

ACIDS, BASES AND SOLUTION EQUILIBRIA

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HILARY TERM

Lecture 3

5. Redox reactions and equilibria

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Sequential electron transfers

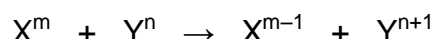
6. Latimer and Frost diagrams

6.1 Inherent stabilities of oxidation states

5. Redox reactions and equilibria

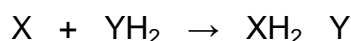
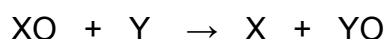
Redox reactions involve a change in the *oxidation numbers* of the species involved.

Electron transfer reactions are the simplest of redox processes:



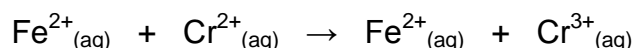
X = oxidant, Y = reductant, and m and n are formal oxidation numbers before the reaction. The term *oxidation number* is a formal assignment. An element is often said to be *in* a certain *oxidation state* and *have* a certain *oxidation number*. In practice, the terms oxidation number and oxidation state are used interchangeably.

Atom transfer reactions are also redox reactions:

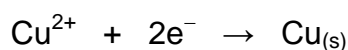


In terms of thermodynamics, electron-transfer and atom transfer reactions can be treated alike. They are related through acid-base chemistry.

Redox reactions can occur entirely in solution, e.g.

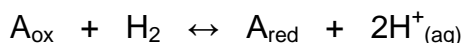


or at the interface, e.g. on an electrode



5.1. Thermodynamics of electron transfer: The Nernst equation

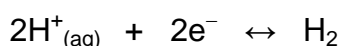
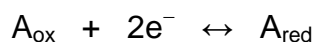
Consider oxidant and reductant in equilibrium with H^+ (unit activity) and H_2 (1atm pressure).



At equilibrium:

$$K = \frac{[A_{red}][H^+]^2}{[A_{ox}][H_2]} = 10^{\left(\frac{-\Delta G^{\circ}_{rxn}}{2.3RT}\right)}$$

If we consider the reaction in terms of electron transfer, we can write the equilibrium as two half-reactions (c.f. proton transfer):



$$\Delta G^{\circ}_{rxn} = \Delta G^{\circ}_A - \Delta G^{\circ}_H$$

however, by definition $\Delta G^{\circ}_H = 0$, so $\Delta G^{\circ}_{rxn} = \Delta G^{\circ}_A$

$$\Delta G^{\circ} = -nE^{\circ}F$$

where E° is the standard reduction potential (vs the Standard Hydrogen Electrode – SHE) of A_{ox} . Another way of putting that is that E° is the difference in standard reduction potentials for the couples A_{ox}/A_{red} and $2H^+/H_2$.

$$E^{\circ} = (2.3RT/nF)\log K$$

For any system: $\Delta G = \Delta G^{\circ} + 2.3RT \log Q$

Where Q is the reaction quotient $\frac{[A_{red}][H^+]^2}{[A_{ox}][H_2]}$, which is equal to $\frac{[A_{red}]}{[A_{ox}]}$ when referenced against SHE.

The Nernst equation

$$E = E^{\circ} - \frac{2.3RT}{nF} \log \left(\frac{[A_{red}]}{[A_{ox}]} \right)$$

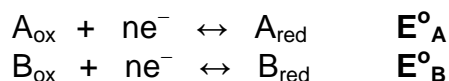
$$E = E^{\circ} + \frac{2.3RT}{nF} \log \left(\frac{[A_{ox}]}{[A_{red}]} \right)$$

$$\text{at 298K: } E = E^{\circ} + 0.059 \log \left(\frac{[A_{\text{ox}}]}{[A_{\text{red}}]} \right)$$

The thermodynamics of any redox reaction can be computed by comparing their E° values. As a result:



Comprises of the two half-reactions:



$$\text{Subsequently: } \log K_{\text{AB}} = (nF / 2.3RT)(E^{\circ}_{\text{A}} - E^{\circ}_{\text{B}})$$

The quantity nE° is the volt-equivalent. It is very important to realise that E° values *cannot* be manipulated without the inclusion of n .

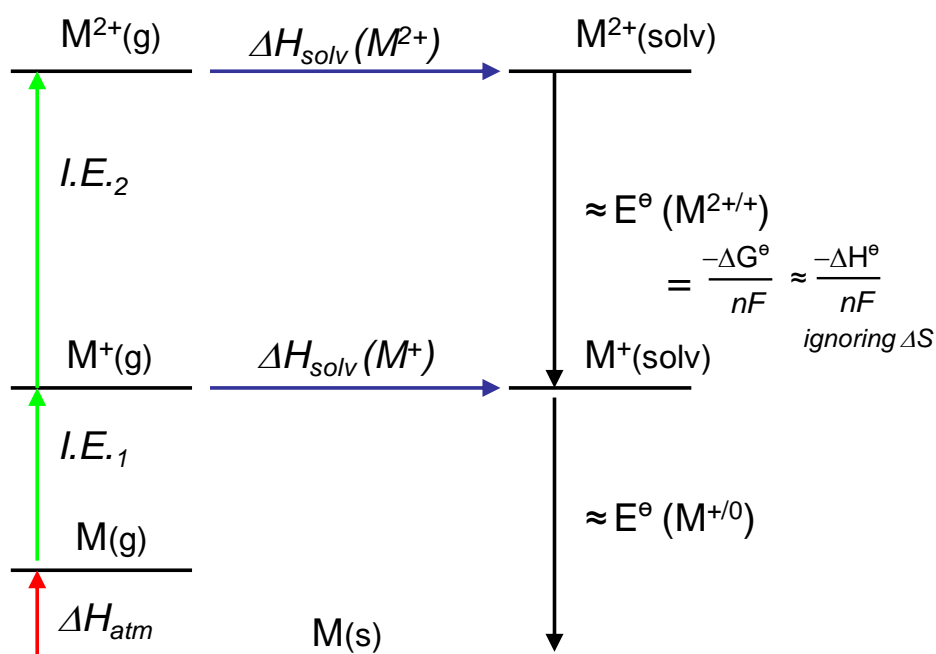
5.2. Reduction potentials, ionisation potentials and solvation effects

Reduction potentials refer to a half-reaction written in the following form:



in which the other half reaction is the reference (SHE), with $E^{\circ} = 0$.

Ignoring entropy terms, standard reduction potentials E° can be related to ionisation potentials and enthalpies of solvation and atomisation using the following thermodynamic cycle:



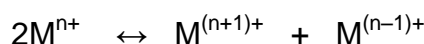
The higher (more positive) E° , the stronger the oxidant.

High oxidation states are favoured (E° lowered) by a strong interaction with solvent.

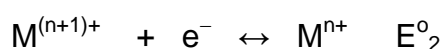
High enthalpies of atomisation decrease the reducing power of metals (raise E°).

Sequential electron transfers

Consider the disproportionation reaction:



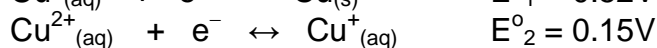
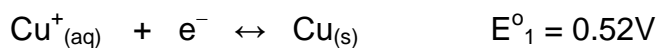
which comprises of the following two half-reactions:



Then $\log K_{\text{disp}} = (nF/2.3RT)(E^\circ_1 - E^\circ_2) = 16.9n (E^\circ_1 - E^\circ_2)$

If $E^\circ_1 > E^\circ_2$, then M^+ is unstable with regard to disproportionation.

Example: Stability of $\text{Cu}^+_{(\text{aq})}$



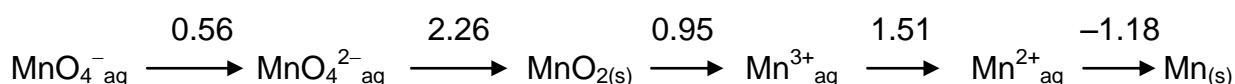
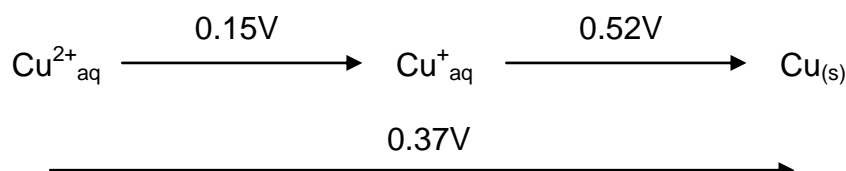
$$\log K_{\text{disp}} = 16.9(0.52 - 0.15) = 6.27$$

$$K_{\text{disp}} = 10^{6.27}$$

6. Latimer and Frost diagrams

Latimer diagrams

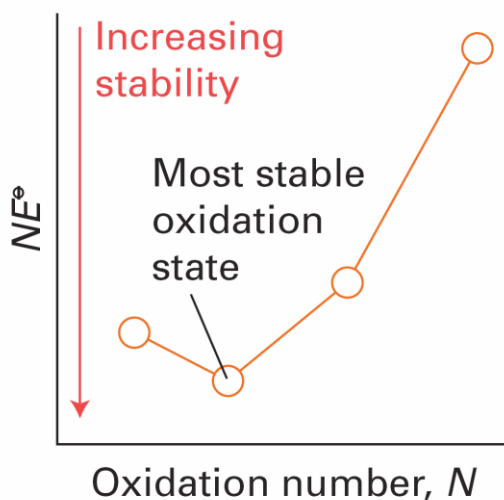
A Latimer diagram is a simple way of representing a series of step-wise half-reactions.



Reduction potentials for transformations between any species in the series are easily calculated. An important point is that E° values alone cannot be used since they are not additive. Instead, it is essential to use *volt-equivalents* (nE°).

Frost diagrams

A Frost diagram is another way of depicting multiple step-wise electron transfers. It is a plot of volt equivalents against oxidation state. The slope of a line joining any two data points is the reduction potential for that process. It is easy to assess whether a species in a redox series will be stable or unstable with regard to disproportionation.

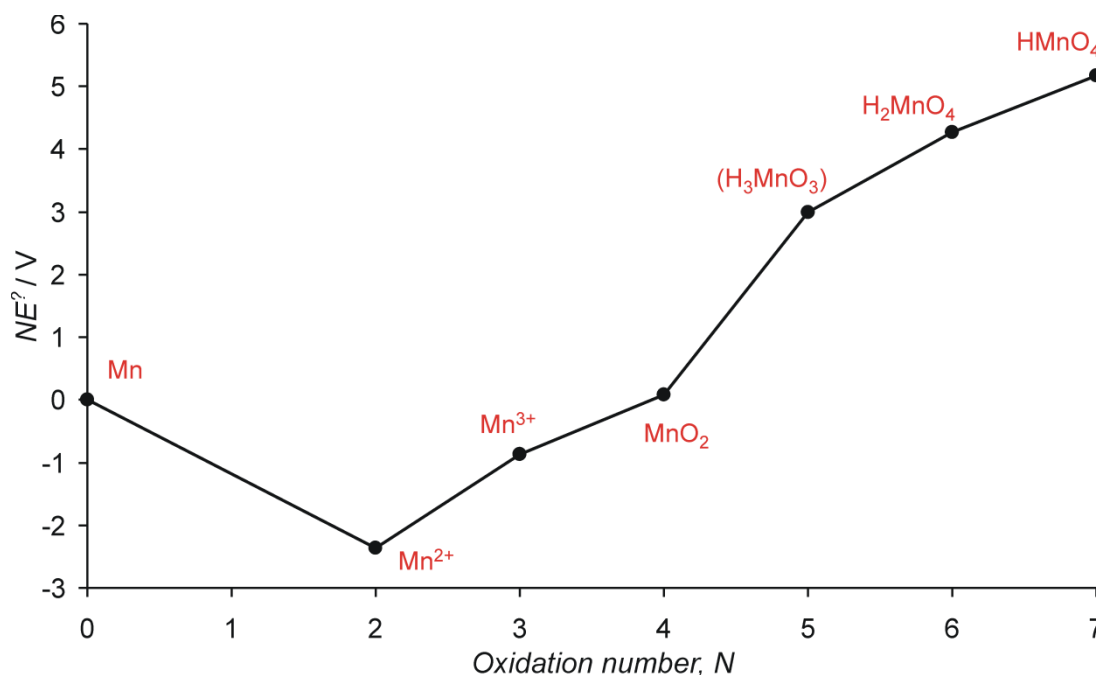


A *Frost diagram* portrays inherent stability and is also a convenient way to see how good (thermodynamically) a species is an oxidising or a reducing agent.

The species lying in the 'well' is *inherently* more stable.

6.1 Inherent stabilities of oxidation states

A Frost diagram for **Manganese** aqua species at pH = 0 is pictured. The 'thermodynamic sink' is Mn(II). Mn(s) is a good reducing agent. Mn^{3+} is inherently unstable.



The Frost diagram for **Nitrogen** aqua species at pH = 0 and pH = 14. The nitrogen molecule (N_2) is inherently very stable. Although note that N_2 should be reducible to NH_4^+ at pH = 0. Hydroxylamine (NH_2OH) is inherently very unstable under both acidic and alkaline conditions. A Frost diagram does not offer us any information on kinetics. Formation of NH_4^+ from N_2 is extremely slow without a catalyst.

