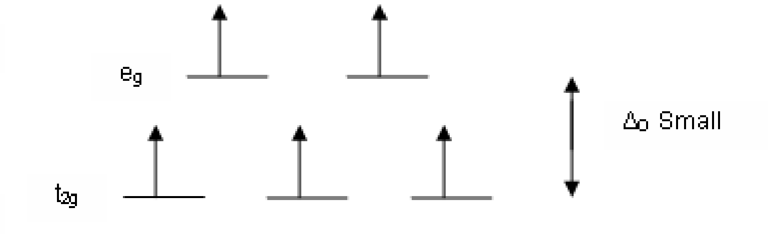
High and Low Spin

Strong-field ligands result in the lower orbitals being filled with paired electrons, thus yielding a low-spin complex with mostly paired electrons. If there are no unpaired electrons, such complexes will be diamagnetic. Weak-field ligands, by contrast, will have unpaired electrons, and hence will be high-spin complexes, exhibiting paramagnetism.

Low spin



High spin



Stability of Metal Complexes

Formation Constant

The formation constant K_f of a complex indicates the binding affinity of the ligand in comparison to water. A large K_f value indicates that the ligand binds more strongly than water.

Stepwise formation constants for multi-ligand replacement reactions are given by the formula:

$$K_{fn} = \frac{[ML_n]}{[ML_{n-1}][L]}$$

The overall formation constant allows us to calculate the concentration of the final product. It can be found by multiplying all of the stepwise formation constants:

$$\beta_n = K_1 K_2 \ldots K_n = \frac{[ML_n]}{[M][L]^n}$$

Since each ligand substitution is energetically favourable, total stability increases as more ligands are substituted out.

Successive Formation Constants

The magnitude of the formation constant tends to decline as the number of bound ligands increases. This occurs because the more water molecules have been substituted out, the less likely it is for the few remaining waters to be removed.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = -RT \ln K$$

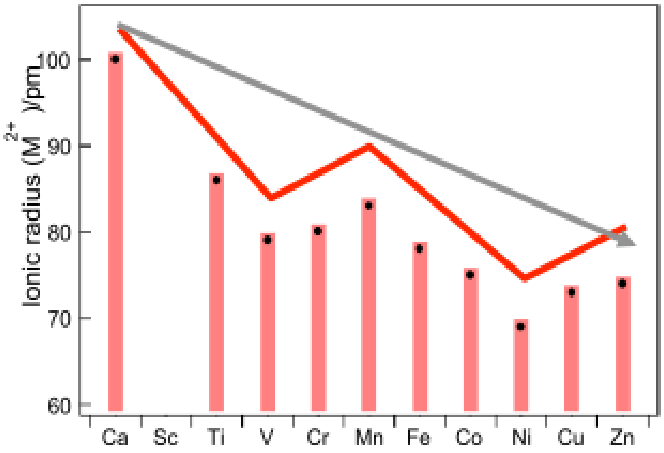
K is the overall formation constant

Irving Williams Series

Different metal ions have different complex stabilities. This stability relation is indicated by the Irving-Williams Series, and is insensitive to the ligands involved.

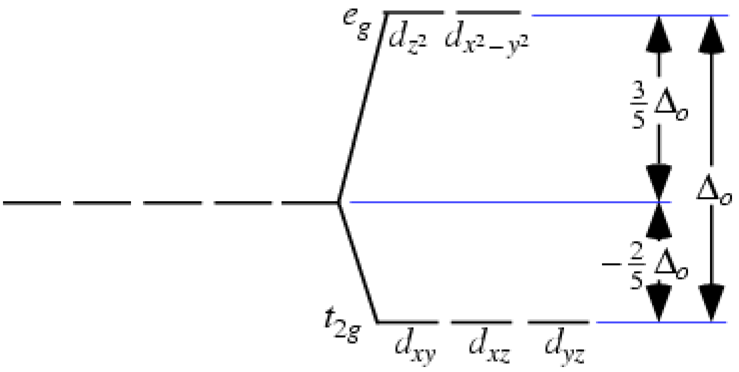
$Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$

Broadly speaking, this relationship is due to the fact that nuclear charge increases moving to the right across the periodic table, this leading to smaller atomic size, and hence causing the d orbitals to be relatively closer to the nucleus. The closer the ligands are able to donate their electrons to the metal nucleus, the more stable the resulting complex will be.



The 'jagged' nature of the line can be explained by crystal field effects for octahedral complexes. The first three electrons are placed in the lower energy orbitals, thus increasing stability, while the next two electrons are relegated to the two remaining higher energy orbitals, thus reducing stability.

octahedral (O_h) crystal field splitting

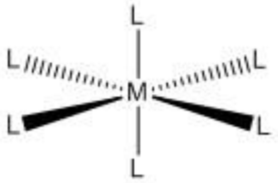


Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
0	0.4	0.8	1.2	0.6	0

Jahn-Teller Distortions

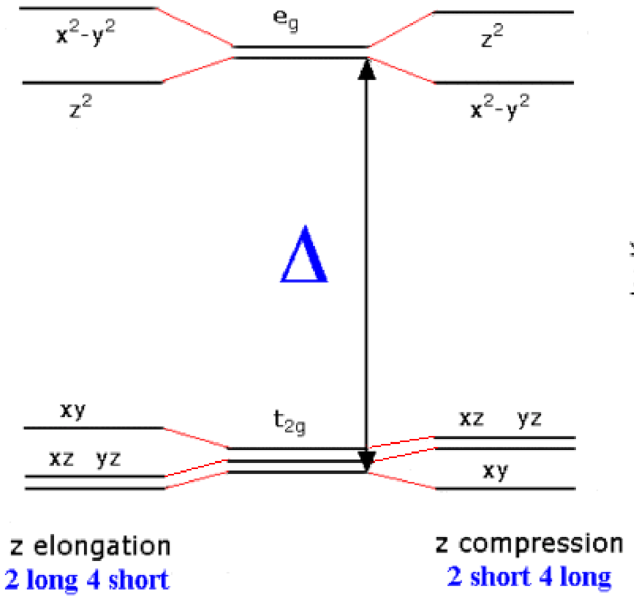
The Jahn–Teller effect describes the geometrical distortion of molecules and ions that is associated with certain electron configurations. The Jahn–Teller theorem essentially states that any nonlinear molecule with a spatially degenerate electronic ground state will undergo a geometrical distortion that removes that degeneracy, because the distortion lowers the overall energy of the species. This is most commonly observed with transition metal octahedral complexes, however, it can be observed in tetrahedral compounds as well.

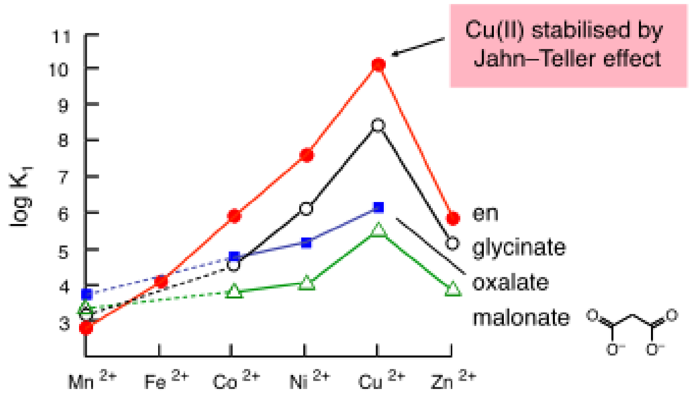
Elongated



Compressed

When an octahedral complex exhibits elongation, the axial bonds are longer than the equatorial bonds. For a compression, it is the reverse; the equatorial bonds are longer than the axial bonds. Elongation and compression effects are dictated by the amount of overlap between the metal and ligand orbitals. Thus, this distortion varies greatly depending on the type of metal and ligands. In general, the stronger the metal-ligand orbital interactions are, the greater the chance for a Jahn-Teller effect to be observed.





Coordinate Complex Reactions

Reaction Rates

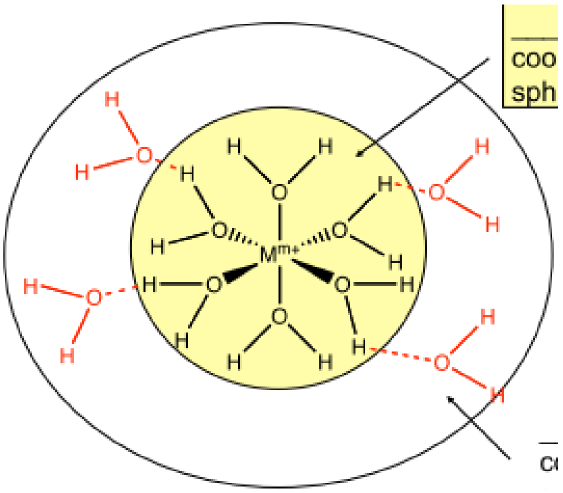
The reaction rate, or the rate at which one complex is converted to another form, is determined by the potential energy activation barrier between the complexes. Large activation energies lead to slow reactions, and are associated with inert substances. Species with a half life of less than one minute are called labile, or reactive.

Rate of Water Exchange

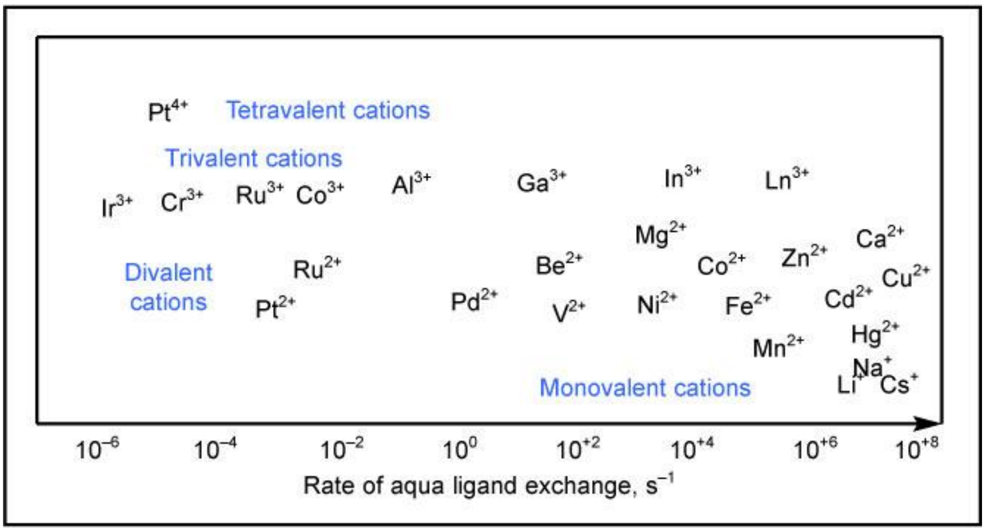
The rate constant for exchange of water molecules between the first coordination sphere and the second (outer) coordination spheres of metal ions is known as k.

$$[M(OH_2)_n]^{m+} + H_2O \xrightarrow{k} [M(OH_2)_{n-1}(OH_2)]^{m+} + H_2O$$

$$\text{Water exchange rate} = nk[M(H_2O)_n{}^{m+}]$$



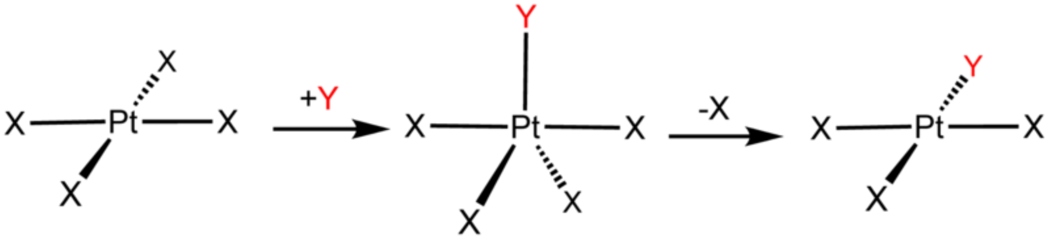
In general, the greatest lability is shown by metal ions of large ionic radius and low charge = low surface charge density.



Reaction Mechanisms

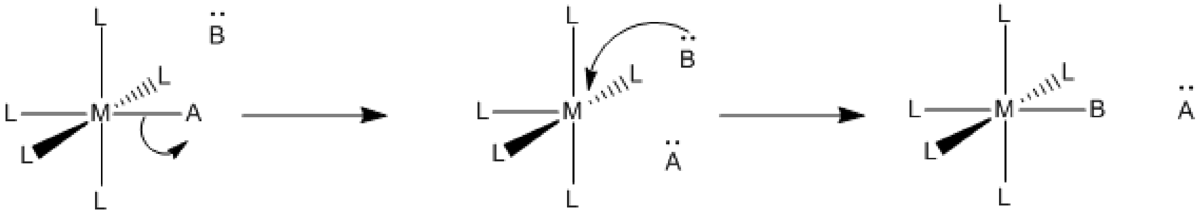
Associative

Associative pathways are characterized by binding of the attacking (nucleophile) to give a discrete, detectable intermediate followed by loss of another ligand. These reactions are second order, as their rate depends upon the concentration of the incoming ligand and the substrate.



Dissociative

Dissociative pathways are characterized by a rate determining step that involves release of a ligand from the coordination sphere of the metal undergoing substitution. The concentration of the substituting nucleophile has no influence on this rate, and an intermediate of reduced coordination number can be detected. These reactions are first order, as the rate limiting step is the dissociation of the departing ligand.



An interchange mechanism is a concerted process in which there is no intermediate species with a different coordination number.

Interchange Associative

In many substitution reactions, well-defined intermediates are not observed, when the rate of such processes are influenced by the nature of the entering ligand, the pathway is called associative interchange.

Interchange Dissociative

Interchange pathways apply to substitution reactions where intermediates are not observed, which is more common than pure dissociative pathways. If the reaction rate is insensitive to the nature of the attacking nucleophile, the process is called dissociative interchange**.**

Rate Laws

Although associative substitution reactions are technically second order, we generally study them as pseudo-first order, under the assumption that if the concentration of the incoming ligand is large, it will not change over the course of the reaction, and hence can be treated as a constant.

An example of the use of rate laws is in the substitution of a ligand for square planar complexes (e.g. cis-platin).

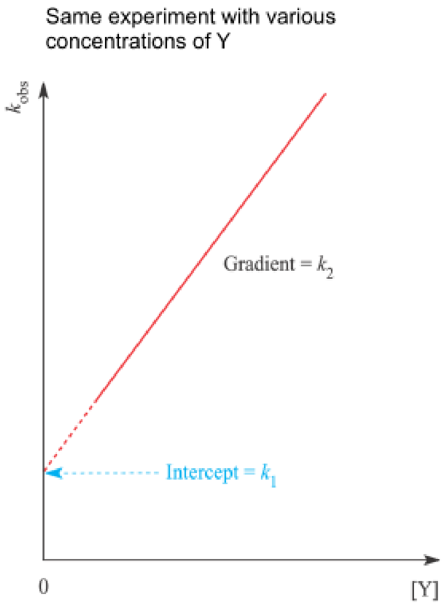
Substitution in square planar d^8 complexes

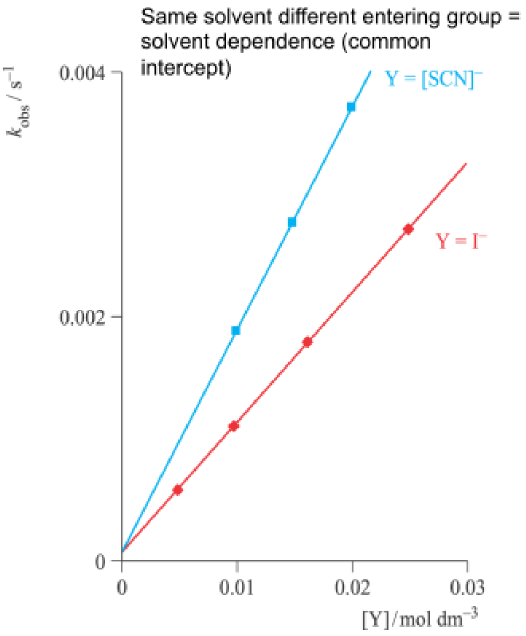
$$\mathrm{PtL_3X} + \mathrm{Y} \longrightarrow \mathrm{PtL_3Y} + \mathrm{X}$$

$$\begin{aligned}\text{Rate} &= -\,\mathrm{d[PtL_3X]/dt} \\ &= k_1[\mathrm{PtL_3X}] + k_2[\mathrm{PtL_3X}][\mathrm{Y}]\end{aligned}$$

$$k_{obs} = k_1 + k_2[\mathrm{Y}]$$

This means that if we fix the concentration of the substrate, we should observe a linear relationship between the reaction rate and the concentration of the incoming ligand. If both the slope and the intercept are positive, this indicates that two distinct associative pathways are occuring.


Same experiment with various concentrations of Y


Same solvent different entering group = solvent dependence (common intercept)

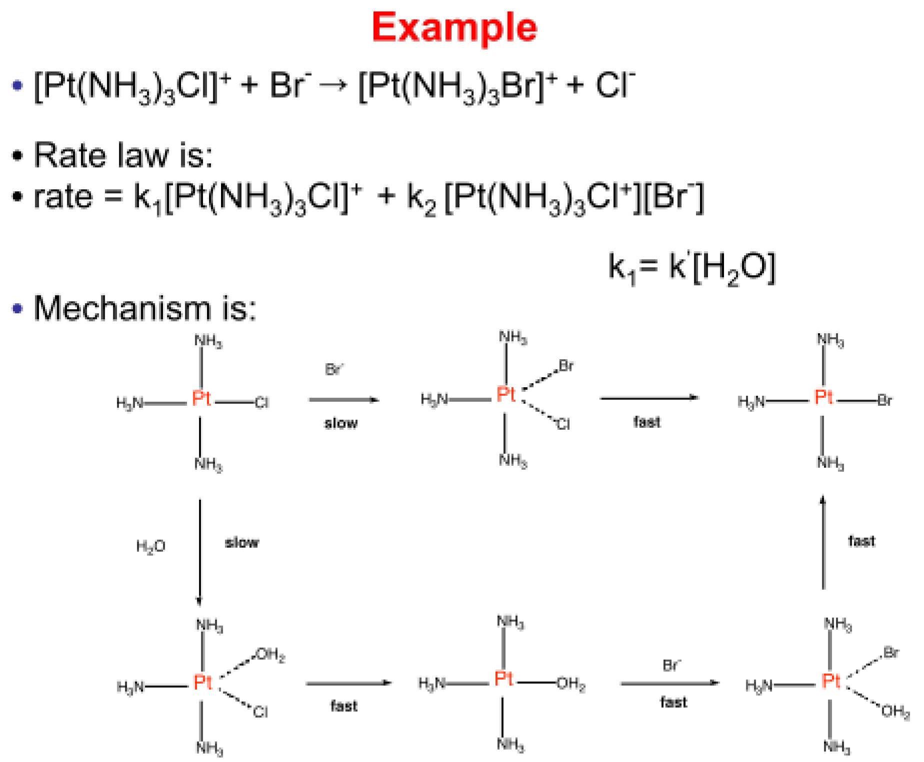
k_1 is determined by the solvent, and indicates the rate of the alternate pathway in which the solvent first replaces a ligand, and then is in turn replaced by the new attacking ligand

k_2 reflects the nucleophilicity of the entering ligand, with higher reaction rates associated with ligands that posses greater nucleophilicity

Order:

$CN^- > PR_3 \approx SCN^- > I^- > N_3^- \approx NO_2^- > py \approx NH_3 \approx Br^- > Cl^- > OH^- > H_2O$

- Correlates with soft Lewis basicity



Example

- $[Pt(NH_3)_3Cl]^+ + Br^- \rightarrow [Pt(NH_3)_3Br]^+ + Cl^-$

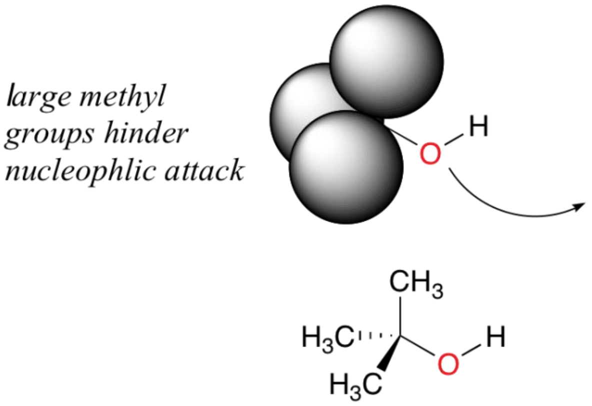
- Rate law is:
- rate = $k_1[Pt(NH_3)_3Cl]^+ + k_2 [Pt(NH_3)_3Cl^+][Br^-]$

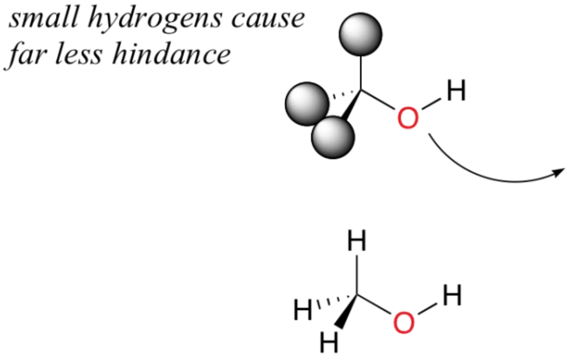
$k_1 = k'[H_2O]$

- Mechanism is:

Steric Effects

Bulky ligands block the approach of an attacking nucleophile, thus slowing the rate of associative reaction by potentially orders of magnitude.

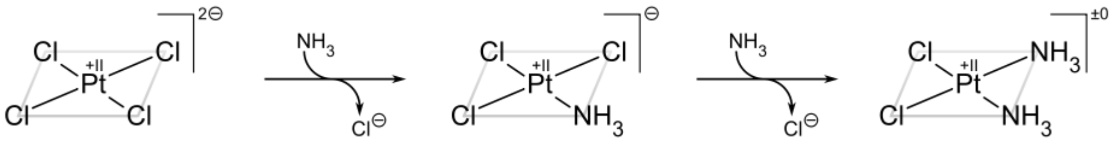




The Trans Effect

The trans effect is the labilization (making unstable) of ligands that are trans to certain other ligands, which can thus be regarded as trans-directing ligands. It is attributed to electronic effects and it is most notable in square planar complexes, although it can also be observed for octahedral complexes.

One way of stating the trans effect is that the position of the substituted ligand is determined by the identity of the existing ligand trans to it. The classic example of the trans effect is the synthesis of cisplatin. The first NH_3 ligand is added to any of the four equivalent positions at random, but the second NH_3 is always added *cis* to the first one, because Cl^- has a larger trans effect than NH_3.



A simplistic way of thinking about why this occurs is that trans-ligands share (or partly share) the same s-orbital in their σ-bonds, so if one ligand forms an especially strong σ-bond with the metal, this leaves 'less' of the electron density available for the ligand in the trans position relative to the first ligand to bind to, thus resulting in a weaker bond, and hence increasing the rate at which that ligand dissociates.

Labile and Inert

Most 2+ metal ions from the first row are labile. For example, Co(II) is reactive, owing to its two unpaired electrons. By contrast, Cr^{3+} and Co^{3+} are inert, as they have no unpaired electrons.

Synthesis

The synthesis of coordination complexes is a fairly straightforward matter:

$$[Ni(OH_2)_6]^{2+} + 6NH_3 \rightarrow [Ni(NH_3)_6]^{2+} + 6H_2O$$

$$[Co(II)(OH_2)_6]^{2+} + 6NH_3 \rightarrow [Co(II)(NH_3)_6]^{2+} + 6H_2O \rightarrow [Co(III)(NH_3)_6]^{3+} + 6H_2O$$

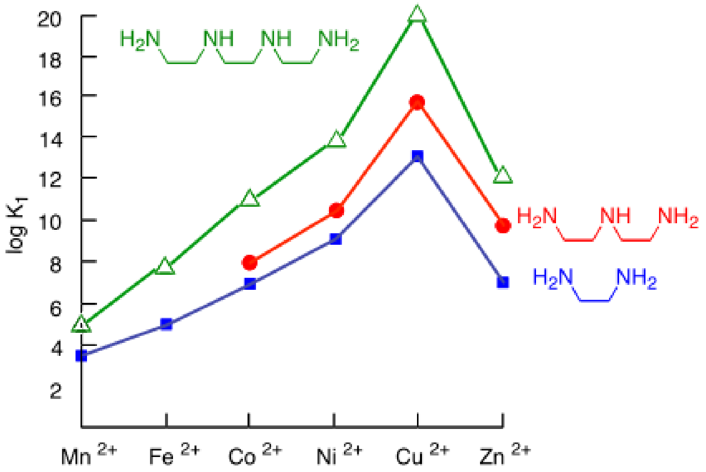
Applications

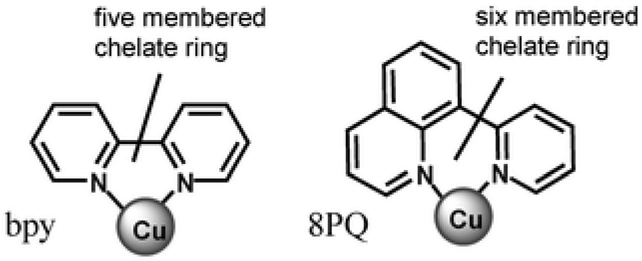
The Chelate Effect

Chelation involves the formation or presence of two or more separate coordinate bonds between a polydentate (multiple bonded) ligand and a single central atom. The chelate effect describes the enhanced affinity of chelating ligands for a metal ion compared to the affinity of a collection of similar nonchelating (monodentate) ligands for the same metal.

This is primarily an entropic effect: displacement of two water ligands by one bidentate (for example) ligand increases the total number of free particles in solution, thus increasing total entropy.

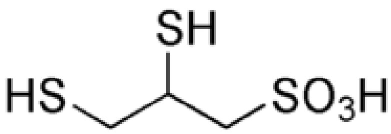
In general, chelates containing five- or six-membered rings are more stable than chelates with four-, seven-, or eight-membered rings.





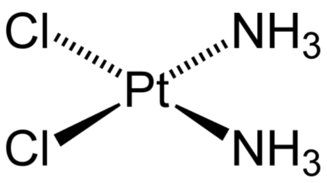
log K_1 Cu(II):	8.1	4.4
Ni(II):	7.0	3.2

DMPS is a particularly useful chelating agent, because it is a strong acid and so is easily soluable in water, making secretion of the chelated ring from the body easier.

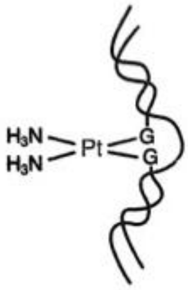


Cisplatin

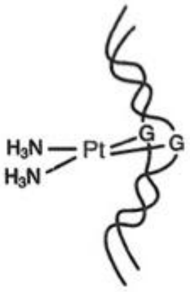
Cisplatin is administered intravenously as short-term infusion in normal saline for treatment of solid malignancies. It is used to treat various types of cancers. It is non-specific, so targets all cells in the body, having particularly strong effects on rapidly proliferating cells (including cancer cells, but also germ cells, hair and skin cells).



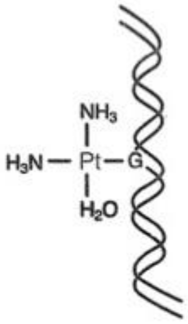
Cisplatin binds to guanine, one of the DNA bases, sometimes causing crosslinking between two different guanine basis, thereby causing a 'bend' to form in the DNA molecule. Complexation of DNA with cisplatin inhibits DNA replication or repair, and the complex can be recognized by proteins which target the cell for apoptosis.



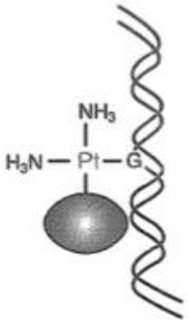
Intra-strand crosslink (96%)



Inter-strand crosslink (1%)

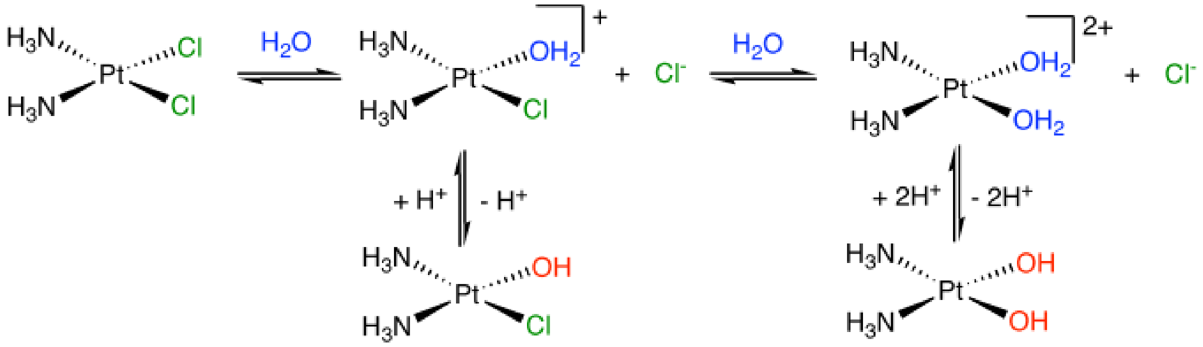


Mono adduct (~2%)

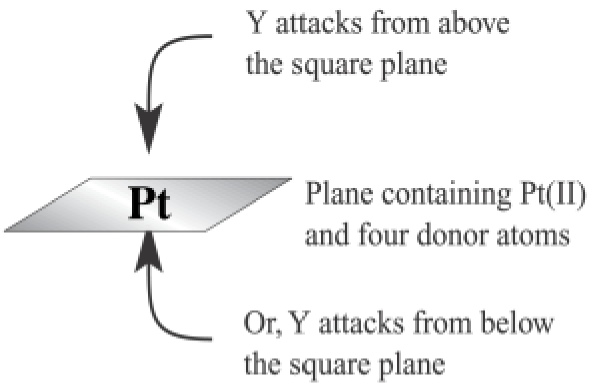


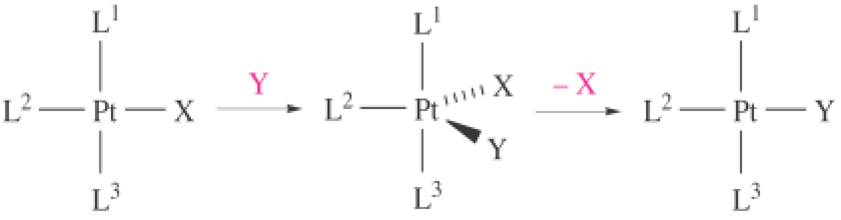
Protein DNA crosslink (<1%)

Cisplatin is administered into the bloodstream, where it remains in dichloro form as a result of the high levels of chloride ions in the blood. Once cisplatin crosses the cell membrane, however, the chlorines are lost to the much lower chloride ion concentrations of the cytoplasm.



Cisplatin is thought to react predominantly by an associative reaction mechanism.





Siderophores

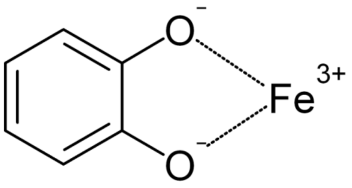
Siderophores are small, high-affinity iron chelating compounds secreted by microorganisms such as bacteria, fungi and grasses. They are an example of hard acid/hard base pairs.

The greater stability of enterobactin compared to catechole is a result of the chelate effect. Enterobactin is hexadentate compared to the bidentate catachole, so it is very unlikely that all six donor oxygen atoms will dissassociate at once.

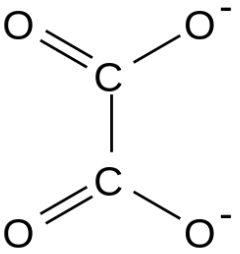
$$LH_6 + Fe^{3+}(aq) \rightarrow [FeL]^{3-} + 6H^+ \qquad K \sim 10^{45}$$

$$3\ catH_2 + Fe^{3+}(aq) \rightarrow [Fe(cat)_3]^{3-} + 6H^+ \qquad K = 10^{33}$$

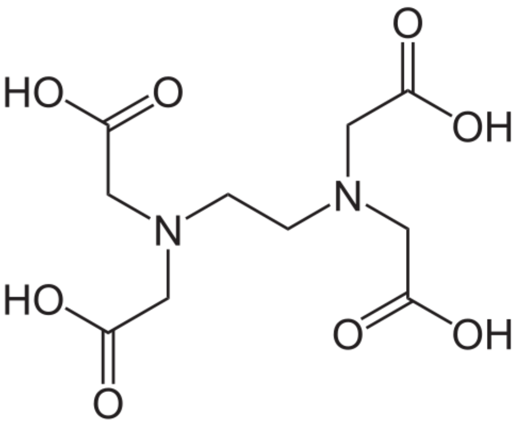
Catecholate



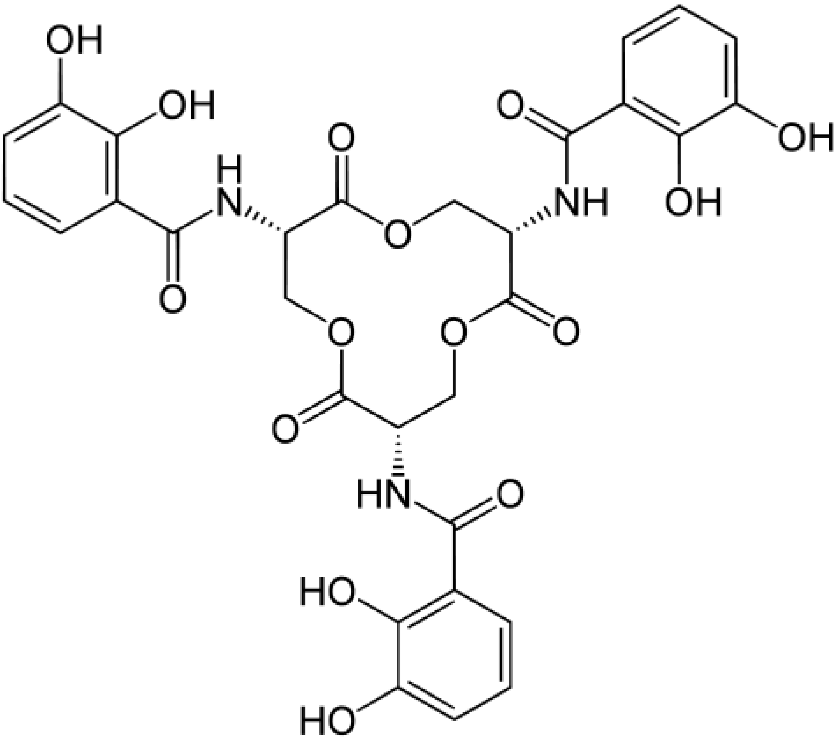
Oxalate



EDTA



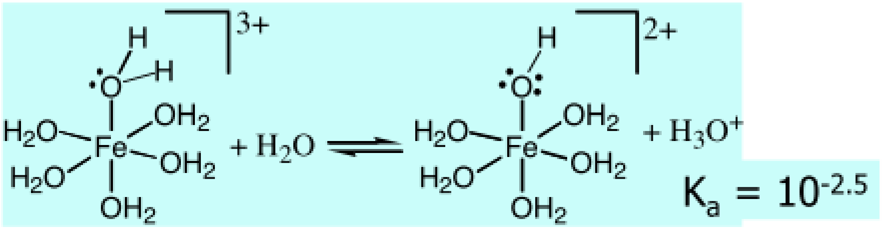
Enterobactin



Catalytic Ligands

The properties of some ligands change dramatically upon coordination with a transition metal. For example, Fe(III) coordination increases the acidity of water by a factor of $10^{11.5}$. Largely this is due to the polarising ability of the metal ion.

$$2\ H_2O\ =\ OH^- + H_3O^+ \qquad\qquad K_w = 10^{-14}$$

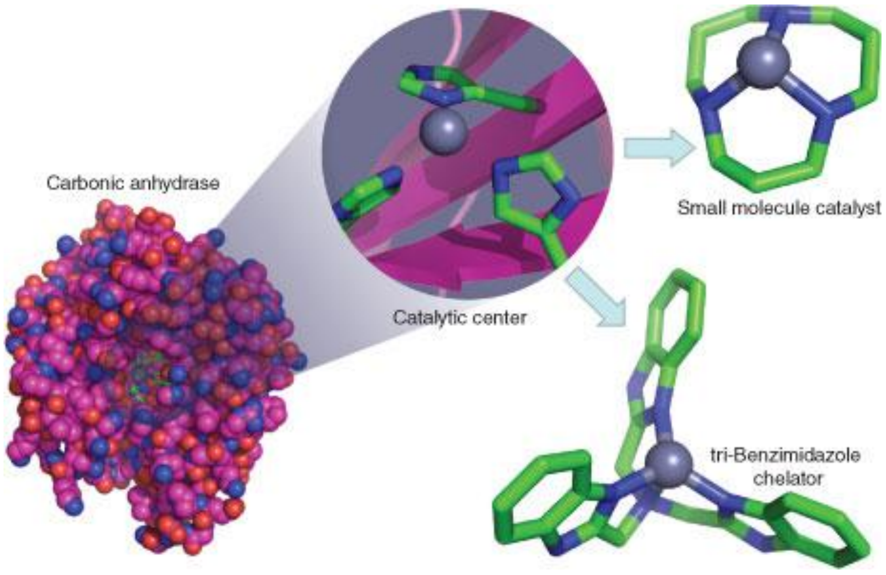


Fe^{3+} increases acidity of water by $10^{11.5}$

Carbonic anhydrase is an enzyme that catalyzes the rapid interconversion of carbon dioxide and water to bicarbonate and protons, a reversible reaction that occurs relatively slowly in the absence of a catalyst. The active site of most carbonic anhydrases contains a zinc ion; they are therefore classified as metalloenzymes.

$$H_2O + CO_2 \rightleftharpoons [HCO_3]^- + H^+$$

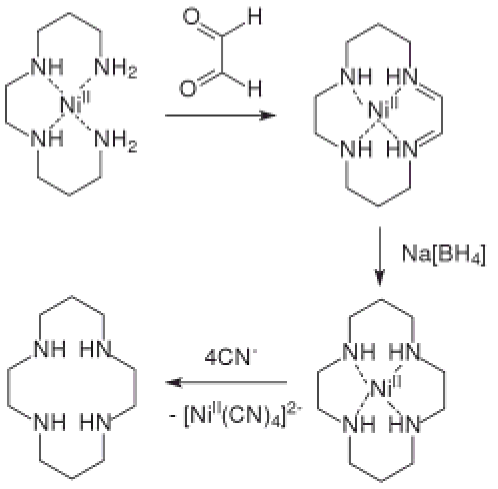
Zinc(II) is a hard metal with a high polarising ability, and is also not redox reactive, owing to its full d shell.. Hence it makes a perfect choice as the catalyst for the carbonic anhydrase reaction.



Template Effect

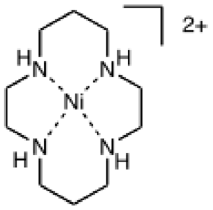
A macrocycle is a cyclic molecule with 3 or more donor atoms in a ring of at least 9 atoms. Macrocycles can be formed by utilising central transition metal atoms as 'templates', around which the ring is formed as connected ligands. Had the metal ion not been present, the ligands would have formed an ill-defined polymer mixture rather than a macrocycle.

There are two types of template reactions. In thermodynamic template effect reactions, the metal is crucial to shift the reaction equilibrium. In kinetic template effect reactions, the macrocycle directs the steric course of the reaction, holding the reacting compounds in the correct orientation by their joint proximity to the metal atom.

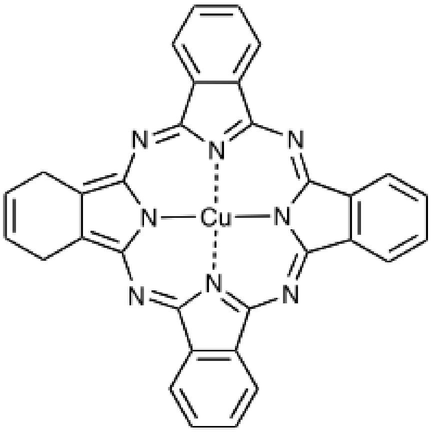


Nickel(II) template synthesis of cyclam (15).

Cyclam: Used as a transition metal ligand

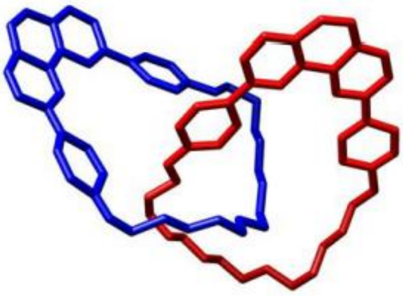


Pthalocyanine: Used as a blue pigment

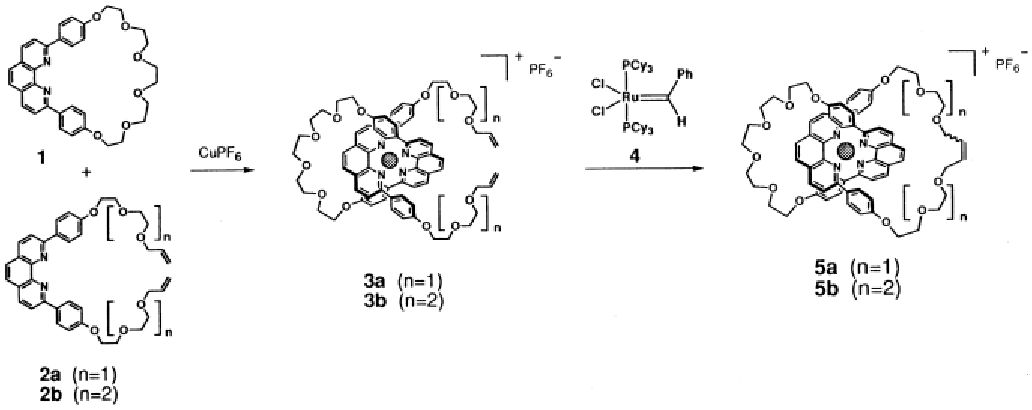


Catenanes

A catenane is a mechanically-interlocked molecular architecture consisting of two or more interlocked macrocycles. The interlocked rings cannot be separated without breaking the covalent bonds of the macrocycles.



Threading in catenane synthesis, catalysed by Cu(I), is one example of how the template effect can be used in synthesis.



Physical Chemistry

The First Law of Thermodynamics

Some Definitions

- Isolated system: no exchange of heat or work with surroundings (e.g. an isolated insulated box of fixed volume), q=0, w=0, $\mathit{\Delta} U = 0$
- Isothermal process: temperature remains constant (ΔT=0), meaning that $\mathit{\Delta} U = 0$
- Adiabatic process: no heat exchange between the system and the surroundings, so q = 0 and thus $\mathit{\Delta} U = w$

First Law

The First Law of Thermodynamics states that the change in the internal energy of a system is equal to the heat transferred plus the work done on that system:

$$\Delta U = q + w$$

- U is the internal energy of the system, sum of translation, vibrational, rotational energies
- Q is the heat transferred into the system (negative for heat transferred to surroundings)
- W is the work done on the system (negative for work done on the surroundings by the system)

Work

Work done on the system

$$w = -\int P_{ex}\, dV$$

Where P_{ex} is the external pressure

Internal Energy

$$\Delta U = C_V \Delta T$$

Where C_V is the constant volume heat capacity

$$dU = dw$$

Enthalpy

Enthalpy is the thing that is increased in a system when energy is transferred to that system. Some of the energy goes to increasing U, and some goes to increasing PV

$$H = U + PV$$

For constant pressure this becomes:

$$\begin{aligned} dH &= dU + d(PV) \\ &= d(q + w) + PdV \\ &= dq + dw + PdV \\ &= dq - PdV + PdV \\ dH &= dq \end{aligned}$$

Can also write:

$$\begin{aligned} dH &= dU + d(PV) \\ &= d(C_V T) + d(nRT) \\ &= C_V dT + nRdT \\ dH &= (C_V + nR)dT \\ \Delta H &= C_p \Delta T \end{aligned}$$

Where C_p is the constant pressure heat capacity

Reversible Adiabatic Process

Note that in this case P is not constant, but can be found by the ideal gas law

$$\begin{aligned} dU &= dw \\ C_V dT &= -PdV \\ C_V dT &= -\frac{nRT}{V} dV \\ \frac{C_V}{T} dT &= -\frac{nR}{V} dV \\ C_V \int \frac{1}{T} dT &= -nR \int \frac{1}{V} dV \\ C_V \log\left(\frac{T_f}{T_i}\right) &= -nR \log\left(\frac{V_f}{V_i}\right) \\ \log\left(\frac{T_f}{T_i}\right)^{C_V} &= \log\left(\frac{V_i}{V_f}\right)^{nR} \\ \left(\frac{T_f}{T_i}\right)^{C_V} &= \left(\frac{V_i}{V_f}\right)^{nR} \\ T_f &= T_i \left(\frac{V_i}{V_f}\right)^{nR/C_V} \end{aligned}$$

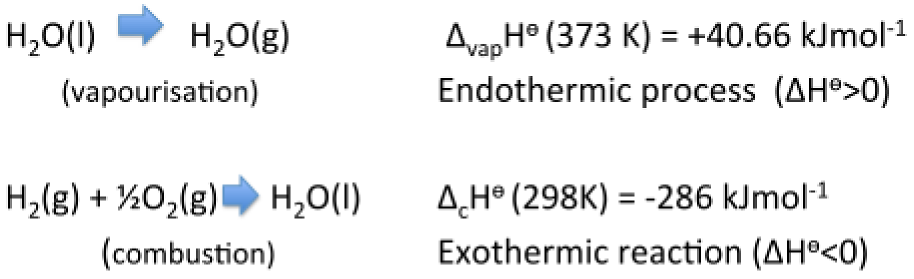
Enthalpy of Formation

The standard enthalpy of formation or standard heat of formation of a compound is the change of enthalpy from the formation of 1 mole of the compound from its constituent elements, with all substances in their standard states at 1 atmosphere.

The formation enthalpy varies with temperature. If the reaction occurs at a different temperature to the standard reference temperature, this needs to be adjusted for:

$$\Delta H^{\Theta}(T_2) = \Delta H^{\Theta}(T_1) + \int_{T_1}^{T_2} \Delta C_P \, dT$$

Where $\Delta C_P = \sum_{\text{prod}} v_p C_p - \sum_{\text{react}} v_r C_p$



$H_2O(l) \rightarrow H_2O(g)$ (vapourisation)

$\Delta_{vap}H^{\ominus}$ (373 K) = +40.66 kJmol^{-1}

Endothermic process ($\Delta H^{\ominus}>0$)

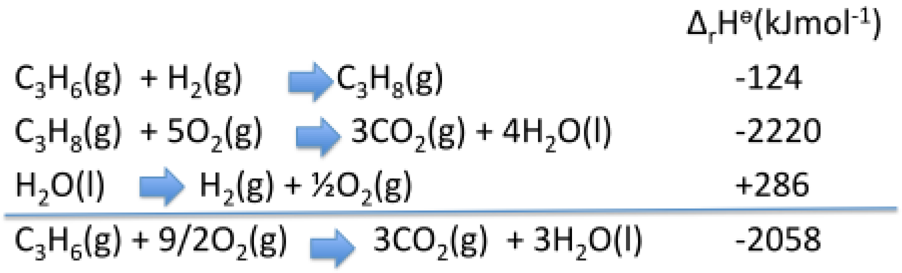
$H_2(g) + ½O_2(g) \rightarrow H_2O(l)$ (combustion)

$\Delta_c H^{\ominus}$ (298K) = -286 kJmol^{-1}

Exothermic reaction ($\Delta H^{\ominus}<0$)

Hess's Law

The standard enthalpy of an overall reaction is the sum of the standard enthalpies for the individual reactions.



	$\Delta_r H^{\ominus}(\mathrm{kJmol}^{-1})$
$C_3H_6(g) + H_2(g) \rightarrow C_3H_8(g)$	-124
$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$	-2220
$H_2O(l) \rightarrow H_2(g) + ½O_2(g)$	+286
$C_3H_6(g) + 9/2O_2(g) \rightarrow 3CO_2(g) + 3H_2O(l)$	-2058

This can also be written as the sum of the enthalpy of the products minus the sum of the enthalpy of the reactants.

$$\Delta_r H^{\ominus} = \Sigma_{prod} \nu_p \, \Delta_f H^{\ominus} - \Sigma_{reac} \nu_r \, \Delta_f H^{\ominus}$$

The Second Law and Entropy

Second Law

The second law states that the entropy of an isolated system increases in the course of spontaneous change.

For reversible processes:

$$dS = \frac{dq_{rev}}{T}$$

Where q_{rev} is the head supplied during a reversible change.

Note that entropy change is given by:

$$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr}$$

Entropy Change - Fixed T Changing V

For an isothermal volume change:

$$\Delta S = \int \frac{1}{T} dq_{rev}$$

$$\Delta S = \frac{q_{rev}}{T}$$

for an isothermal process $\Delta U = 0$ so $\Delta q = -w$, and hence:

$$\Delta S = -\frac{w_{rev}}{T}$$

$$= -\frac{1}{T}\left[-\int P_{ex}\, dV\right]$$

Since the process is reversible we set $p = p_{ex}$for all stages of the reaction, and hence:

$$= \frac{1}{T}\int \frac{nRT}{V}\,dV$$

$$\Delta S = nR\log\left(\frac{V_f}{V_i}\right)$$

Entropy Change - Fixed V Changing T

For a temperature change with constant volume:

$$\Delta S = \int \frac{1}{T}\,dq_{rev}$$

Since $w = 0$ if $\Delta V = 0$ then we have $dU = dq$ and thus $dU = nC_V dT$:

$$\Delta S = \int \frac{1}{T} nC_V\,dT$$

$$= nC_V \int \frac{1}{T}\,dT$$

$$\Delta S = nC_V \log\left(\frac{T_f}{T_i}\right)$$

Entropy Change - Phase Transition

For a phase transition:

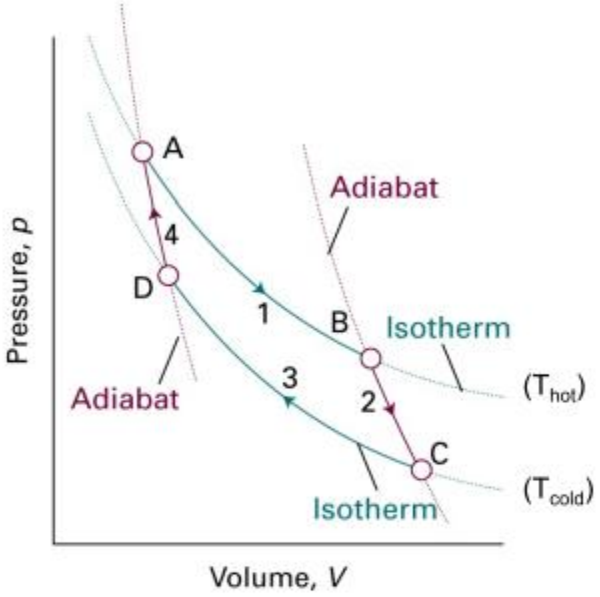
$$\Delta S = \int \frac{1}{T}\,dq_{rev}$$

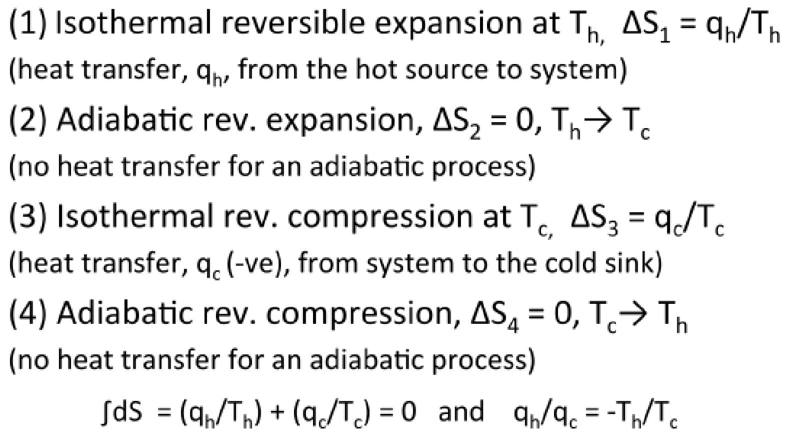
$$\Delta S = \frac{q_{rev}}{T}$$

$$\Delta S = \frac{\Delta_{trs}H}{T_{trs}}$$

At the transition temperature, any heat exchange between system and surroundings is reversible (as no temperature change), so the change in the entropy of the surroundings will simply be the negative of the change in entropy of the system.

The Carnot Cycle





(1) Isothermal reversible expansion at $T_{h,}$ $\Delta S_1 = q_h/T_h$

(heat transfer, q_h, from the hot source to system)

(2) Adiabatic rev. expansion, $\Delta S_2 = 0$, $T_h \rightarrow T_c$

(no heat transfer for an adiabatic process)

(3) Isothermal rev. compression at $T_{c,}$ $\Delta S_3 = q_c/T_c$

(heat transfer, q_c (-ve), from system to the cold sink)

(4) Adiabatic rev. compression, $\Delta S_4 = 0$, $T_c \rightarrow T_h$

(no heat transfer for an adiabatic process)

$$\int dS = (q_h/T_h) + (q_c/T_c) = 0 \quad \text{and} \quad q_h/q_c = -T_h/T_c$$

The efficiency of a heat engine is given as:

$$\begin{aligned}\eta &= \frac{w}{q_h}\\ &= \frac{q_h - q_c}{q_h}\\ &= 1 - \frac{q_c}{q_h}\\ \eta &= 1 - \frac{T_c}{T_h}\end{aligned}$$

Third Law

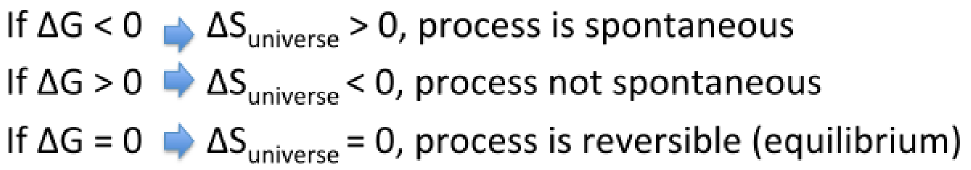
The entropy of all perfect crystalline substances at zero Kelvin is zero.

Free Energy

The Gibbs free energy (SI units J/mol) is the maximum amount of non-expansion work that can be extracted from a closed system; this maximum can be attained only in a completely reversible process.

The Gibb's Free Energy is given as:

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



If $\Delta G < 0$ ➡ $\Delta S_{universe} > 0$, process is spontaneous

If $\Delta G > 0$ ➡ $\Delta S_{universe} < 0$, process not spontaneous

If $\Delta G = 0$ ➡ $\Delta S_{universe} = 0$, process is reversible (equilibrium)

Inorganic Thermodynamics

Pyrometallurgy

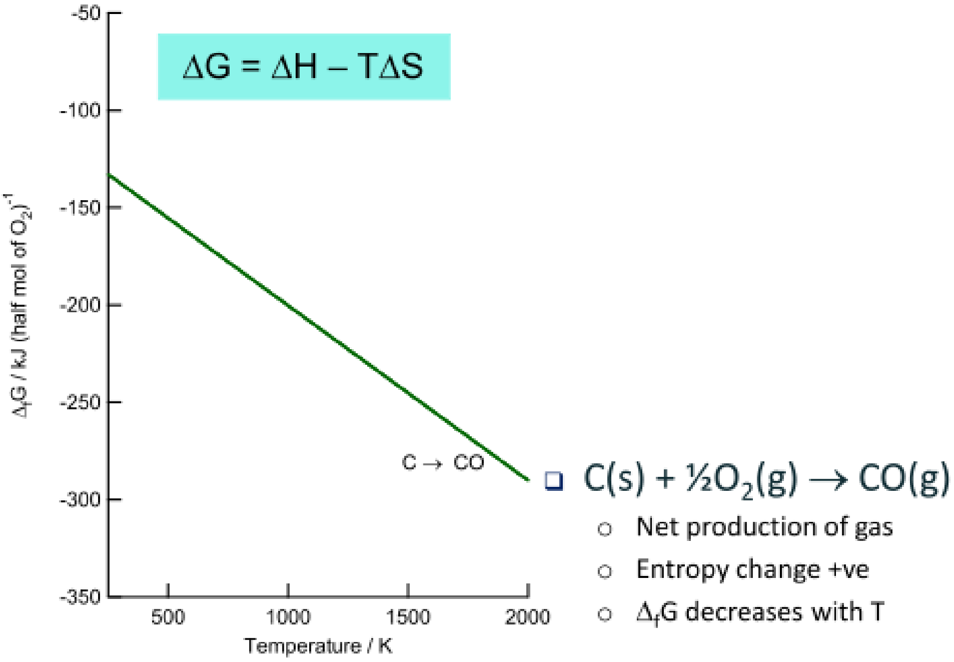
This process refers to the treatment of metal-ores by heating them with carbon to yield oxidised forms of carbon, and the refined metal. General equation given by:

$$MO + C \rightarrow M + CO$$

Such reactions are energetically favourable because of the increase in the number of moles of gas:

$$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$$

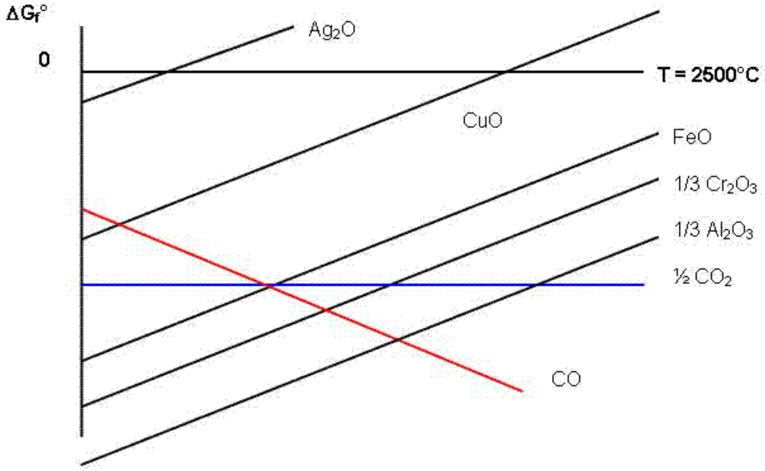
This reaction also becomes more favourable at higher temperatures:

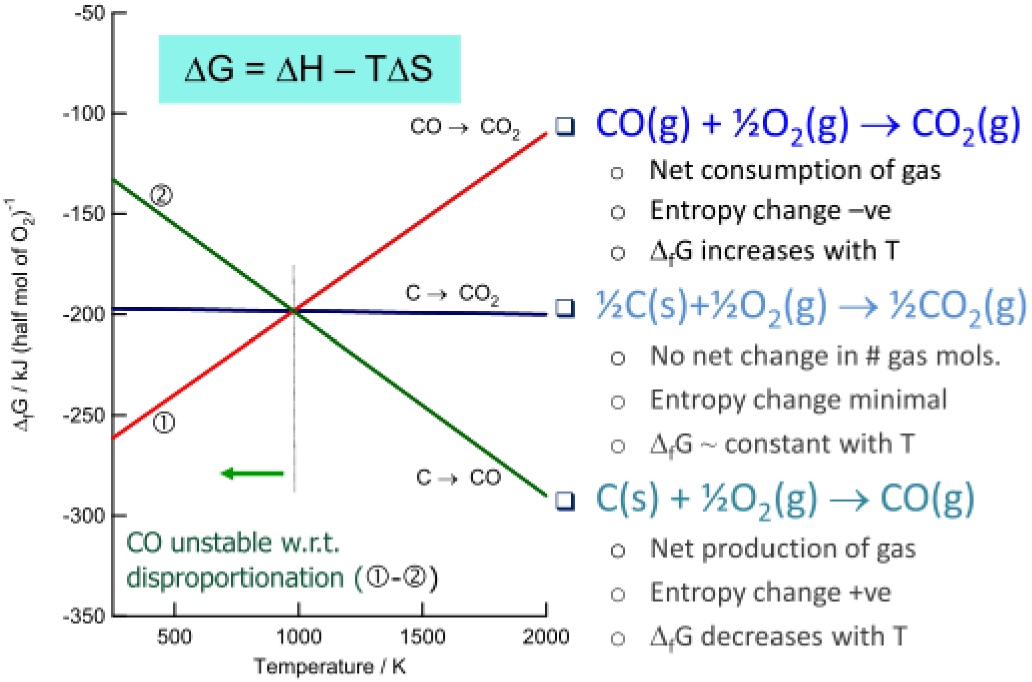


- ☐ $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$
  - ○ Net production of gas
  - ○ Entropy change +ve
  - ○ $\Delta_f G$ decreases with T

Ellingham Diagrams

An Ellingham diagram is a graph showing the temperature dependence of the stability for compounds. This analysis is usually used to evaluate the ease of reduction of metal oxides. The analysis is thermodynamic in nature, and ignores reaction kinetics. Thus, processes that are predicted to be favourable by the Ellingham diagram can still be slow. Note that reactions are always given in terms of 1/2 moles of O_2.

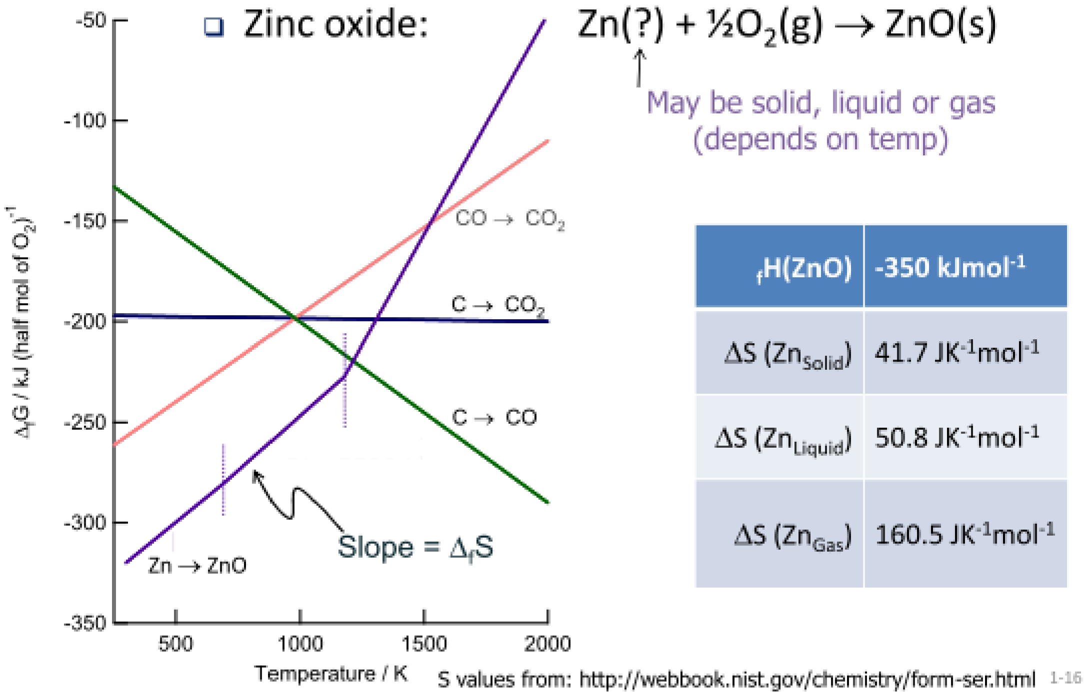




CO unstable w.r.t. disproportionation (①-②)

- ☐ $CO(g) + ½O_2(g) \rightarrow CO_2(g)$
  - ○ Net consumption of gas
  - ○ Entropy change –ve
  - ○ $\Delta_f G$ increases with T
- ☐ $½C(s)+½O_2(g) \rightarrow ½CO_2(g)$
  - ○ No net change in # gas mols.
  - ○ Entropy change minimal
  - ○ $\Delta_f G$ ~ constant with T
- ☐ $C(s) + ½O_2(g) \rightarrow CO(g)$
  - ○ Net production of gas
  - ○ Entropy change +ve
  - ○ $\Delta_f G$ decreases with T

Changes in the slope indicate changes in the entropy of a substance as it changes state



☐ Zinc oxide: $Zn(?) + ½O_2(g) \rightarrow ZnO(s)$

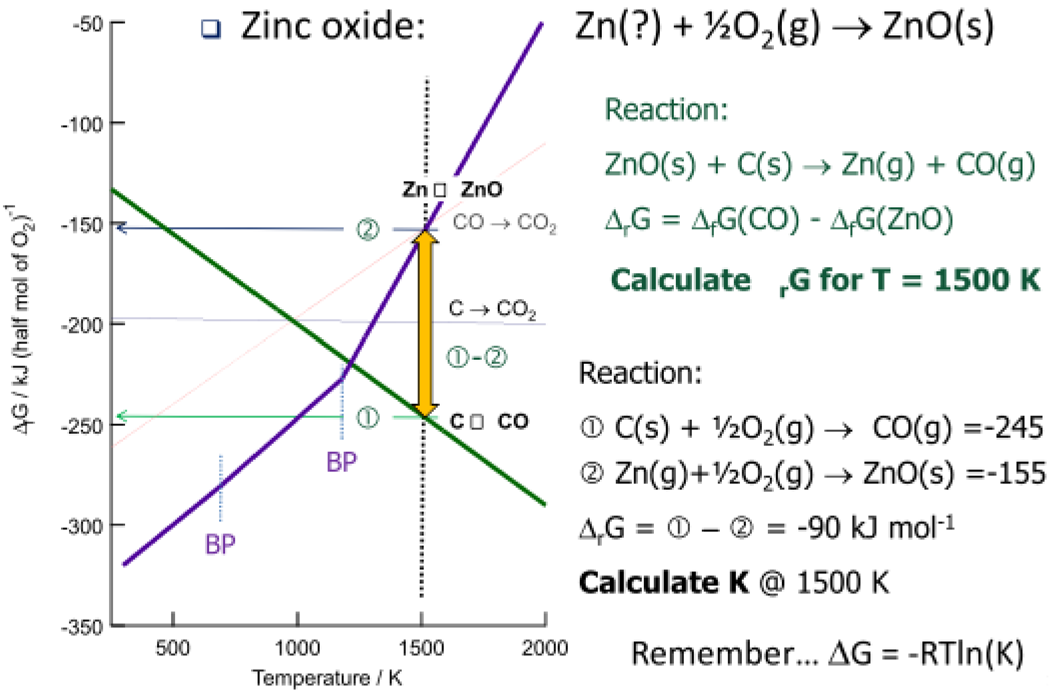
May be solid, liquid or gas (depends on temp)

$_f$H(ZnO)	-350 $kJmol^{-1}$
ΔS (Zn_{Solid})	41.7 $JK^{-1}mol^{-1}$
ΔS (Zn_{Liquid})	50.8 $JK^{-1}mol^{-1}$
ΔS (Zn_{Gas})	160.5 $JK^{-1}mol^{-1}$

S values from: http://webbook.nist.gov/chemistry/form-ser.html 1-16

The slope on an Ellingham diagram is calculated using rise over run, working from left to right.

If an oxide curve is above any of the carbon curves at a particular temperature, that means that said oxide is unstable at that temperature, and will tend to be reduced into a pure metal. This means that the uppermost reaction will always run in reverse.



❑ Zinc oxide: $Zn(?) + \frac{1}{2}O_2(g) \rightarrow ZnO(s)$

Reaction:

$ZnO(s) + C(s) \rightarrow Zn(g) + CO(g)$

$\Delta_r G = \Delta_f G(CO) - \Delta_f G(ZnO)$

Calculate $_r$G for T = 1500 K

Reaction:

① $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$ =-245

② $Zn(g) + \frac{1}{2}O_2(g) \rightarrow ZnO(s)$ =-155

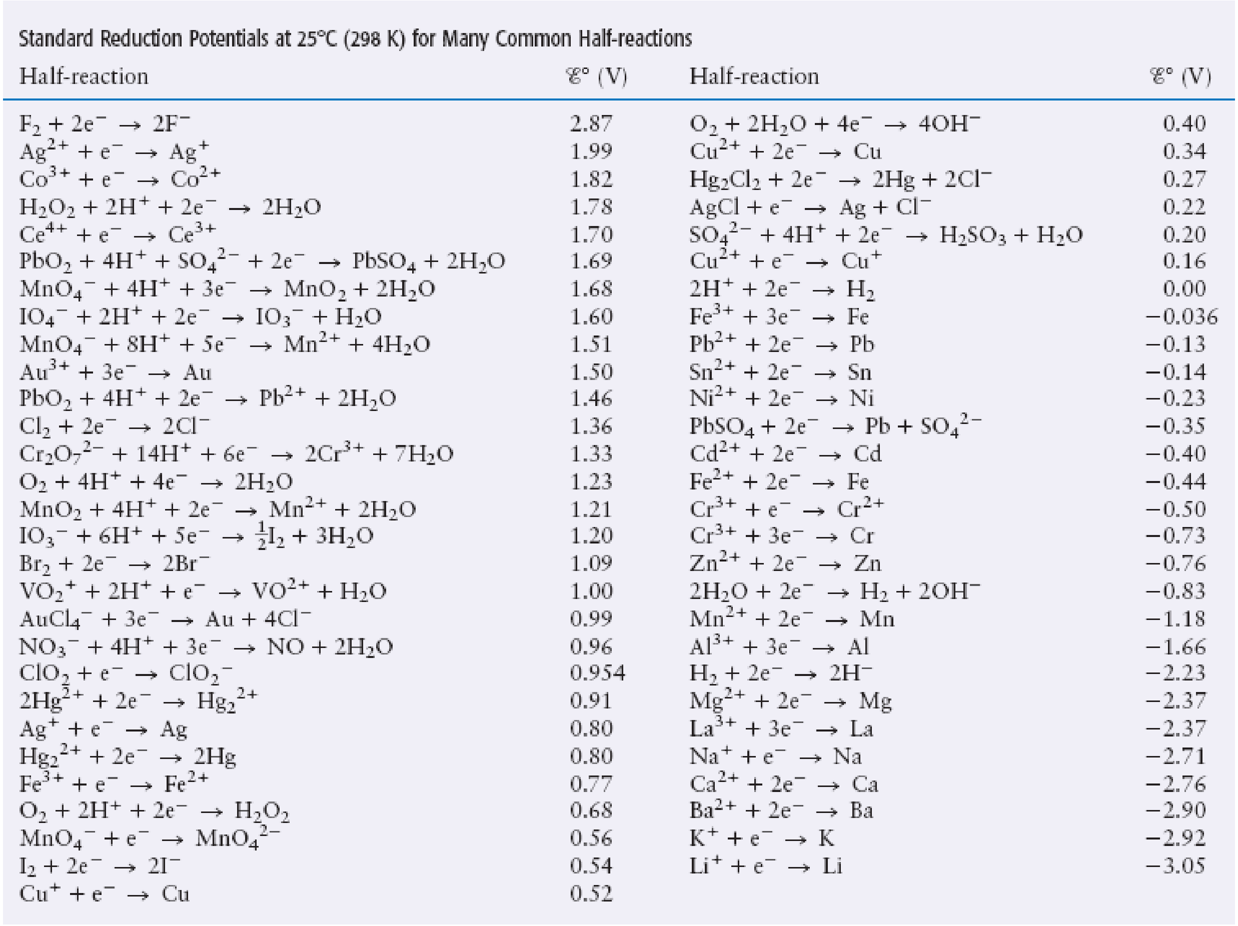
$\Delta_r G$ = ① – ② = -90 kJ mol^{-1}

Calculate K @ 1500 K

Remember... $\Delta G = -RT\ln(K)$

The top-most equation is always run in reverse, and represents the species that is reduced. The lower equation represents the species that is oxidised. One species may reduce another if its line is below the other species.

Standard Reduction Potentials

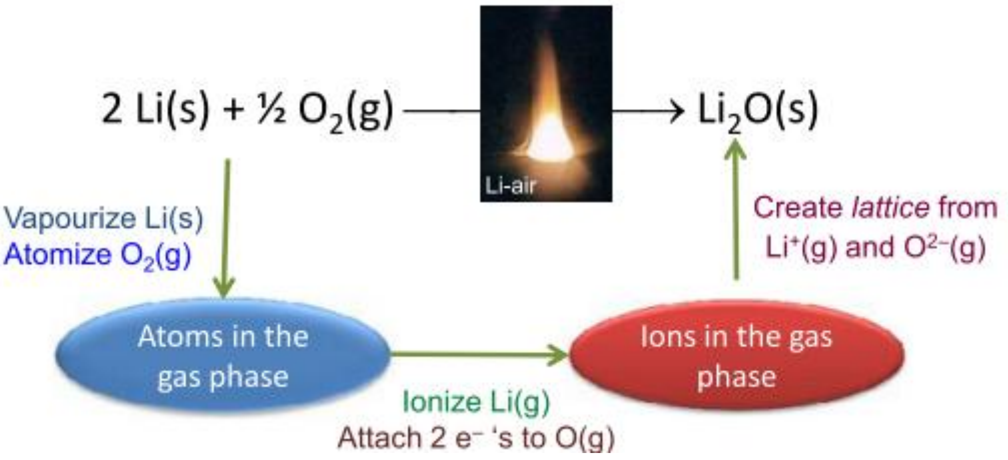


Standard Reduction Potentials at 25°C (298 K) for Many Common Half-reactions

Half-reaction	$\mathcal{E}^\circ$ (V)	Half-reaction	$\mathcal{E}^\circ$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$IO_4^- + 2H^+ + 2e^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	−0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	−0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	−2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	−2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	−2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	−2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	−2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	−2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	−3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		

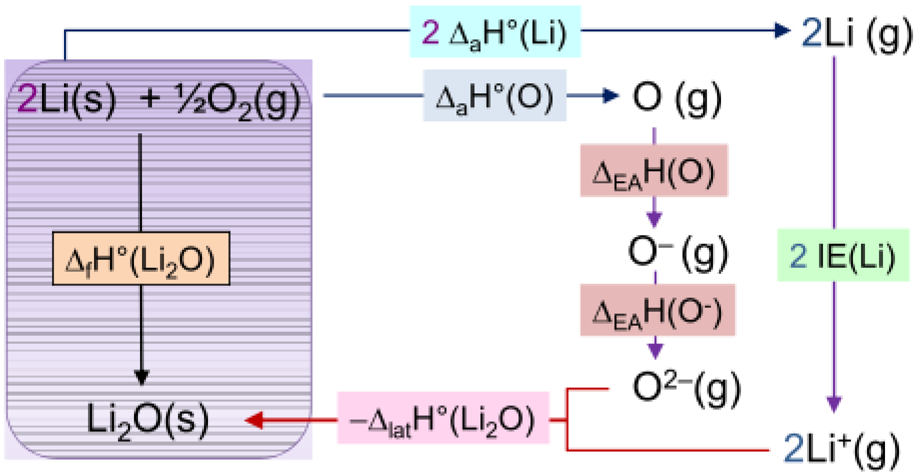
Born-Haber Cycle

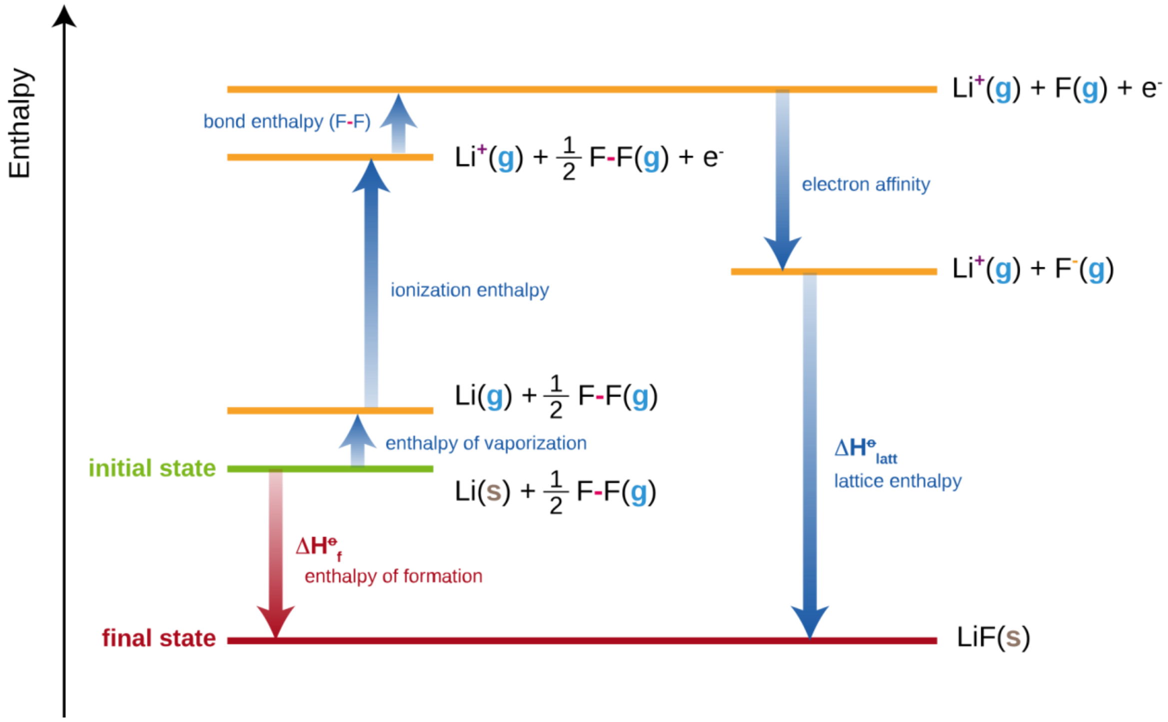
The Born–Haber cycle is an approach to analyze reaction energies. The cycle is concerned with the formation of an ionic compound from the reaction of a metal (often a Group I or Group II element) with a halogen.



The steps for constructing a Born-Haber cycle are as follows:

1. Begin with elements in their standard phases and states, or as stated in reactants
2. Vapourize any solids into the gas phase: $(\Delta_a H^\circ)$
3. Break up any solid lattices that need to be broken up $(\Delta_{\text{lat}} H^\circ)$
4. Atomise any diatomic gas molecules into individual atoms: enthalpy of atomization $(\Delta_a H^\circ)$
5. Ionise the cation (possibly more than once) -> the maximum enthalpy condition: $(\Delta_{IE} H^\circ)$
6. React the electron with the anion: electron affinity $(\Delta_{EA} H^\circ)$
7. Bring the cation and anion together to form the crystal lattice: lattice enthalpy $(\Delta_{\text{lat}} H^\circ)$. Usually we make the simplification that $\Delta_{\text{lat}} H^\circ = \Delta_{\text{lat}} U^\circ$



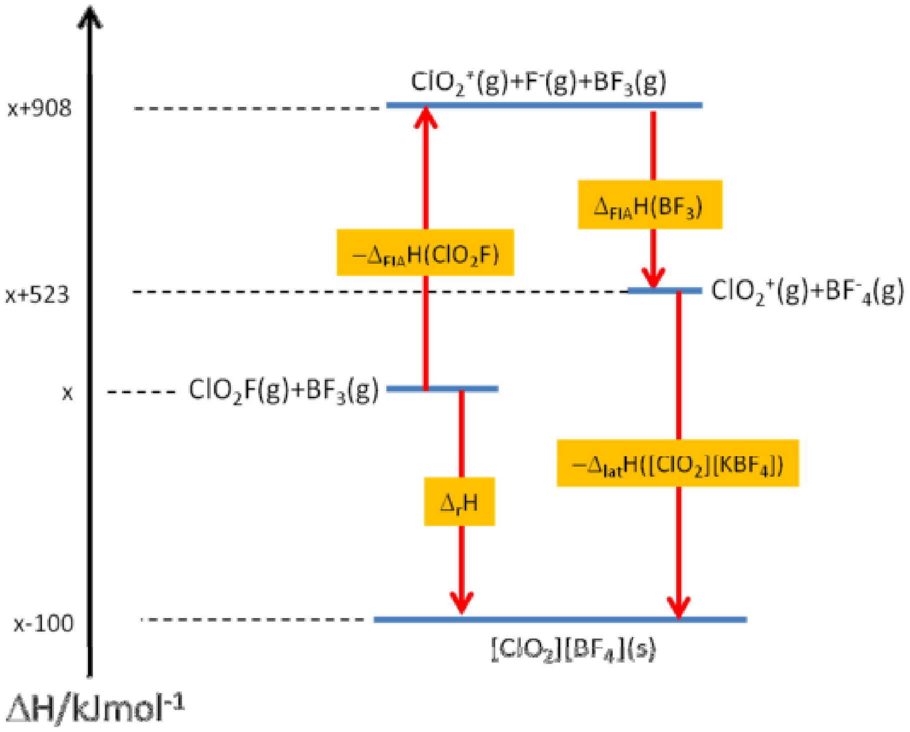


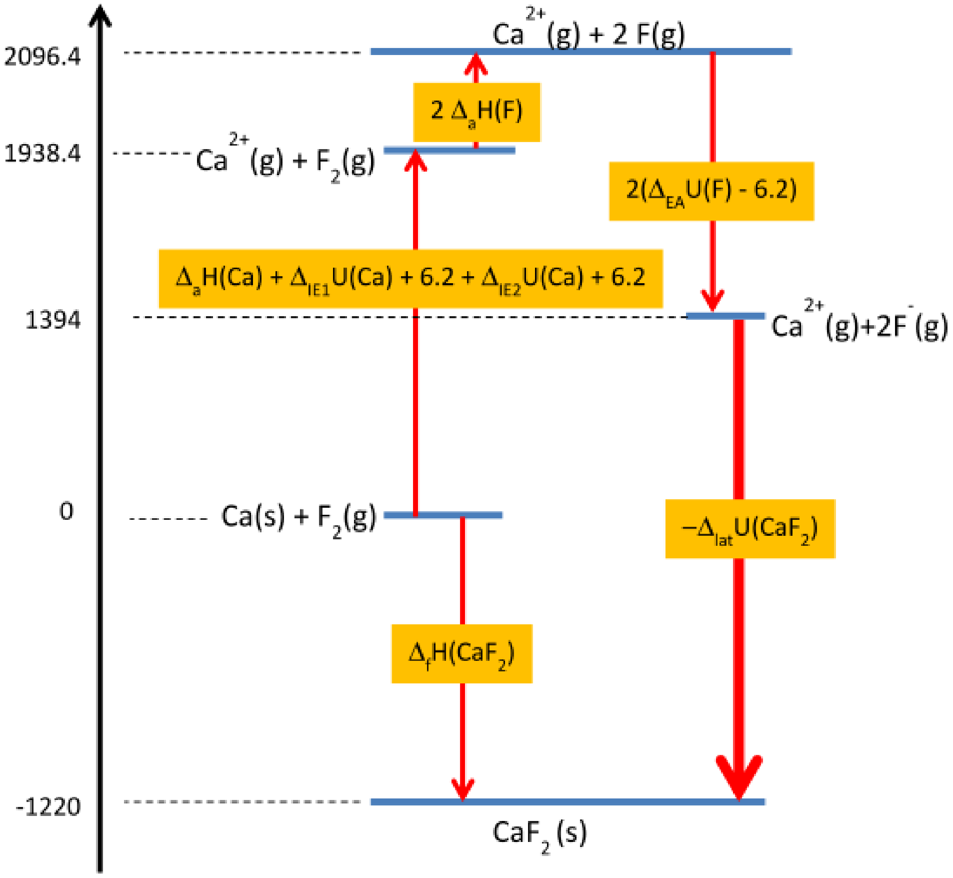
Note that for ionization energy (loss of electrons):

$$\Delta H = \Delta U + \frac{5}{2}nRT$$
$$\Delta H = \Delta U + 6.2n$$

Note that for electron affinity (gain of electrons):

$$\Delta H = \Delta U - \frac{5}{2}nRT$$
$$\Delta H = \Delta U - 6.2n$$





Lattice Enthalpy

The lattice energy of a crystalline solid is usually defined as the energy of formation of the crystal from infinitely-separated ions, molecules, or atoms. Since lattices are energetically favourable, when a lattice is being formed the enthalpy change will be negative.

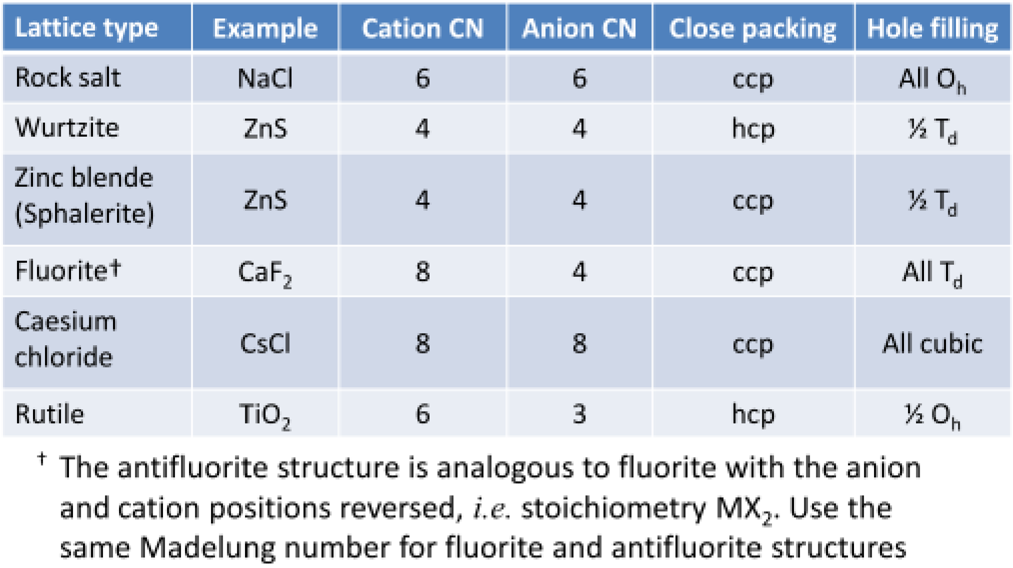
The energy between two ions is simply given by Coulomb's Law:

$$\Delta U_C = \frac{|z_+ z_-|\, e^2}{4\pi\varepsilon_0 d_\pm}$$

For an infinite lattice, however, this becomes an infinite sum:

$$\Delta U_C = \frac{|z_+ z_-|\, e^2}{4\pi\varepsilon_0 d_\pm} \boxed{\left[6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} \ldots \right]}$$

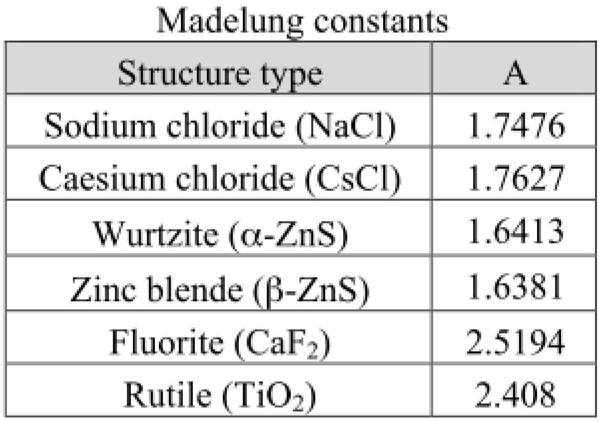
The constant in the box is called the Madelung constant, and varies depending upon the type of crystal structure. The larger this value is, the more stable will be the resulting crystal compound.



Lattice type	Example	Cation CN	Anion CN	Close packing	Hole filling
Rock salt	NaCl	6	6	ccp	All O_h
Wurtzite	ZnS	4	4	hcp	½ T_d
Zinc blende (Sphalerite)	ZnS	4	4	ccp	½ T_d
Fluorite†	CaF_2	8	4	ccp	All T_d
Caesium chloride	CsCl	8	8	ccp	All cubic
Rutile	TiO_2	6	3	hcp	½ O_h

† The antifluorite structure is analogous to fluorite with the anion and cation positions reversed, *i.e.* stoichiometry MX_2. Use the same Madelung number for fluorite and antifluorite structures

To remember these, use the mnemonic of the cation number: "684486"



Madelung constants

Structure type	A
Sodium chloride (NaCl)	1.7476
Caesium chloride (CsCl)	1.7627
Wurtzite (α-ZnS)	1.6413
Zinc blende (β-ZnS)	1.6381
Fluorite (CaF_2)	2.5194
Rutile (TiO_2)	2.408

Combining this analysis of the attractive forces within the lattice with some additional terms for the repulsive interactions (not discussed here), we arrive at the Born-Mayer equation:

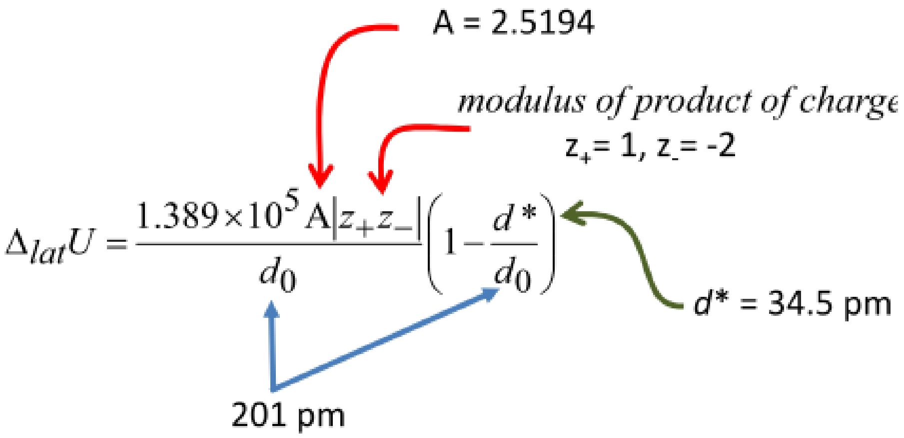
$$\Delta_{lat}U = \frac{N_A A|z_+z_-|e^2}{4\pi\varepsilon_0 d_0}\left(1-\frac{d^*}{d_0}\right)$$

d_0= equilibrium inter-ion separation
d^*= empirical factor = 34.5 pm

Applying the known constants:

$$\Delta_{lat}U = \frac{1.389\times10^5 A|z_+z_-|}{d_0}\left(1-\frac{d^*}{d_0}\right)$$

Note that to use this equation we need to know d_0, the inter-ion distance, and also A, the Madelung constant (which means we need to know the type of crystal structure.



An alternative method for calculating lattice enthalpies which does not require knowledge of the lattice structure (and hence is particularly useful for new substances), is called the Kapustinskii equation:

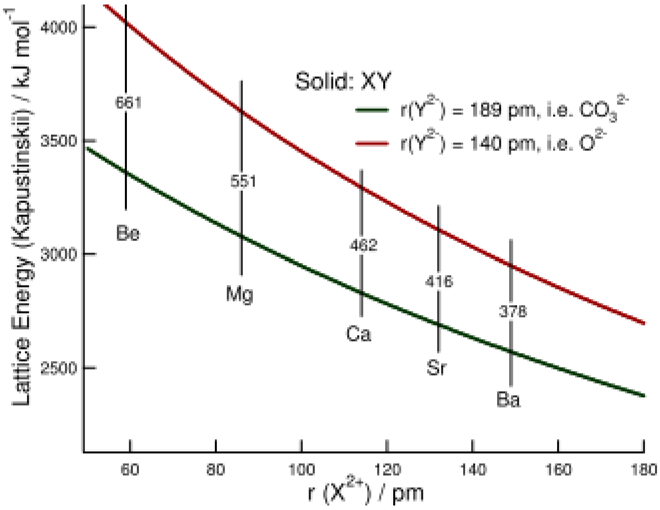
$$\Delta_{lat}U = \frac{1.21\times10^5 n|z_+z_-|}{r_+ + r_-}\left(1-\frac{d^*}{r_+ + r_-}\right)$$

Note that d_0 has been replaced by the sum of 6-coordinate ionic radii, and $\frac{A}{n}$ is constant for a fairly wide range of solids, so A has been substituted out for the ionic salt value. The only other value we need to know is n, which is equal to the total number of ions in a single bond (e.g. two for NaCl).

Thermal Decomposition of Carbonates

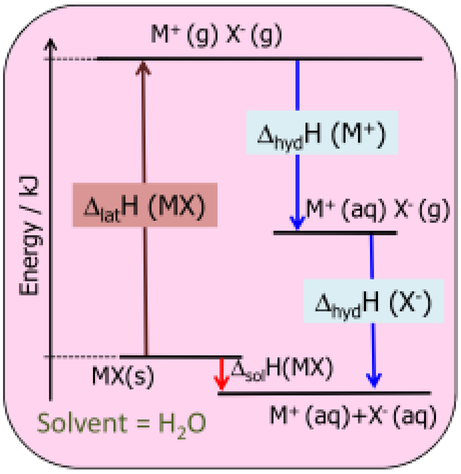
Thermal decomposition of compounds occurs at different temperatures depending upon the lattice energy. The higher the lattice energy, the more stable is the crystal structure, and hence the higher is the thermal decomposition temperature. Thus, the bigger the difference in the lattice energies between the two different lattices, the more favourable will be the decomposition.

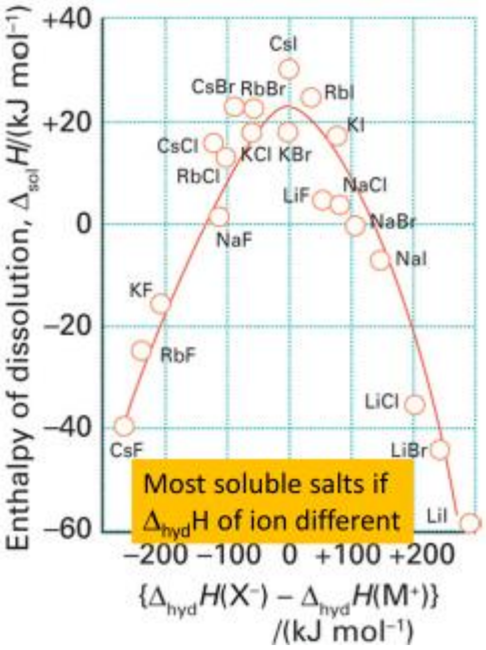
	$MgCO_3$	$CaCO_3$	$SrCO_3$	$BaCO_3$
ΔG°	+48	+130	+184	+218 $kJmol^{-1}$
ΔH°	+101	+178	+235	+269 $kJmol^{-1}$
ΔS°	+175	+161	+171	+172 $Jmol^{-1}K^{-1}$
T_{dec}	300	840	1100	1300 °C



Solubility

The solubility of a particular compound will depend upon the relative sizes of the solvent energy versus the hydration energies, which of course depend on the solvent.





Generally speaking, soluble salts have anion and cations different in size, whereas insoluble salts have similarly sized anions and cations.

Electrochemistry and Energetics

The Nernst Equation

Nernst Equation is given by:

$$E = E° - \frac{RT}{nF}\ \ln Q = E° - \frac{2.303RT}{nF}\ \log_{10} Q$$

Where:
R = gas constant = 8.3145 $J(K.mol)^{-1}$
T = absolute temperature (25°C = 298.13 K)
F = Faraday constant = 96,485 $C.mol^{-1}$
n = # electrons transferred for given reaction (note use of ν in IC)

$RT/F = 0.02569$ V and $\boxed{2.303RT/F = 0.0592\text{ V}}$

For a general redox reaction:

$$\overbrace{\text{a Red}_1 + \text{b Ox}_2 \rightarrow \text{c Ox}_1}\ \ \text{+ d Red}_2$$

$$\text{a Red}_1 + \underbrace{\text{b Ox}_2 \rightarrow \text{c Ox}_1 + \text{d Red}_2}$$

Reaction quotient, Q : $\dfrac{[Ox_1]^c[Red_2]^d}{[Red_1]^a[Ox_2]^b}$ ← **Do not include solids or solvents**

$\Delta G = \Delta H - T\Delta S$ (for constant temperature)

$\Delta_r G^\circ = -RT \ln K$

$\Delta_r G = \Delta_r G^\circ + RT \ln Q_r$ (see Chemical equilibrium)

$\Delta G = -nFE$

$\Delta G^\circ = -nFE^\circ$

and rearranging gives

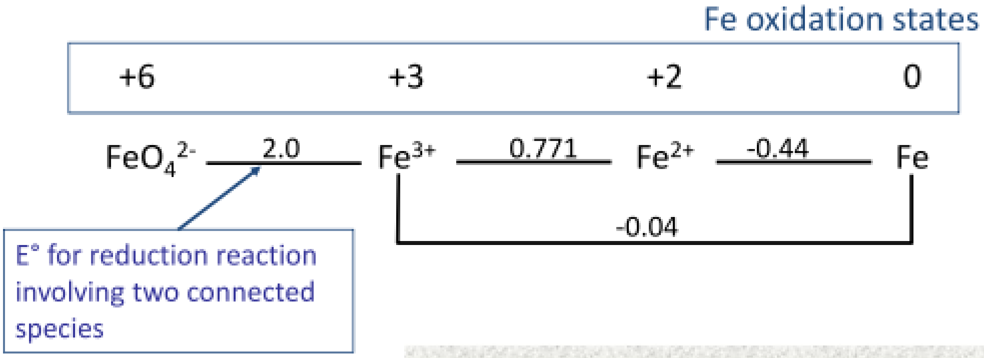
$$nFE^\circ = RT \ln K$$

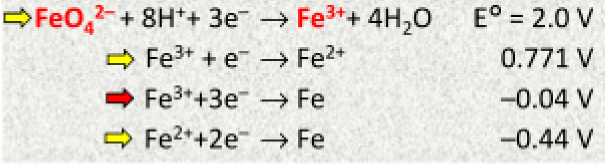
$$nFE = nFE^\circ - RT \ln Q_r$$

$$E = E^\circ - \frac{RT}{nF} \ln Q_r$$

Latimer Diagrams

Latimer diagrams are convenient ways of representing the different oxidation states of a metal in a concise manner. The most highly oxidized form of the element is on the left, with successively lower oxidation states to the right. The species are connected by an arrow, and the numerical value of the standard potential (in volts) for the reduction is written over the arrow.



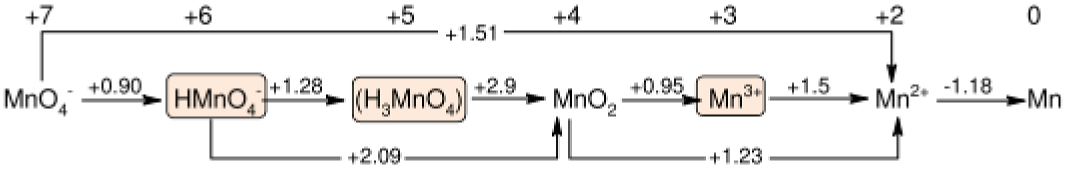


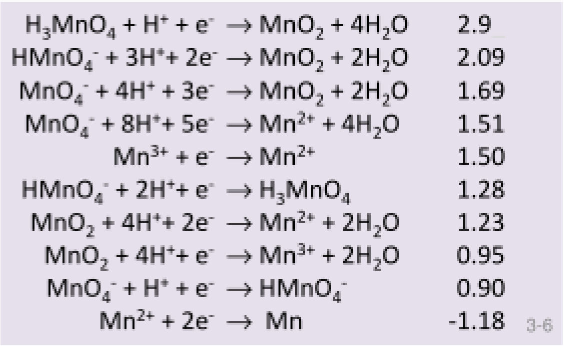
⇨ $FeO_4^{2-} + 8H^+ + 3e^- \rightarrow Fe^{3+} + 4H_2O$	E° = 2.0 V
⇨ $Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.771 V
➡ $Fe^{3+} + 3e^- \rightarrow Fe$	−0.04 V
⇨ $Fe^{2+} + 2e^- \rightarrow Fe$	−0.44 V

To calculate the potential between non-adjacent species, the following equation is used:

$$\Delta G_{a+b} = \Delta G_a + \Delta G_b$$
$$-(n_a + n_b)FE_{a+b} = -n_aFE_a - n_bFE_b$$
$$E_{a+b} = \frac{n_aE_a + n_bE_b}{n_a + n_b}$$

Where n_i is the number of electrons transferred in reaction i



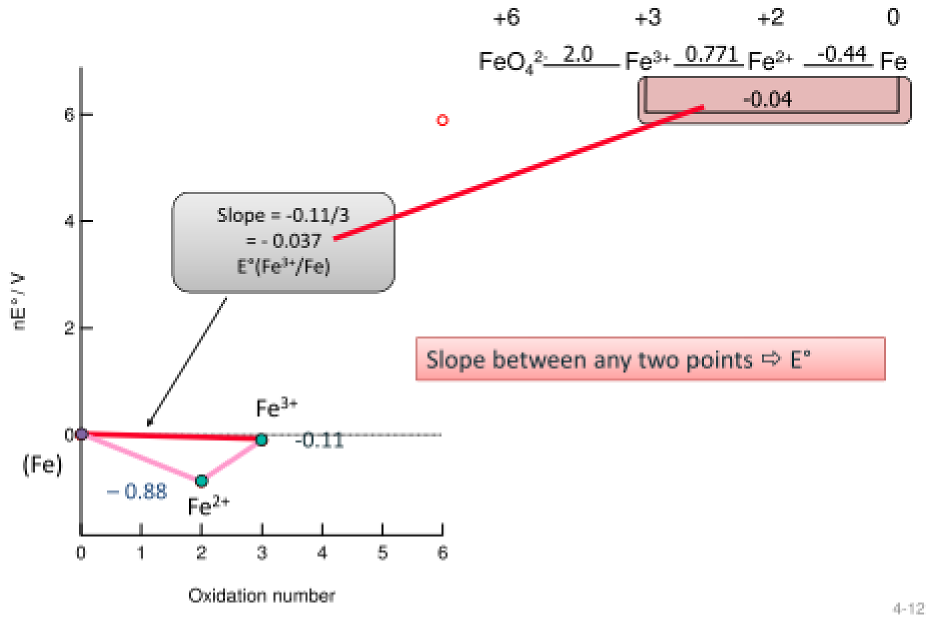


$H_3MnO_4 + H^+ + e^- \rightarrow MnO_2 + 4H_2O$	2.9
$HMnO_4^- + 3H^+ + 2e^- \rightarrow MnO_2 + 2H_2O$	2.09
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.69
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51
$Mn^{3+} + e^- \rightarrow Mn^{2+}$	1.50
$HMnO_4^- + 2H^+ + e^- \rightarrow H_3MnO_4$	1.28
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.23
$MnO_2 + 4H^+ + e^- \rightarrow Mn^{3+} + 2H_2O$	0.95
$MnO_4^- + H^+ + e^- \rightarrow HMnO_4^-$	0.90
$Mn^{2+} + 2e^- \rightarrow Mn$	-1.18

3-6

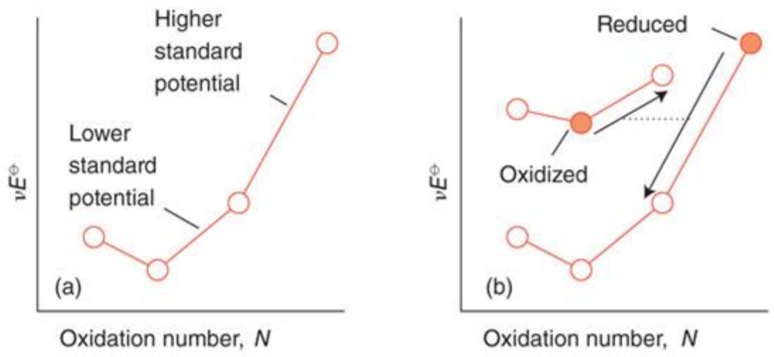
Frost Diagrams

A Frost diagram is a type of graph used to illustrate the relative stability of a number of different oxidation states of a particular substance by plotting free energy against oxidation number. Frost diagrams will be different at different pHs, so the pH must be specified. The slope between any two points in a Frost diagrams is equal to the cell potential between those two substances.



The relative position in diagram represents relative stability of species, however this is not necessarily the most stable species in the presence of other oxidising or reducing agents. The most powerful oxidising agent is the most oxidised member (rightmost) of the pair connected by the line of steepest slope, and the most powerful reducing agent is the most reduced member of the pair.

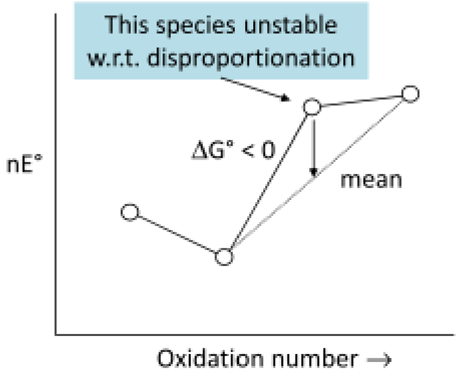
When consideration a reaction between two couples, the rightmost species in the couple with the most positive slope is liable to undergo reduction, while leftmost species of the couple with the least positive (most negative) slope is liable to undergo oxidation.



An oxidising agent is reduced, so if you want to see how good an oxidising agent is, check the slope of the line going to the left (i.e. being reduced). The more positive is that slope, the better an oxidising agent it is. To see how good a reducing agent a species is, look to the line on its right. The more negative is that slope, the better a reducing agent it is.

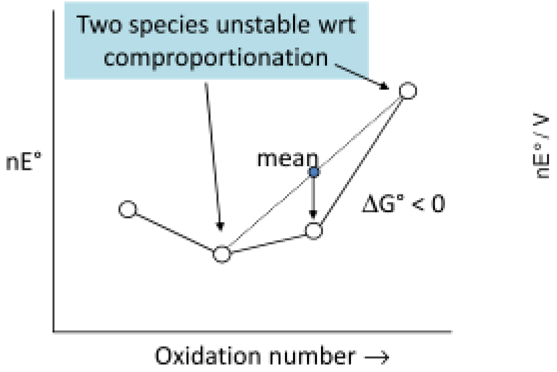
A single species disproportionates if it can form two products of lower mean free energy:

$$e.g.\ \mathrm{Cu^{I}} \rightarrow \tfrac{1}{2}\,\mathrm{Cu^{0}} + \tfrac{1}{2}\,\mathrm{Cu^{II}}$$



Comproportionation will occur if free energy of product is lower than the mean free energy of the two reactants:

$$e.g.\ {}^{1}/_{3}\,\mathrm{Mn^{0}} + {}^{2}/_{3}\,\mathrm{Mn^{III}} \rightarrow \mathrm{Mn^{II}}$$

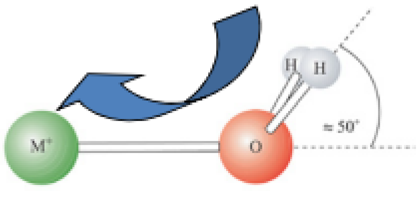


Hydrolysis reactions (oxidising the metals) will occur if the slope of the line joining metal species to higher oxidation number is less positive than that of O_2/H_2O (1.23 V).

Metal Oxide Species

An oxoacid is an acid that contains oxygen. Because they possess both protons and oxygen atoms, they can interact via both electrochemical and acid-base reactions, making their chemistry more complicated.

$$K_a = \frac{[\mathrm{M(OH)}][\mathrm{H^+}]}{[\mathrm{M(OH_2)}]}$$



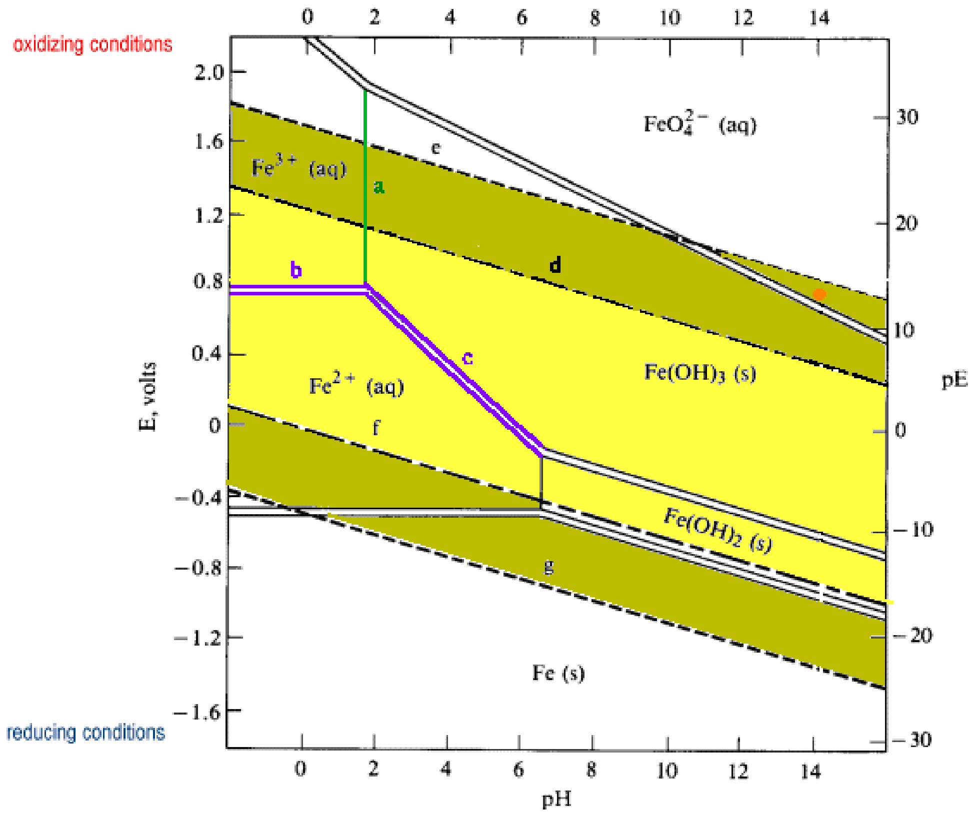
Metals with high charge/size ratios draw electron density away from the water oxygen, making it a weaker base, and the aqua ligand a stronger acid 5-5

$z = 1+$, $pK_{a1} > 13$
$z = 2+$, $pK_{a1} \sim 7\text{-}13$
$z = 3+$, $pK_{a1} \sim 2\text{-}6$

Pourbaix Diagrams

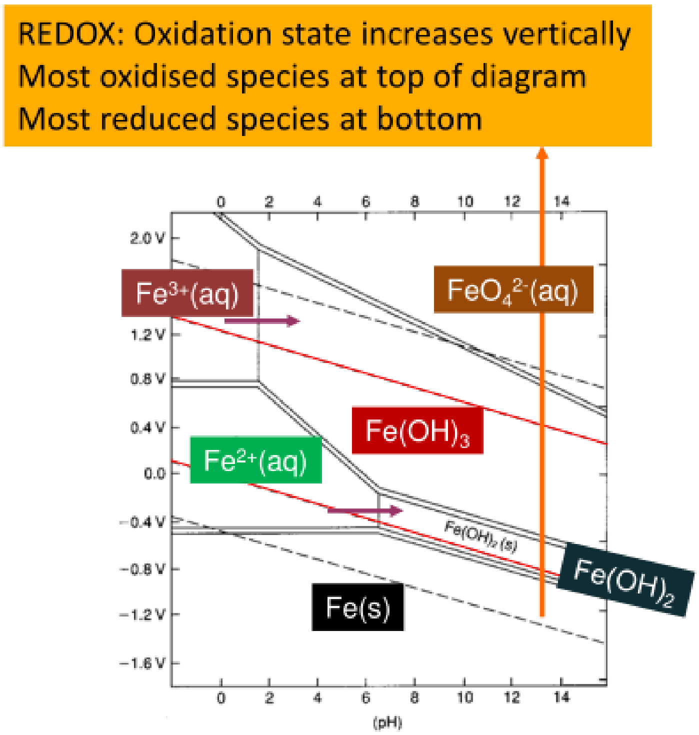
A Pourbaix diagram, also known as a potential/pH diagram, maps out possible stable (equilibrium) phases of an aqueous electrochemical system. Predominant ion boundaries are represented by lines. The regions indicate conditions in which a species is thermodynamically stable, and are labelled as per the predominate species found in those conditions.

The vertical axis is labeled EH for the voltage potential with respect to the standard hydrogen electrode (SHE) as calculated by the Nernst equation. On the horizontal axis, low E (or pE) values represent a reducing environment. High E values represent an oxidizing environment.



Interpreting the diagram

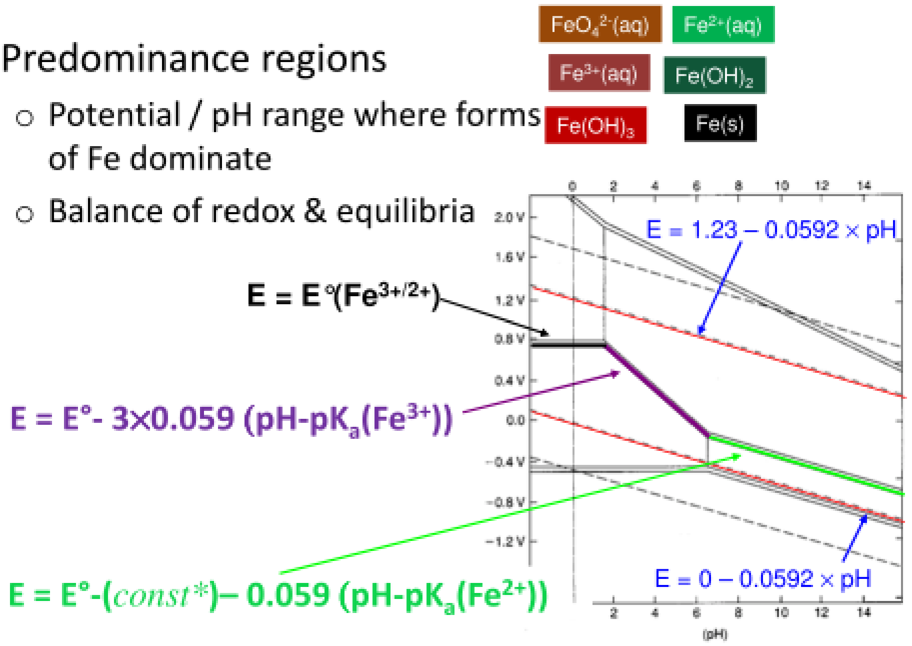
- Solid lines separate species related by acid-base equilibria. For example, line a shows the pH at which half of the 1 M iron is Fe^{3+} and half is precipitated as $Fe(OH)_2$
- Solid double lines separate species related by redox equilibria
- Redox equilibria of species not involving hydrogen or hydroxide ions appear as horizontal boundaries (line b)
- Redox species of species involving hydrogen or hydroxide appear as diagonal boundaries becuase they are in part acid-base equilibria (line c)
- Diagonal boundaries slope from upper left to lower right because basic solutions tend to favor the more oxidized species
- As with Ellingham diagrams, one species may reduce another (including water) if it is below that species on the diagram. The further below, the more vigorous the reaction will be



REDOX: Oxidation state increases vertically
Most oxidised species at top of diagram
Most reduced species at bottom

Constructing a Pourbaix diagram

- Any reactions between species that do not involve H^+ ions will not vary with pH, and hence appear as horizontal lines on the diagram
- Any reactions which are not redox reactions will not vary with potential, and hence will appear as vertical lines on the diagram
- For reactions which involve both redox and acid/base chemistry, the slope of the line separating the two relevant species will be equal to the 0.0592 times the H^+/e ratio
- The intercept of the line is simply the standard potential for that reduction reaction (that is, it is the potential when pH equals zero)



Predominance regions

- ○ Potential / pH range where forms of Fe dominate
- ○ Balance of redox & equilibria

$E = E°(Fe^{3+/2+})$

$E = E° - 3\times0.059\ (pH - pK_a(Fe^{3+}))$

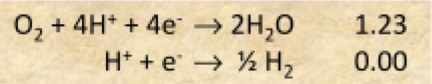
$E = E° - (const^*) - 0.059\ (pH - pK_a(Fe^{2+}))$

$E = 1.23 - 0.0592 \times pH$

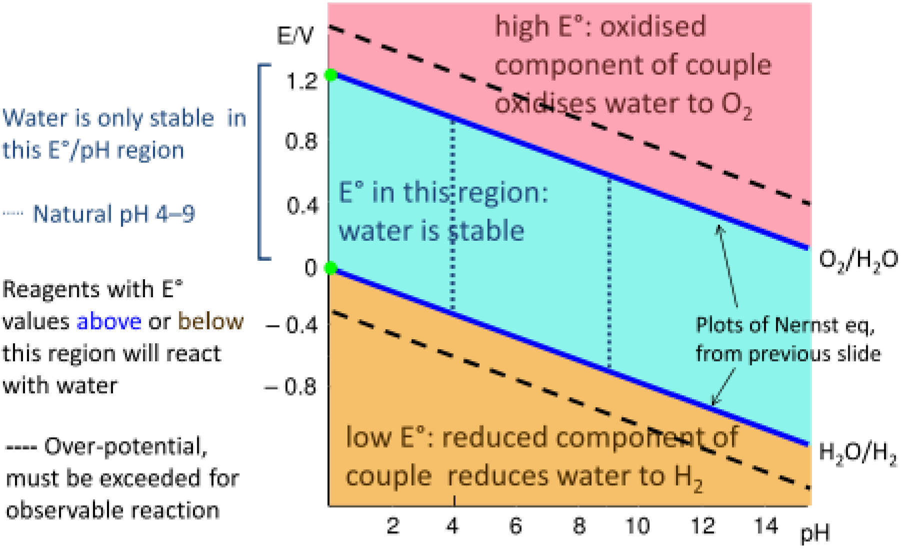
$E = 0 - 0.0592 \times pH$

Natural Waters

Water can act both as an oxidising or a reducing agent, depending upon the prevailing electrochemical and pH conditions.



$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23
$H^+ + e^- \rightarrow \tfrac{1}{2} H_2$	0.00



Theory of Materials

Polymers

Brownian Motion

Theoretical mean-squared displacement for Brownian motion, where a is step length:

$$\langle r^2 \rangle = Na^2 = 3\sigma^2$$

Empirical mean-squared displacement for particles in solution, where D is the diffusion coefficient:

$$\langle r^2 \rangle = 6Dt$$

Hence we have:

$$6Dt = Na^2$$

Mean-squared velocity:

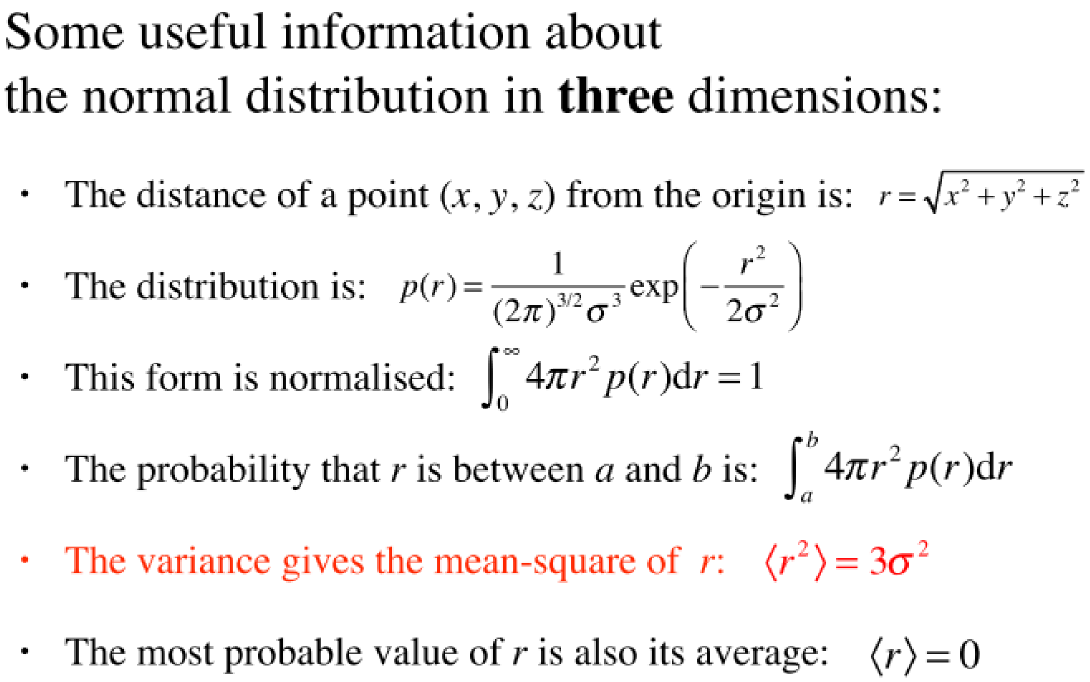
$$\langle v^2 \rangle = \frac{3kT}{m}$$

Diffusion constant is given by:

$$D = \frac{kT}{6\pi\eta R_B}$$

Where η is the viscosity of the solvent and R_B is the particle radius

The Normal Distribution



Some useful information about
the normal distribution in **three** dimensions:

- The distance of a point (x, y, z) from the origin is: $r = \sqrt{x^2 + y^2 + z^2}$
- The distribution is: $p(r) = \dfrac{1}{(2\pi)^{3/2}\sigma^3}\exp\left(-\dfrac{r^2}{2\sigma^2}\right)$
- This form is normalised: $\int_0^\infty 4\pi r^2 p(r)\mathrm{d}r = 1$
- The probability that r is between a and b is: $\int_a^b 4\pi r^2 p(r)\mathrm{d}r$
- The variance gives the mean-square of r: $\langle r^2 \rangle = 3\sigma^2$
- The most probable value of r is also its average: $\langle r \rangle = 0$

Polymer Entropy

The probability that a polymer with N monomers and monomer separation a has ends separated by a vector $\tilde{r}$ is given by:

$$P(\tilde{r}) = \left(\frac{3}{2\pi N a^2}\right)^{\frac{3}{2}} e^{-\left(\frac{3r^2}{2Na^2}\right)}$$

The exponential term is directly proportional to the entropy of the polymer (since probability is related to the number of microstates):

$$\begin{aligned} S &= k \log W \\ &= k \log e^{-\left(\frac{3r^2}{2Na^2}\right)} \\ S &= -k\frac{3r^2}{2Na^2} \end{aligned}$$

Monomer Repulsion

Repulsion between monomers becomes important when monomers are packed closely together. The total number of pairs in contact will depend upon the concentration per unit volume (number of monomers in contact), and also the volume of the polymer:

$$\begin{aligned} E_r &\propto E_{pair} \times V \times N_{in-contact} \\ E_r &\propto E_{pair} \times r^3 c^2 \end{aligned}$$

If the repulsion energy per pair E_{pair} is given by $\frac{A}{2}$, we have:

$$\begin{aligned} E_r &= \frac{A}{2} r^3 c^2 \\ &= \frac{A}{2} r^3 \left(\frac{N}{r^3}\right)^2 \end{aligned}$$

$$E_r = \frac{A}{2}\frac{N^2}{r^3}$$

Free Energy of a Polymer

Given both the energy and the entropy, we can find the free energy of the polymer:

$$\begin{aligned} F &= E - TS \\ &= \frac{A}{2}\frac{N^2}{r^3} - T\left(-k\frac{3r^2}{2Na^2}\right) \\ F &= \frac{A}{2}\frac{N^2}{r^3} + kT\frac{3r^2}{2Na^2} \end{aligned}$$

At equilibrium the free energy does not change with the polymer length (otherwise it wouldn't be equilibrium and the polymer would change size):

$$\begin{aligned} \frac{dF}{dr} &= -3\frac{A}{2}\frac{N^2}{r^4} + kT\frac{3r}{Na^2} \\ 3\frac{A}{2}\frac{N^2}{r^4} &= kT\frac{3r}{Na^2} \\ \frac{Aa^2}{2kT}N^3 &= r^5 \\ r &\propto N^{3/5} \end{aligned}$$

Comparing this to the pure random walk case where $r \propto N^{1/2}$, we find that incorporating repulsions causes the polymer chain length to increase more rapidly with N.

Stretch a Polymer

Suppose we have a polymer of length $r_i = \sqrt{Na^2}$. Its entropy is given by:

$$\begin{aligned} S_i &= -k\frac{3r_i^2}{2Na^2} \\ &= -k\frac{3\left(\sqrt{Na^2}\right)^2}{2Na^2} \\ S_i &= -\frac{3}{2}k \end{aligned}$$

Now double the length and calculate the new entropy:

$$\begin{aligned} S_f &= -k\frac{3r_f^2}{2Na^2} \\ &= -k\frac{3\left(2\sqrt{Na^2}\right)^2}{2Na^2} \\ &= -k\frac{3 \times 4}{2} \\ S_f &= -6k \end{aligned}$$

Thus we see that stretching the polymer lowers its entropy, which means that when released the polymer will tend to snap back to its higher entropy, shorter length configuration.

Compress a Polymer

Take the equation for the free energy of a polymer:

$$F = \frac{A}{2}\frac{N^2}{r^3} + kT\frac{3r^2}{2Na^2}$$

Let $a = 1$ and $\mathrm{A} = kT$ for simplicity

$$\frac{F}{kT} = \frac{1}{2}\frac{N^2}{r^3} + \frac{3r^2}{2N}$$

The probability of a fluctuation away from equilibrium is given by the Boltzmann distribution:

$$P(\Delta F) = Ce^{-\frac{\Delta F}{kT}}$$

We wish to find the probability that the polymer squashes into half its original length, where $r \to \frac{r}{2}$:

$$\frac{F}{kT} = \frac{1}{2}\frac{N^2}{\left(\frac{r}{2}\right)^3} + \frac{3\left(\frac{r}{2}\right)^2}{2N}$$
$$\frac{F}{kT} = \frac{4N^2}{r^3} + \frac{3r^2}{8N}$$

Now calculate the resulting change in free energy:

$$\begin{aligned}
\frac{\Delta F}{kT} &= \frac{F_f}{kT} - \frac{F_i}{kT} \\
&= \left(\frac{4N^2}{r^3} + \frac{3r^2}{8N}\right) - \left(\frac{1}{2}\frac{N^2}{r^3} + \frac{3r^2}{2N}\right) \\
&= \frac{4N^2}{r^3} - \frac{N^2}{2r^3} + \frac{3r^2}{8N} - \frac{3r^2}{2N} \\
\frac{\Delta F}{kT} &= \frac{7N^2}{2r^3} - \frac{9r^2}{8N}
\end{aligned}$$

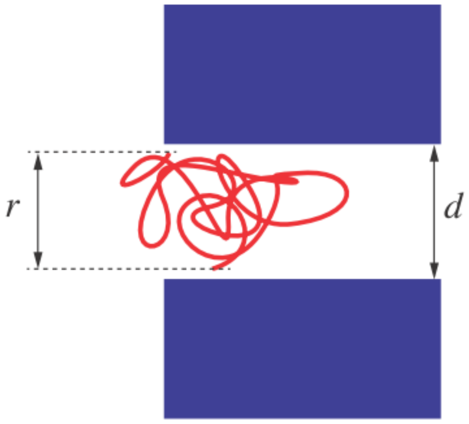
Using the expression derived earlier for how r changes with N, namely $r = \left(\frac{1}{2}\right)^{\frac{1}{5}} N^{\frac{3}{5}}$:

$$\begin{aligned}
\frac{\Delta F}{kT} &= \frac{7N^2}{2\left(\left(\frac{1}{2}\right)^{\frac{1}{5}} N^{\frac{3}{5}}\right)^3} - \frac{9\left(\left(\frac{1}{2}\right)^{\frac{1}{5}} N^{\frac{3}{5}}\right)^2}{8N} \\
&= \frac{7N^2}{2\left(\frac{1}{2}\right)^{\frac{3}{5}} N^{\frac{9}{5}}} - \frac{9\left(\frac{1}{2}\right)^{\frac{2}{5}} N^{\frac{6}{5}}}{8N} \\
&= \frac{7N^{\frac{1}{5}}}{2^{\frac{2}{5}}} - \frac{9 \times 2^{-\frac{2}{5}} N^{\frac{1}{5}}}{8} \\
\frac{\Delta F}{kT} &= 4.18 \times N^{\frac{1}{5}}
\end{aligned}$$

Suppose N=100:

$$\begin{aligned} P(\Delta F) &= Ce^{-\frac{\Delta F}{kT}} \\ &= Ce^{-4.18\times 100^{\frac{1}{5}}} \\ P(\Delta F) &= Ce^{-10.5} \end{aligned}$$

Crucially, the probability becomes small as N becomes large.



$$\text{prob.} \propto \exp\left(\frac{\Delta S_{\text{TOT}}}{k}\right) = \exp\left(-\frac{\Delta F}{kT}\right)$$

Entropy and Thermodynamics

Entropy

Entropy is the measure of the number of microstates any given macrostate possesses.

Microstate: a detailed configuration of the individual atoms

Macrostate: the observed state of the material

Laws of Thermodynamics

1. Energy is conserved: $\Delta U = q + w$
2. The entropy of an ***isolated system*** increases in the course of spontaneous change: $\Delta S_{\text{TOT}} > 0$

The Clausius Inequality

$$dS \geq \frac{dq}{T}$$

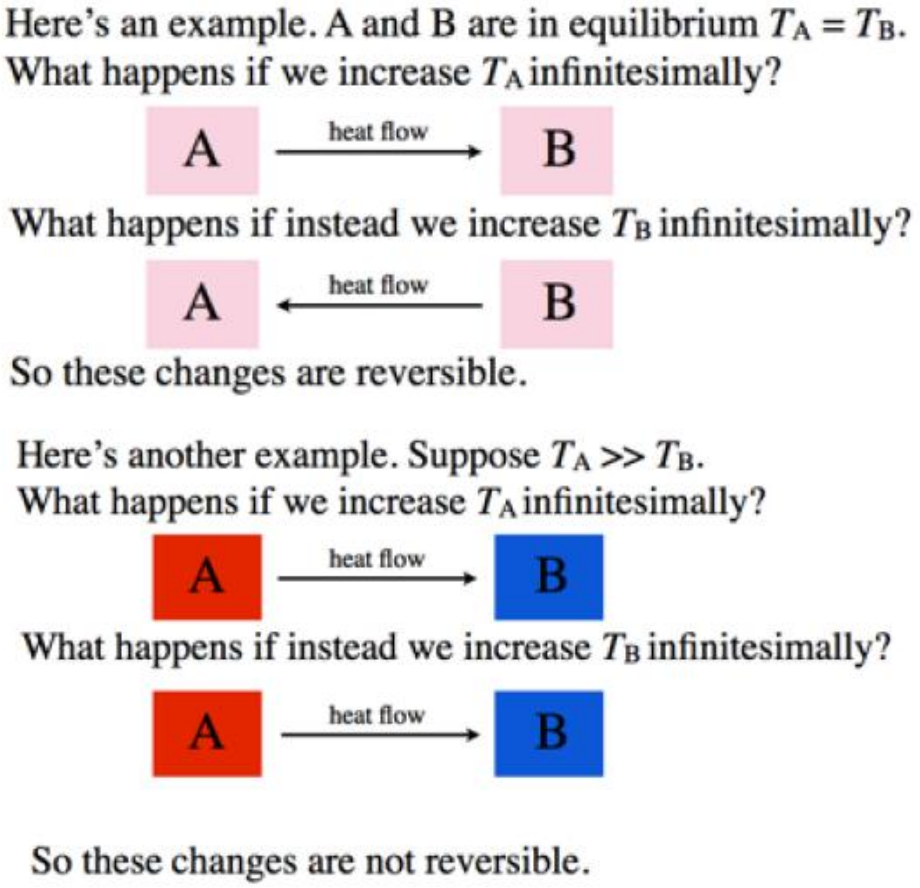
For a reversible change this becomes:

$$dS = \frac{dq_{rev}}{T}$$

Why is there a factor of $\frac{1}{T}$ in dS? Imagine dumping some heat, dq, into a system that’s very cold. This system will be made more random by this process. Imagine instead dumping the same heat into a system that is very, very hot. It's already completely random, so its entropy won't be changed. We need the change in the system's entropy to go to zero as the temperature becomes large.

Reversible Changes

These are changes which can be reversed by an infinitesimal change of a variable, and in which the system is therefore kept infinitesimally close to equilibrium with its surroundings at all times.



Here's an example. A and B are in equilibrium $T_A = T_B$.
What happens if we increase T_A infinitesimally?

What happens if instead we increase T_B infinitesimally?

So these changes are reversible.

Here's another example. Suppose $T_A >> T_B$.
What happens if we increase T_A infinitesimally?

What happens if instead we increase T_B infinitesimally?

So these changes are not reversible.

Gibbs Free Energy

Take enthalpy:

$$H = U + PV$$

Fix temperature and pressure

$$\Delta H = \Delta q + \Delta w + P\Delta V$$

At constant pressure the only work is expansion work in changing volume:

$$\Delta H = \Delta q - P\Delta V + P\Delta V$$
$$\Delta H = \Delta q$$

Thus the Clausius inequality becomes:

$$dS \geq \frac{dq}{T}$$
$$dS \geq \frac{dH}{T}$$

$$dS - \frac{dH}{T} \geq 0$$
$$TdS - dH \geq 0$$
$$dH - TdS \leq 0$$

Since T is constant this can be written as:

$$dH - d(TS) \leq 0$$
$$d(H - TS) \leq 0$$

Thus we define $H - TS$ as the Gibbs free energy, being the quantity that always decreases when temperature and pressure are constant. If $dG = 0$ then the change is reversible. The change in free energy as a system relaxes to equilibrium is the maximum amount of work we can get the system to perform during this relaxation.

The Fundamental Equations

$$dU = dq + dw$$
$$dU = dq_{rev} + dw_{rev}$$

From the Clausius inequality:

$$dS = \frac{dq_{rev}}{T}$$
$$dq_{rev} = TdS$$

With only reversible (expansion) work, we also have:

$$dw_{rev} = -pdV$$

Thus we arrive at:

$$dU = TdS - pdV$$

Maxwell's Relations

Let us write dU in total differential form:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

Using the fundamental equation:

$$TdS - pdV = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

Thus we have:

$$T = \left(\frac{\partial U}{\partial S}\right)_V$$
$$-p = \left(\frac{\partial U}{\partial V}\right)_S$$

Now take derivatives:

$$\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial}{\partial V} T$$

$$\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial}{\partial S}(-p)$$

So we have:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

Phase Changes

At a phase transition boundary, the two phases are in equilibrium with one another, meaning that a small change of the substance from one state to the other is reversible.

$$dS = \frac{dq_{rev}}{T}$$

Since temperature and pressure are constant:

$$dS = \frac{dH}{T}$$

If we're below the freezing point, the crystal is the stable state with the lower free energy. If we're above the freezing point, the liquid is the stable state with the lower free energy. At the melting point the molar free energy of the two phases is the same, so there's no free energy cost to converting a mole of ice into a mole of liquid water.

Thermodynamic Equilibrium

Given two objects or systems in contact:

- If heat can flow between the two, their temperatures are the same at equilibrium.
- If the two can exchange volume, their pressures are the same at equilibrium.
- If matter can flow between the two, the chemical potentials of all species are the same in the two at equilibrium
- Chemical potential of two substances in a mixture is given as $G = \mu_A n_A + \mu_B n_B$, and equilibrium occurs when $\mu_B = \mu_A$

Solutions and Crystallisation

Nucleation and Crystal Formation

Let us examine the formation of spherical crystals in a supersaturated solution of species A. The reaction is thus given by:

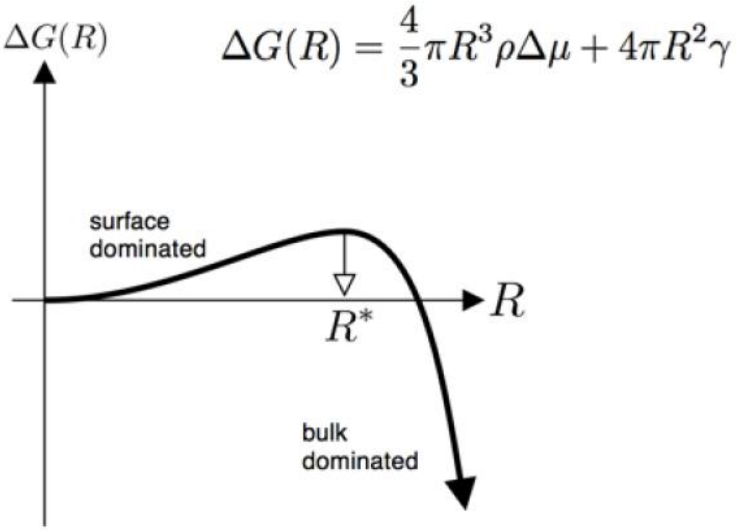
$$A_{aq} \rightleftharpoons A_s$$

The change in free energy of the formation of a single crystal is:

$$\Delta G(R) = \frac{4}{3}\pi R^3 \rho \Delta\mu + 4\pi R^2 \gamma$$

Where ρ is the number of particles per unit volume of the crystal, $\Delta\mu$ is the change in chemical potential for a single particle of A going from supersaturated solution to the crystal, and γ is the work needed to create the crystal/solution surface interface - the interfacial tension.

The fact that the solution is supersaturated means that the crystal is the more stable form, and hence we know that $\Delta\mu < 0$. Thus the bulk and surface contributions will be offsetting, and hence there will be a critical radius R^*:



The critical radius R^* is the crystal size above which further crystal growth is spontaneous. Some thermal fluctuation is first needed to get over this energy barrier. To find R^* we simply maximise the free energy function:

$$\begin{aligned}
\frac{\partial \Delta G(R)}{\partial R} &= 4\pi R^2 \rho \Delta\mu + 8\pi R\gamma \\
4\pi R^2 \rho \Delta\mu &= -8\pi R\gamma \\
R\rho\Delta\mu &= -2\gamma \\
R^* &= -\frac{2\gamma}{\rho\Delta\mu}
\end{aligned}$$

The probability of a thermal fluctuation of sufficient size occurring to push the system over this potential barrier is equal to:

$$P(R^*) = Ae^{-\left(\frac{\Delta G(R^*)}{kT}\right)} \propto \text{rate of crystal formation}$$

Gibbs Free Energy of Mixing

We know that for a mixed system:

$$G = \mu_A n_A + \mu_B n_B$$

Where μ_i is the partial molar free energy for substance i:

$$\mu_i = \frac{\partial G}{\partial n_i}$$

Note that for a pure substance, the chemical potential is the same as the molar Gibbs free energy:

$$\mu = G_m$$

We also have an expression for the chemical potential of a gas:

$$\mu = \mu^o + RT\log\left(\frac{p}{p^o}\right)$$

The Gibbs free energy of mixing is thus given by:

$$\Delta_{mix}G = n_A RT\ln\frac{p_A}{p} + n_B RT\ln\frac{p_B}{p}$$

Gibbs Reaction Energy

We can also solve for the reaction free energy between the two substances in terms of pressures:

$$\begin{aligned}
\Delta_r G &= \mu_B - \mu_A \\
&= \left(\mu_B^o + RT\ln\frac{p_B}{p^o}\right) - \left(\mu_A^o + RT\ln\frac{p_A}{p^o}\right) \\
&= (\mu_B^o - \mu_A^o) + \left(RT\ln\frac{p_B}{p^o} - RT\ln\frac{p_A}{p^o}\right) \\
&= \mu_B^o - \mu_A^o + RT\ln\frac{p_B}{p_A} \\
\Delta_r G &= \Delta_r G^o + RT\ln\frac{p_B}{p_A}
\end{aligned}$$

At equilibrium we have:

$$\begin{aligned}
0 &= \mu_B^o - \mu_A^o + RT\ln\frac{p_B}{p_A} \\
\ln\frac{p_B}{p_A} &= -\frac{(\mu_B^o - \mu_A^o)}{RT} \\
\ln\frac{p_B}{p_A} &= -\frac{\Delta_r G^o}{RT} \\
\frac{p_B}{p_A} &= e^{-\frac{\Delta_r G^o}{RT}}
\end{aligned}$$

Thus we find the equilibrium constant:

$$K = \frac{p_B}{p_A} = e^{-\frac{\Delta_r G^o}{RT}}$$

Activity

In chemical thermodynamics, activity (a) is a measure of the “effective concentration” of a species in a mixture, in the sense that the species' chemical potential depends on the activity of a real solution in the same way that it would depend on concentration for an ideal solution.

$$\begin{aligned}
\text{ideal gas:} \qquad & a = \frac{p}{p^\circ} \\
\text{solute in dilute solution:} \qquad & a = \frac{c}{c^\circ} \\
\text{pure liquid or solid:} \qquad & a = 1
\end{aligned}$$

The reaction quotient can thus be defined as:

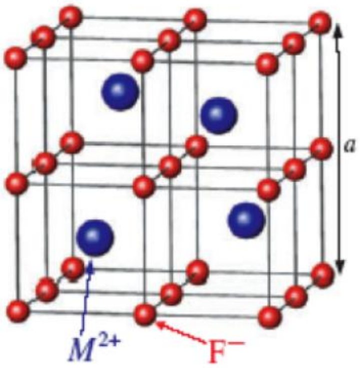
$$Q = \frac{\text{product activity}}{\text{reactant activity}}$$

We can thus write:

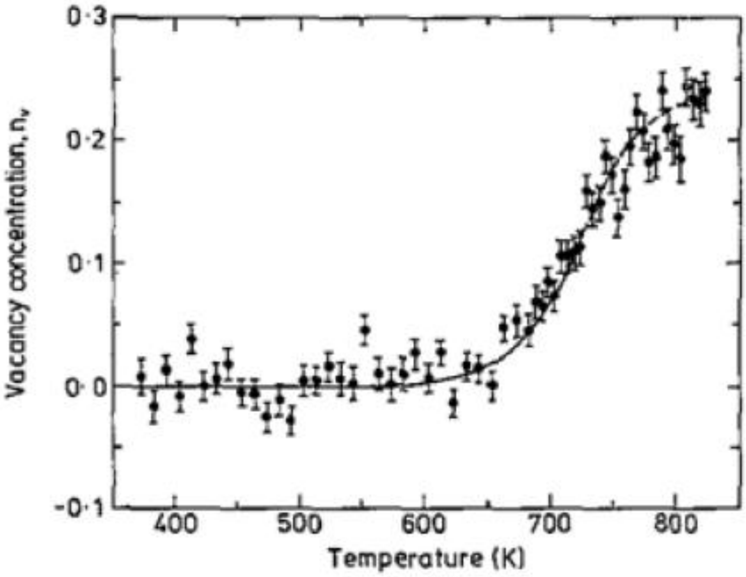
$$\Delta_r G = \Delta_r G^o + RT \ln Q$$

Conducting Crystals

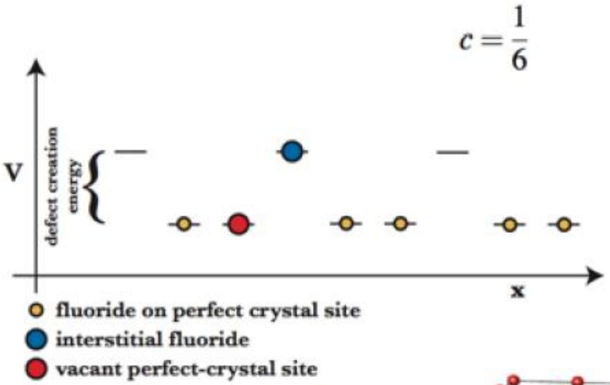
The flourite crystal structure is particularly important, because when oxides of this structure are heated, the oxide ions begin to flow freely throughout the crystal structure, which itself remains intact. Thus such crystals are very useful as solid electrolytes in fuel cells.

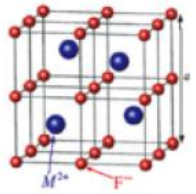


Note that the transition from the perfect, insulating crystal to the electrolyte state doesn't happen at a sharp temperature, but smoothly over a range of temperatures.



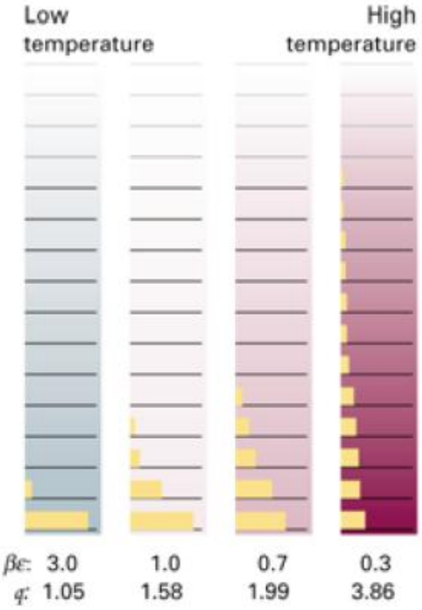
An anion can move from its perfect crystal site into one of the empty cubes in the lattice of anions (the ones that don't contain cations). This disorder allows the anions to move freely through the lattice.





Phase Change

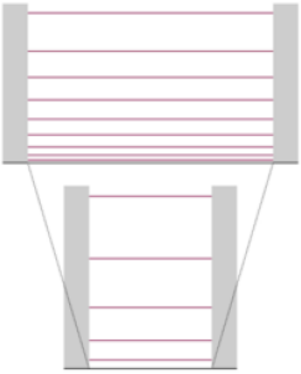
Any molecule or group of molecules can only have one of a discrete set of energies, called energy levels, as a consequence of quantum mechanics. The diagram below shows that at a fixed energy the macrostate with the most energy levels (or microstates) is the one that we will most often see. The lower the energy level, the more likely is the system to be found in that energy state.



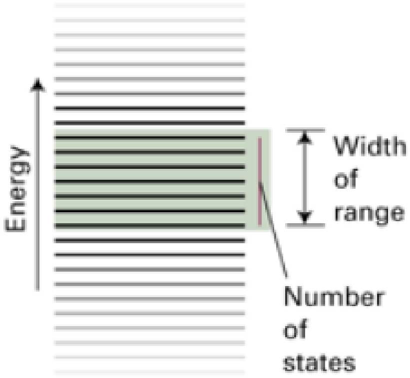
From the Boltzmann distribution, the probability of the ith energy level being occupied is:

$$P_i = Ae^{-\frac{E_i}{k_B T}}$$

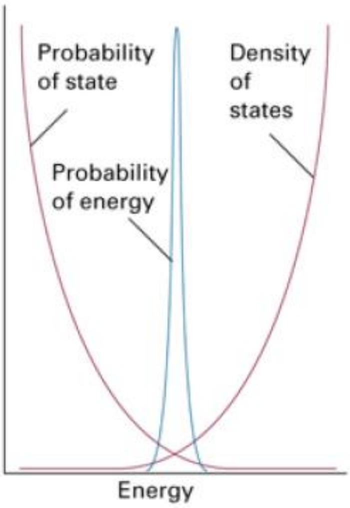
Compressing a system causes the energy levels to move further apart.



Density of states refers to the number of possible microstates per unit of energy within some defined energy range. The higher the density of states, the more likely the system is to be found in that state.



Combining these two ideas, we see that the higher the energy level, the less probable is that corresponding state, but the higher the density of states becomes. For example, there are many more ways of arranging water molecules at liquid-like energies that at crystal energies. These two curves multiply together to give a very sharply peaked probability density of energy levels.



Averaging over a large number of molecules means that we only ever see one particular macrostate - a glass of water is not seen to occasionally boil or freeze.

Raoult's Law

This law states that the partial vapor pressure of each component of an ideal mixture of liquids is equal to the vapor pressure of the pure component multiplied by its mole fraction in the mixture. The total vapor pressure of the ideal solution is then directly dependent on the vapor pressure of each chemical component and the mole fraction of the component present in the solution.

This can be stated as:

$$p_A = x_A p_A^*$$

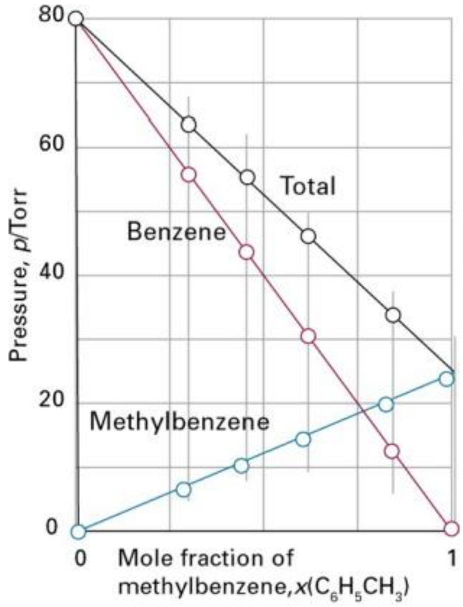
Where x_A is the fraction of the molecules in the mixture that are A, μ_A^* is the chemical potential of pure liquid and p_A^* is the vapour pressure above pure liquid.

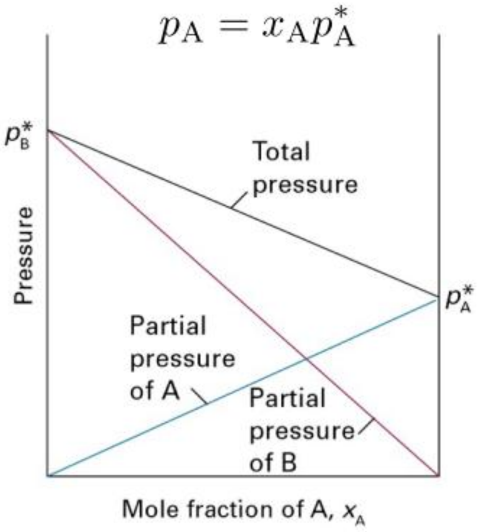
Hence we can modify our chemical potential expression:

$$\mu_A = \mu_A^* + RT\log(x_A)$$

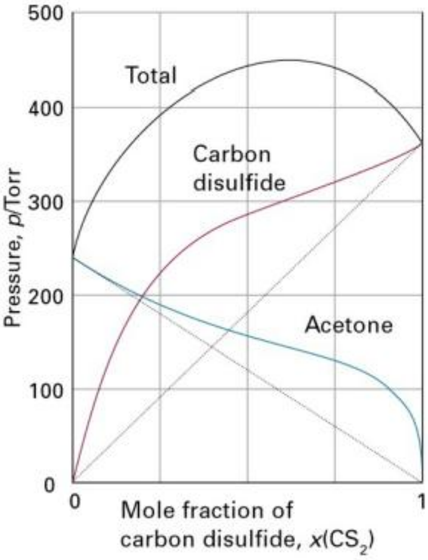
You can see that we can measure the chemical potential of the pure liquid simply by measuring the equilibrium vapour pressure of the vapour above that fluid.

Two similar liquids behave almost ideally





Dissimilar liquids (e.g. polar and non-polar) deviate from ideal behaviour

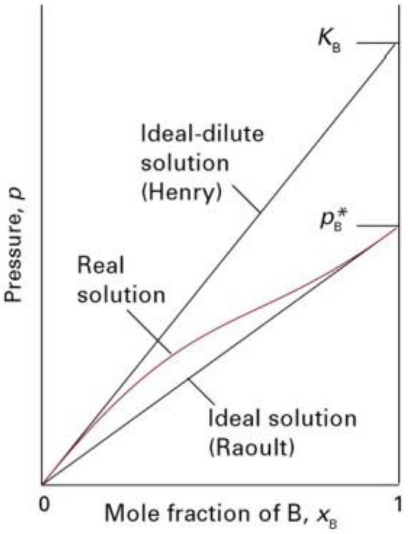


Henry's Law

In an ideal-dilute solution, the partial pressure above the mixture depends linearly on the proportion of species A, without regard to vapour pressure of that substance.

$$p_A = x_A K_A$$

Thus, although Rauolt's and Henry's laws are similar, they do yield different predictions.



The Hydrophobic Effect

The reluctance of non-polar molecules of many types to dissolve in water, and the reluctance of water and oil to form interfaces at which the two meet, are together called the hydrophobic effect. The hydrophobic effect is an equilibrium phenomenon, whose origin is not well understood.