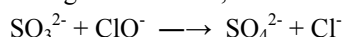


CHEM3012 - Core Chemistry 3

Inorganic Reaction Mechanisms

5. Mechanisms of electron transfer between metal ions

This section of the course is concerned with the mechanisms of electron transfer reactions, principally involving transition metal redox couples. The study of main group electron transfer reactions has been less extensively pursued, although there is a significant body of data relating to oxoanions, such as the following reaction:

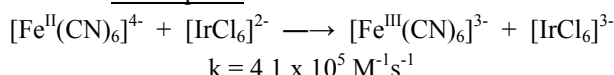


The above reaction can be considered as a two electron redox reaction or as a nucleophilic attack by sulphite on the oxygen atom of chlorate(I). Such oxoanion chemistry is beyond the scope of the current course.

5.1. Transition metal electron transfer reactions

During the 1950's Taube (1983 Nobel Prize) recognised that electron transfer reactions are of two types:

(a) No change occurs in the coordination sphere of either transition metal complex during the electron transfer - such electron transfer reactions are known as "outer-sphere" electron transfer reactions



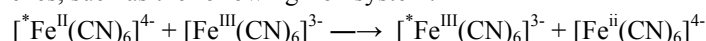
(b) The coordination sphere of the products of the electron transfer reaction differs from that of the starting materials. The electron transfer occurs through a bridging ligand and such reactions are known as "inner-sphere" electron transfer reactions.



The importance of electron transfer reactions cannot be overemphasised, many biologically important processes involve metallo-enzymes, for example the absorption of iron in the gut involves the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple.

5.2. Electron transfer without change in coordination sphere ("outer-sphere")

This mechanism is best considered by first considering the degenerate electron transfer reaction using radioactive (or other) labelled metal complexes, such as the following iron system:



- These complexes are low spin d^5 and d^6 complexes - ligand substitution is slow compared with electron transfer
- Rate Law is first order in both starting complexes
- Rate constants cover 18 orders of magnitude

Complexes	no of d electrons	k (dm ³ mol ⁻¹ s ⁻¹)
$[\text{W}(\text{CN})_8]^{3-}$ $[\text{W}(\text{CN})_8]^{4-}$	$d^1 \rightarrow d^2$	10^5
$[\text{IrCl}_6]^{2-}$ $[\text{IrCl}_6]^{3-}$	$d^4 \rightarrow d^5$	10^5
$[\text{Mo}(\text{CN})_8]^{3-}$ $[\text{Mo}(\text{CN})_8]^{4-}$	$d^1 \rightarrow d^2$	10^4
MnO_4^- MnO_4^{2-}	$d^0 \rightarrow d^1$	10^3
$[\text{Fe}(\text{CN})_6]^{3-}$ $[\text{Fe}(\text{CN})_6]^{4-}$	$d^5 \rightarrow d^6$	10^2
$[\text{Co}(\text{phen})_3]^{3+}$ $[\text{Co}(\text{phen})_3]^{2+}$	$d^6 \rightarrow d^7$	1
$[\text{Co}(\text{en})_3]^{3+}$ $[\text{Co}(\text{en})_3]^{2+}$	$d^6 \rightarrow d^7$	10^{-4}
$[\text{Co}(\text{NH}_3)_6]^{3+}$ $[\text{Co}(\text{NH}_3)_6]^{2+}$	$d^6 \rightarrow d^7$	10^{-12}

The factors which need to be considered are (i) how does the electron transfer occur, (ii) can we predict electron transfer rates, and (iii) how do electron transfer rates vary with d electron count?

The theory which rationalises this data is due to Marcus and Hush (Marcus's theory) and can get highly mathematical - only an overview will be considered.

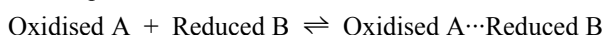
The Marcus equation can be derived in two ways:

- (a) RIGOROUSLY by a highly mathematical combination of thermodynamics, collision theory, kinetics;
- (b) from thermodynamics.

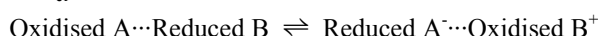
5.2.1. Outline of Marcus theory from kinetics etc.

In order to discuss this derivation it is necessary to first consider a suitable mechanism for the electron transfer process. The mechanism which is accepted involves three steps. These are: (i) formation of a precursor complex or ion pair; (ii) electron transfer; and (iii) diffusion apart of the new species.

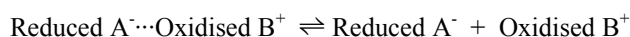
Formation of the encounter pair, with equilibrium constant K_a



Electron transfer with rate constant k_{el}



Rapid diffusion apart of the products



For such a mechanism the observed rate constant = $k_{obs} = K_a k_{el}$

Consider the various parts of this mechanism

(a) the formation of the encounter pair can be treated using the principles of electrostatics. This allows us to calculate the energy need to bring the two ions from infinite separation into contact.

- Calculate the energy needed to bring the two ions into contact
- For like charge complexes, the encounter pair concentration will be low.

(b) The electron transfer step. It is less easy to visualise the factors that contribute to the electron transfer rate constant, k_e . Consider how the energy of one ion pair (say $[\text{Fe}(\text{H}_2\text{O})_6]^{2+/3+}$) varies as the electron is transferred. The reactants initially have the bond lengths of Fe(II) and Fe(III) and the reaction corresponds to motion in which the bonds of Fe(II) shorten and those of Fe(III) lengthen.

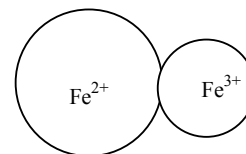
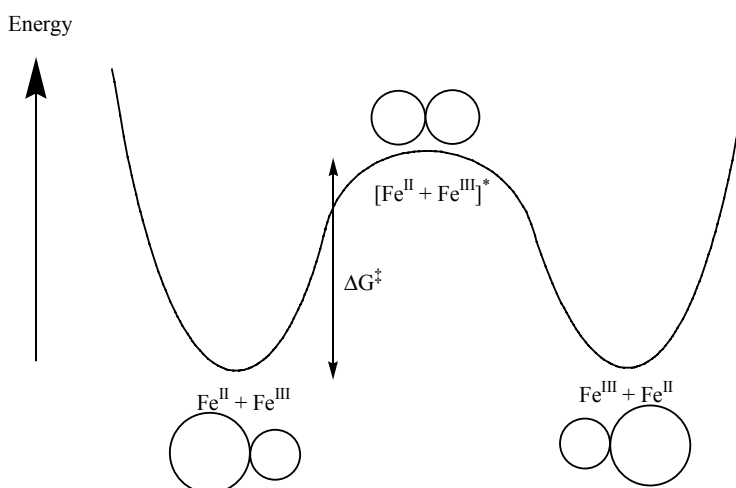


Figure: A simplified reaction profile for the electron exchange in a symmetrical reaction. On the left of the graph, the nuclear coordinates correspond to Fe(II) and $^*\text{Fe(III)}$; on the right, the ligands and solvent molecules have adjusted positions and the nuclear coordinates now correspond to Fe(III) and $^*\text{Fe(II)}$, where * denotes an isotopically labelled Fe atom.

The activated complex occurs at the crossing of the two energy curves, but the non-crossing rule states that energy curves of the same symmetry do not cross, but split - as a consequence of orbital interactions.

The starting materials in their ground states slowly distort (change their bond lengths) and transform into the products in their electronic ground states. The electron transfer occurs instantaneously (as required by the Franck-Condon principle) at the energy maximum.



5.2.2. What energy is required to come to the transition state?

It is possible to identify a number of energy terms which are important in producing the transition state from the encounter pair complex. These include energy terms required for: (i) $\Delta G_{\text{inner}}^\ddagger$, the change in the M-ligand bond lengths/strengths (within the complex), and (ii) $\Delta G_{\text{outer}}^\ddagger$, the change in the solvation energy of these ions (outwith the complex).

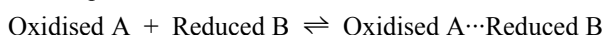
$$\Delta G^\ddagger = \Delta G_{\text{inner}}^\ddagger + \Delta G_{\text{outer}}^\ddagger$$

If we know these activation energies, or can calculate them, k_{el} can be calculated

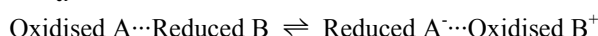
- $\Delta G_{\text{inner}}^\ddagger$ can be deduced from vibrational frequencies
- $\Delta G_{\text{outer}}^\ddagger$ is more difficult to deduce, but equations have been proposed

5.2.3. What influences the rate of the electron transfer reaction?

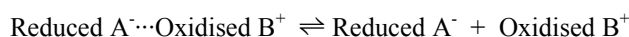
Formation of the encounter pair, with equilibrium constant K_a



Electron transfer with rate constant k_{el}



Rapid diffusion apart of the products

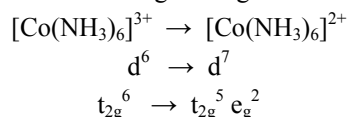


observed rate constant = $k_{\text{obs}} = K_a k_{\text{el}}$

For a fast electron transfer reaction we need to:

(a) Maximise the value of K_a , the equilibrium constant for the formation of the encounter complex. This is mainly determined by electrostatics. The value of K_a can be maximised for small charges, large ions (charge/size ratio), solvent dielectric constant, ionic strength

(b) Lower the activation energy, increase the rate constant for the electron transfer step k_{el} . In order to do this we need to (i) minimise the change in M-L bond lengths, and (ii) minimise the change in electron arrangement. If we remember that t_{2g} electrons are π -bonding and σ -non-bonding, and that e_g electrons are σ -antibonding then the role of electron configuration of the metal complexes which are being oxidised or reduced can be evaluated. Electron transfer reactions involving changes in t_{2g} and e_g occupancy can result in large changes in M-L bond lengths, and slow electron transfer.

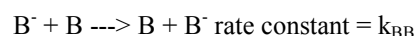
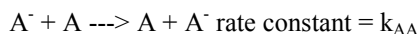


One final factor is that complexes containing large ligands require less reorganisation of the solvent sphere

5.2.4. The Marcus cross relationship

It is possible to provide expressions for K_a and k_{el} in the previous description, and to thus derive the Marcus relationship. However, this involves some serious physical chemistry, and some not very friendly mathematics. This material is omitted from this course, but you might meet it later in your Physical chemistry course. For the moment we will just use the Marcus cross relationship without attempting to prove or derive it.

The Marcus cross relationship relates to the rate of the "cross" reaction, k_{AB} , given that the rate of the self-exchange reactions, k_{AA} and k_{BB} are known, or can be found in some fashion.:



$$k_{\text{AB}} = \left(k_{\text{AA}} k_{\text{BB}} K_{\text{AB}} \frac{Z_{\text{AB}}^2}{Z_{\text{AA}} Z_{\text{BB}}} \right)^{\frac{1}{2}}$$

or $k_{\text{AB}} = (k_{\text{AA}} k_{\text{BB}} K_{\text{AB}} F_{\text{AB}})^{1/2}$

Where K_{AB} is the EQUILIBRIUM CONSTANT for the cross reaction.

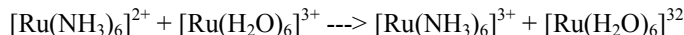
The factor F_{AB} is in fact a collision factor. It is often assumed that $F_{\text{AB}} \sim 1$, which is reasonable for ionic reactions with charge symmetry (e.g., $\text{A}^{2+} + \text{B}^{3+} \rightarrow \text{A}^{3+} + \text{B}^{2+}$), but deviations from $F_{\text{AB}} = 1$ can become a problem for less symmetrical systems.

The Marcus cross relationship means that if we know the rate constants for the self exchange reactions of two redox couples (k_{AA} and k_{BB}), together with their standard reduction potentials (E° for A/A^- and B/B^- and hence K_{AB}) then we can calculate the rate constant for the cross reaction.

Note that the rate constant for the cross reaction depends on how thermodynamically favoured it is:

5.2.5. How do we use the Marcus cross relationship?

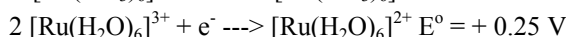
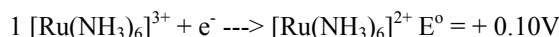
As a problem for the student. Calculate the rate constant for the reaction:



given the rate constants for the self exchange reactions and the standard reduction potentials are:

$$[\text{Ru}(\text{NH}_3)_6]^{3+}/\text{Ru}^{2+} \quad k = 2 \times 10^4 \text{ M}^{-1}\text{s}^{-1}, \quad E^\circ = +0.10 \text{ V}$$

$$[\text{Ru}(\text{H}_2\text{O})_6]^{3+}/\text{Ru}^{2+} \quad k = 32 \text{ M}^{-1}\text{s}^{-1}, \quad E^\circ = +0.25 \text{ V}$$



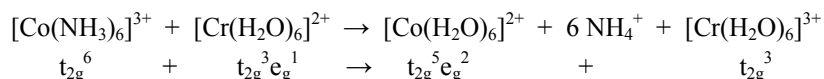
Desired equation is 2 minus 1, hence $E^\circ = 0.25 - 0.10 = 0.15 \text{ V}$

$\Delta G^\circ = -n F E^\circ = -RT \ln K$ hence $\ln K = n F E^\circ / R T$ and then $K = 344$

using $k_{AB} = (k_{AA}k_{BB}K_{AB}F_{AB})^{1/2}$ gives $k_{AB} = (2 \times 10^4 \times 32 \times 344)^{1/2}$ from which $k_{AB} = 1.4 \times 10^4$

5.3. Electron transfer with change in coordination sphere

The following reaction is rather slow ($k = 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$):



Aside: Remember that Co^{3+} is stable as the amine complex, but the aquo complex will oxidise water, Co^{2+} is substitutionally labile and so the product is the aquo complex.

The following reaction is almost the same, but the starting material has one NH_3 ligand on $\text{Co}(\text{III})$ replaced by a Cl^- . This reaction is substantially faster ($k = 6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$):



This enhanced rate suggests that a different mechanism may be operating, a point first made by Taube. This mechanism is known as the Inner Sphere electron transfer mechanism. The important characteristics are that during the electron transfer reaction, a ligand has also been transferred. This suggests that the ligand and the electron may have been transferred simultaneously.

5.3.1. Proof of inner sphere electron transfer

The observation that the reaction above involves transfer of both an electron and also a ligand is an important clue to the mechanism. BUT, it is necessary to first exclude the possibility that the ligand transfer and the electron transfer steps do not take place simultaneously.

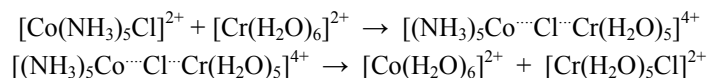
The reaction outlined above involves two starting complexes and two products. These are:

- $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ is $\text{Cr}^{2+} d^4$, and so is substitution labile
- $\text{Co}(\text{H}_2\text{O})_6^{2+}$ is $\text{Co}^{3+} d^7$ and so also labile
- $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ is $\text{Co}^{3+} d^6$, low spin and so inert
- $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$ is $\text{Cr}^{3+} d^3$ and so also inert

Thus the Co^{III} starting material is substitution inert, and the Cl^- ligand will not be released from the Co^{III} metal centre. Similarly, the Cr^{III} product is inert to ligand substitution, and so it is not possible to attach the Cl^- ligand to the Cr^{III} metal centre AFTER the electron transfer step has taken place. Since both the M-Cl complexes are inert to ligand substitution, the Cl^- ligand must have been transferred during the electron transfer step. One more piece of evidence is that if this reaction is performed in a solution containing radioactive $^{36}\text{Cl}^-$ there is no incorporation of $^{36}\text{Cl}^-$ into the products.

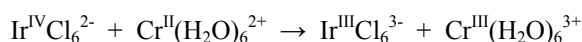
The accepted mechanism is as follows; (a) the labile Cr^{II} complex substitutes an H_2O ligand by a bridging Cl^- ligand

(Aside for the student, is this reaction I_a or I_d? What limitations does this imply for the bridging ligand?), (b) the resulting bimetallic complex has the two metals held in close proximity and electron transfer occurs, (c) after the electron transfer has occurred the bimetallic complex contains Co^{II} which is labile, and all of the ligands attached to Co^{II} (including the bridging Cl) are replaced rapidly by the solvent, H₂O.



When he proposed this mechanism, Taube observed that "The inner sphere electron transfer mechanism can be unequivocally assigned when both oxidant and oxidised product are substitution inert, and when ligand transfer accompanies electron transfer"

Inner sphere electron transfer requires (i) reducing agents which is labile, and (ii) a ligand on the oxidising agent which is capable of bridging, bridging ligands can be: Cl⁻, Br⁻, I⁻, N₃⁻, NCS⁻, bipyridines. Inner sphere electron transfer reactions are usually identified by the observation of ligand transfer at the same time as electron transfer, however there are some cases where the ligand is NOT transferred:



In this reaction the electron transfer does occur via an inner sphere electron transfer reaction, but it is then necessary to consider how the resulting Ir^{III}--Cr^{III} product bimetallic complex breaks apart. In this case the Ir-Cl bond is stronger than the Cr-Cl bond and the Cl ligand remains with the Ir^{III}.