

ACIDS, BASES AND SOLUTION EQUILIBRIA

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HILARY TERM

Lecture 4

7. Coupling between electron transfer and acid-base reactions

- 7.1. Stabilisation of different oxidation states by preferential complexation
- 7.2. pH dependence of reduction potentials
- 7.3. Oxo-transfer reactions
- 7.4. Pourbaix diagrams
Example: Iron species in aerobic aqueous media

8. Questions

7. Coupling between electron transfer and acid-base reactions

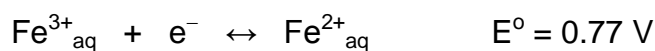
7.1. Stabilisation of different oxidation states by preferential complexation (i.e. adduct formation)

Consider a redox reaction involving metal complexes, such as the hexacyano- complexes of Fe(II) and Fe(III):



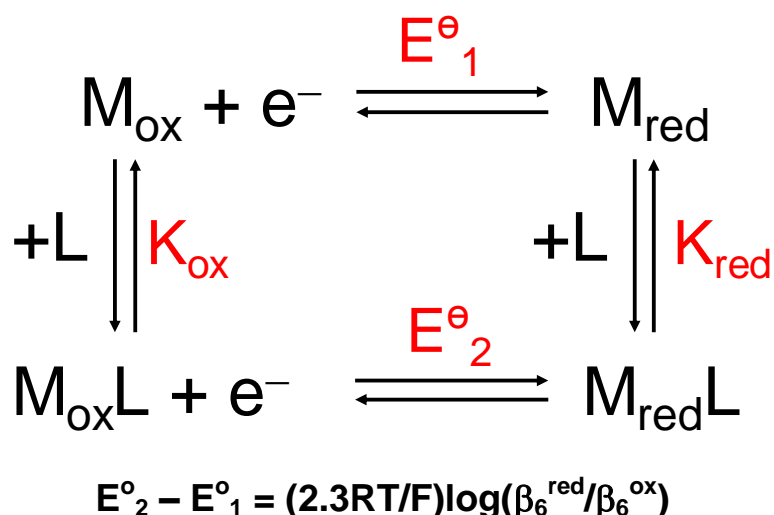
The standard reduction potential indicates that $[\text{Fe}(\text{CN})_6]^{3-}$ is a weak oxidant.

However, for the aqua ions:



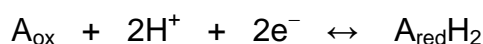
The standard reduction potential indicates that $\text{Fe}^{3+}_{(\text{aq})}$ is a relatively strong oxidant.

Obviously, complexation by CN^- stabilizes Fe(III) relative to Fe(II). The stabilisation can be calculated using a thermodynamic cycle.



7.2. pH dependence of reduction potentials

We consider the simple case where the reduced form of the redox couple is an extremely strong Brønsted base, whereas the oxidised form is a very weak base. Consider the reaction:



This could be a typical organic reaction, equivalent to reduction by two H-atoms or H_2 .

The Nernst equation now includes the H^+ -acidity.

$$E = E^\ominus + \frac{2.3RT}{2F} \log \left(\frac{[A_{\text{ox}}][H^+]^2}{[A_{\text{red}}H_2]} \right)$$

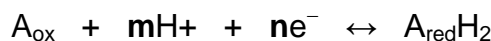
$$E = E^\ominus + \frac{2.3RT}{2F} \log \left(\frac{[A_{\text{ox}}]}{[A_{\text{red}}H_2]} \right) - 2 \left(\frac{2.3RT}{2F} \right) \text{pH}$$

$$E = E^\ominus + \frac{2.3RT}{2F} \log \left(\frac{[A_{\text{ox}}]}{[A_{\text{red}}H_2]} \right) - \left(\frac{2.3RT}{F} \right) \text{pH}$$

pH-dependent term

The reduction potential thus *decreases* by $2.3RT/F = 0.059 \text{ V}$ per pH unit.

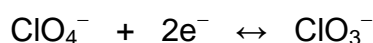
In general, for a reaction that can be written:



The pH dependence is given by $-(0.059\text{ m/n})\text{pH}$

7.3. Oxo-transfer reactions

Consider a reduction reaction involving the loss of an O atom, e.g. the reduction of ClO_4^- to ClO_3^- .



Both species are strong acids, however the reaction releases O_2^- , which is an extremely strong base, therefore 2H^+ are consumed.



The reaction is therefore pH dependent with $m/n = 1$.

7.4. Pourbaix diagrams

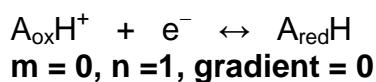
The principles outlined above can be extended to include reactions in which the concentrations of the ligand are not sufficient to saturate oxidised or reduced states of the redox couple, or where the pH range includes values for protonation constants.

A good rule is that the reduced form of a redox couple is a much better Brønsted base than the oxidised form. Exceptions imply that a large structural change has occurred.

Over a wide pH range several situations can arise.

Consider a simple one-electron system.

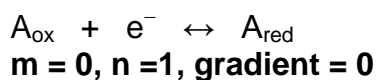
At $\text{pH} < \text{pH}_{\text{ox}}$:



At $\text{pK}_{\text{ox}} < \text{pH} < \text{pH}_{\text{red}}$:

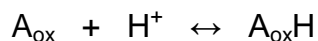


At $\text{pH} > \text{pH}_{\text{red}}$:

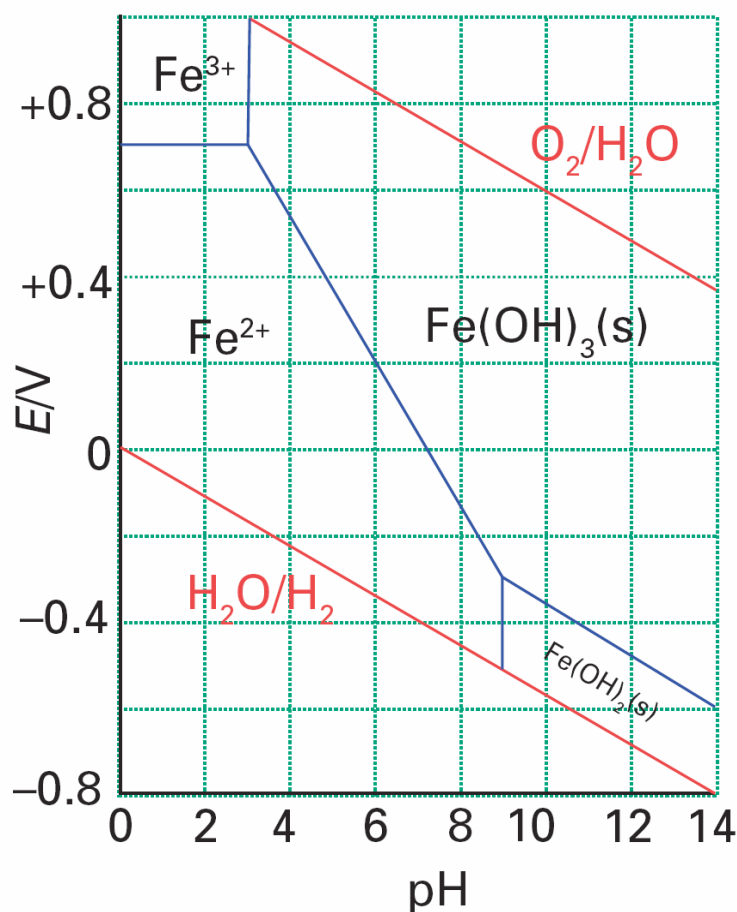


Pourbaix diagrams are charts of E° vs. pH. They describe proton and electron transfer together.

Proton transfer reactions can be treated (trivially) within the framework of the Nernst equation. For:

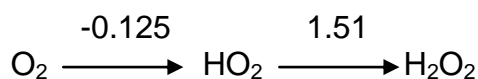


We can think of this reaction as having $m = 1$, $n = 0$ and subsequently a gradient $= \infty$.



8. Questions

- 1) Write two half reactions for disproportionation of H_2O_2 in acid solution and show how the reaction should be independent of $[\text{H}^+]$ in the range pH 1-7.
- 2) From the following Latimer diagram (in acid solution):

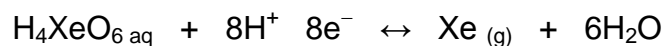


Calculate ΔG° for the reaction: $2\text{HO}_2(\text{aq}) \rightarrow \text{O}_2(\text{g}) + \text{H}_2\text{O}_2(\text{aq})$

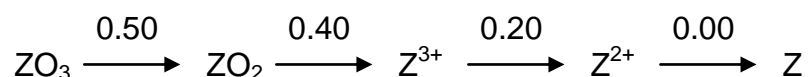
- 3) Discuss how the equilibrium: $\text{Cu}^{2+}_{(\text{aq})} + \text{Cu}_{(\text{s})} \leftrightarrow 2\text{Cu}^{+}_{(\text{aq})}$

can be shifted by complexation with Cl^{-} ions.

- 4) Calculate E° for the following reaction:

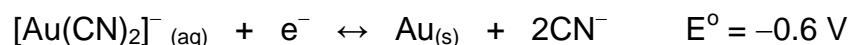
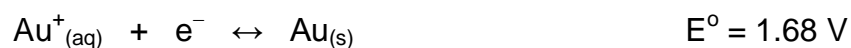


- 5) The hypothetical element Z has the following Latimer diagram in aqueous solution.



Construct a Frost diagram for Z, identify any species prone to disproportionation, and write an appropriate equation for the reaction that occurs.

- 6) Using the following standard reduction potentials:



Calculate the formation constant β_2 for the reaction of Au(I) with CN^{-}

