Semester IV

CHE-HC-4014: INORGANIC CHEMISTRY-III

Topic: Oxidation-Reduction (Redox)

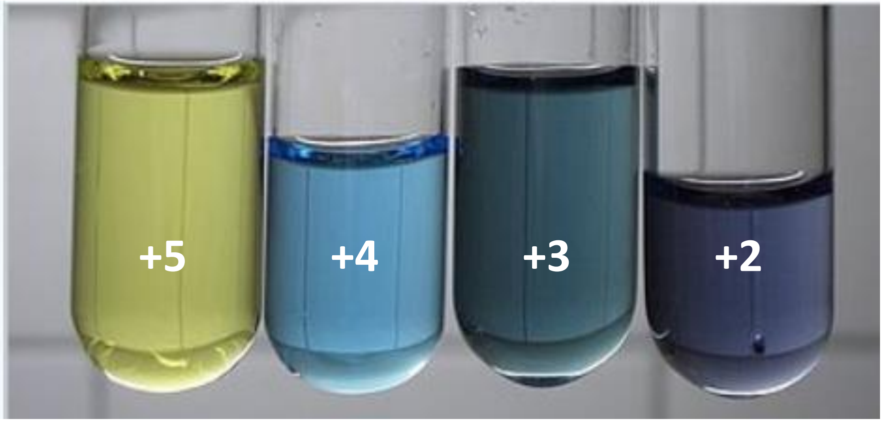
Prelude to Redox Reactions

- ☐ A large class of reactions of inorganic compounds can be regarded as occurring by the transfer of electrons from one species to another.
- ☐ ***Electron gain*** is called ***reduction*** and ***electron loss*** is called ***oxidation***; the joint process is called a ***redox reaction***.
- ☐ The species that *supplies electrons* is the **reducing agent** (or '**reductant**') and the species that *removes electrons* is the **oxidizing agent** (or '**oxidant**').
- ☐ Redox reactions are often analyzed in terms of oxidation numbers; oxidation then corresponds to an increase in the oxidation number of an element and reduction corresponds to a decrease in its oxidation number.
- ☐ If an element in a reaction do not undergo a change in oxidation number, then the reaction is not classified as redox.
- ☐ Many redox reactions release a great deal of energy and they are exploited in combustion or battery technologies.

Examples of Redox Reactions

- The metabolism of sugars to CO_2, which stores energy in the form of ATP, is an example of redox reaction.
- In a car engine, hydrocarbons in the fuel are oxidized to carbon dioxide and water, while oxygen is reduced to water.
- Corrosion (i.e., the formation of rust on iron) is a redox reaction involving oxidation of a metal.
- Production of O_2 from water by an ‘Mn_4’ cofactor contained in one of the photosynthetic complexes of plants.
- Li-ion and Li-polymer batteries (https://www.youtube.com/watch?v=rViC90fSN7Q).

The four oxidation states of vanadium forms the basis of a vanadium flow battery, a storage device for electricity generated from sunlight and wind.



Oxidation states of vanadium in acidic solution

Reduction potentials

Redox half-reactions

- ☐ A redox reaction as the combination of two conceptual half reactions in which the electron loss (oxidation) and gain (reduction) are displayed explicitly.
- ☐ The oxidized and reduced species in a half-reaction constitute a redox couple. A couple is written with the oxidized species before the reduced.
- ☐ It is useful to represent oxidation half-reactions by the corresponding reduction half-reaction. To do so, we simply reverse the equation for the oxidation half-reaction.

In a reduction half-reaction, a substance gains electrons, as in $2\,H^+(aq) + 2\,e^- \rightarrow H_2(g)$	In an oxidation half-reaction, a substance loses electrons, as in $Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-$

- ☐ The reduction half-reaction associated with the oxidation of zinc is written

$$Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)$$

- ☐ A redox reaction in which zinc is oxidized by hydrogen ions is

$$Zn(s) + 2\,H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

Combining half-reactions

Balancing Redox Reactions: The ion-electron method

Q: Write a balanced equation for the oxidation of Fe^{2+} by permanganate ions (MnO$_4^-$) in acid solution.

A systematic approach of balancing redox reactions is as follows:

1. Write the unbalanced half-reactions for the two species as reductions.

2. Balance the elements other than hydrogen.

3. Balance O atoms by adding H_2O to the other side of the arrow.

4. If the solution is acidic, balance the H atoms by adding H$^+$; if the solution is basic, balance the H atoms by adding OH$^-$ to one side and H_2O to the other.

5. Balance the charge by adding **'e'**.

6. Multiply each half-reaction by a factor to ensure that the numbers of e match.

7. Subtract one half-reaction from the other and cancel redundant terms.

Combining half-reactions

Balancing Redox Reactions: The ion-electron method

Q: ***Write a balanced equation for the oxidation of Fe^{2+} by permanganate ions (MnO_4^-) in acid solution.***

Ans: The half-reaction for the reduction of Fe^{3+} is straightforward as it involves only the balance of charge:

$$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$$

The unbalanced half-reaction for the reduction of MnO_4^- is

$$MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$$

Balance the O with H_2O:

$$MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4\,H_2O(l)$$

Balance the H with $H^+(aq)$:

$$MnO_4^-(aq) + 8\,H^+(aq) \rightarrow Mn^{2+}(aq) + 4\,H_2O(l)$$

Balance the charge with e^-:

$$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \rightarrow Mn^{2+}(aq) + 4\,H_2O(l)$$

To balance the number of electrons in the two half-reactions the first is multiplied by 5 and the second by 2 to give $10\,e^-$ in each case. Then subtracting the iron half-reaction from the permanganate half-reaction and rearranging so that all stoichiometric coefficients are positive gives

$$MnO_4^-(aq) + 8\,H^+(aq) + 5\,Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 5\,Fe^{3+}(aq) + 4\,H_2O(l)$$

Self-test 5.1 Use reduction half-reactions to write a balanced equation for the oxidation of zinc metal by permanganate ions in acid solution.

Balancing Redox Reactions: The ion-electron method

Example 1: Balancing in a Neutral Solution

Balance the following reaction

$$\mathrm{Cu^{+}(aq) + Fe(s) \rightarrow Fe^{3+}(aq) + Cu(s)}$$

Solution

Step 1: Separate the half-reactions. By searching for the reduction potential, one can find two separate reactions:

$$\mathrm{Cu^{+}(aq) + e^{-} \rightarrow Cu(s)}$$

and

$$\mathrm{Fe^{3+}(aq) + 3\,e^{-} \rightarrow Fe(s)}$$

The copper reaction has a higher potential and thus is being reduced. Iron is being oxidized so the half-reaction should be flipped. This yields:

$$\mathrm{Cu^{+}(aq) + e^{-} \rightarrow Cu(s)}$$

and

$$\mathrm{Fe(s) \rightarrow Fe^{3+}(aq) + 3\,e^{-}}$$

Step 2: Balance the electrons in the equations. In this case, the electrons are simply balanced by multiplying the entire $Cu^{+}(aq) + e^{-} \rightarrow Cu(s)$ half-reaction by 3 and leaving the other half reaction as it is. This gives:

$$\mathrm{3\,Cu^{+}(aq) + 3\,e^{-} \rightarrow 3\,Cu(s)}$$

and

$$\mathrm{Fe(s) \rightarrow Fe^{3+}(aq) + 3\,e^{-}}$$

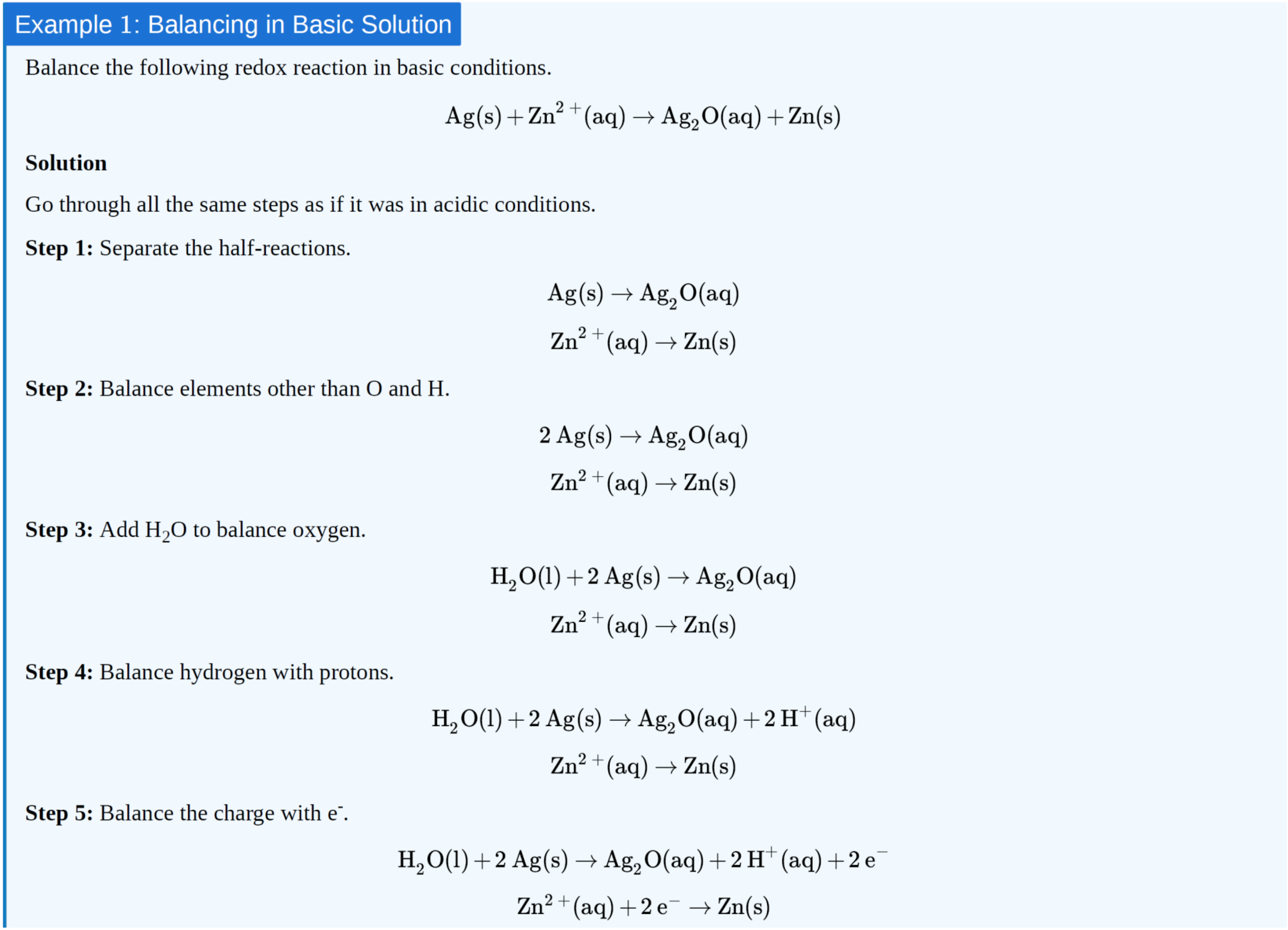
Step 3: Adding the equations give:

$$\mathrm{3\,Cu^{+}(aq) + 3\,e^{-} + Fe(s) \rightarrow 3\,Cu(s) + Fe^{3+}(aq) + 3\,e^{-}}$$

The electrons cancel out and the balanced equation is left.

$$\mathrm{3\,Cu^{+}(aq) + Fe(s) \rightarrow 3\,Cu(s) + Fe^{3+}(aq)}$$

Balancing Redox Reactions: The ion-electron method



Example 1: Balancing in Basic Solution

Balance the following redox reaction in basic conditions.

$$\mathrm{Ag(s) + Zn^{2+}(aq) \rightarrow Ag_2O(aq) + Zn(s)}$$

Solution

Go through all the same steps as if it was in acidic conditions.

Step 1: Separate the half-reactions.

$$\mathrm{Ag(s) \rightarrow Ag_2O(aq)}$$

$$\mathrm{Zn^{2+}(aq) \rightarrow Zn(s)}$$

Step 2: Balance elements other than O and H.

$$\mathrm{2\,Ag(s) \rightarrow Ag_2O(aq)}$$

$$\mathrm{Zn^{2+}(aq) \rightarrow Zn(s)}$$

Step 3: Add H_2O to balance oxygen.

$$\mathrm{H_2O(l) + 2\,Ag(s) \rightarrow Ag_2O(aq)}$$

$$\mathrm{Zn^{2+}(aq) \rightarrow Zn(s)}$$

Step 4: Balance hydrogen with protons.

$$\mathrm{H_2O(l) + 2\,Ag(s) \rightarrow Ag_2O(aq) + 2\,H^+(aq)}$$

$$\mathrm{Zn^{2+}(aq) \rightarrow Zn(s)}$$

Step 5: Balance the charge with e^-.

$$\mathrm{H_2O(l) + 2\,Ag(s) \rightarrow Ag_2O(aq) + 2\,H^+(aq) + 2\,e^-}$$

$$\mathrm{Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)}$$

Balancing Redox Reactions: The ion-electron method

Step 6: Scale the reactions so that they have an equal amount of electrons. In this case, it is already done.

Step 7: Add the reactions and cancel the electrons.

$$H_2O(l) + 2\,Ag(s) + Zn^{2+}(aq) \rightarrow Zn(s) + Ag_2O(aq) + 2\,H^+(aq).$$

Step 8: Add OH$^-$ to balance H$^+$. There are 2 net protons in this equation, so add 2 OH$^-$ ions to each side.

$$H_2O(l) + 2\,Ag(s) + Zn^{2+}(aq) + 2\,OH^-(aq) \rightarrow Zn(s) + Ag_2O(aq) + 2\,H^+(aq) + 2\,OH^-(aq).$$

Step 9: Combine OH$^-$ ions and H$^+$ ions that are present on the same side to form water.

$$\cancel{H_2O(l)} + 2\,Ag(s) + Zn^{2+}(aq) + 2\,OH^-(aq) \longrightarrow Zn(s) + Ag_2O(aq) + \cancel{2}H_2O(l)$$

Step 10: Cancel common terms.

$$2\,Ag(s) + Zn^{2+}(aq) + 2\,OH^-(aq) \rightarrow Zn(s) + Ag_2O(aq) + H_2O(l)$$

Home Assignments

Question 1: Use reduction half-reactions to write a balanced equation for the oxidation of zinc metal by permanganate ions in acid solution.

Question 2: Balance the following redox reaction in acidic condition

$$Cr_2O_7^{2-}(aq) + HNO_2(aq) \rightarrow Cr^{3+}(aq) + NO_3^-(aq)$$

Standard potentials and spontaneity

- ✓ The thermodynamic criterion of spontaneity is that, at constant temperature and pressure, the reaction Gibbs energy change, $\Delta_r G$ is negative.
- ✓ It is usually sufficient to consider the standard reaction Gibbs energy, $\Delta_r G°$, which is related to the equilibrium constant through

$$\Delta_r G^{\ominus} = -RT \ln K$$

- ✓ A negative value of $\Delta_r G°$ corresponds to $K > 1$ and therefore to a ‘favourable’ reaction.
- ✓ The overall chemical equation is the difference of two reduction half-reactions, the standard Gibbs energy of the overall reaction is the difference of the standard Gibbs energies of the two half-reactions.
- ✓ However, because reduction half-reactions always occur in pairs in any actual chemical reaction, only the difference in their standard Gibbs energies has any significance.
- ✓ Therefore, we can choose one half-reaction to have $\Delta_r G° = 0$ and report all other values relative to it.
- ✓ By convention, the specially chosen half-reaction is the reduction of hydrogen ions (at all temperatures) $\mathrm{H^+(aq) + e^- \rightarrow \frac{1}{2}H_2(g)} \quad \Delta_r G^{\ominus} = 0$

Standard potentials and spontaneity

- ✓ Standard reaction Gibbs energies may be measured by setting up a galvanic cell, an electrochemical cell in which a chemical reaction is used to generate an electric current.
- ✓ The potential difference between its electrodes is then measured. The **cathode** is the electrode at which **reduction** occurs and the **anode** is the site of **oxidation**.
- ✓ The measured potential difference can be converted to a reaction Gibbs energy by using

$$\Delta_r G = -\nu F E$$

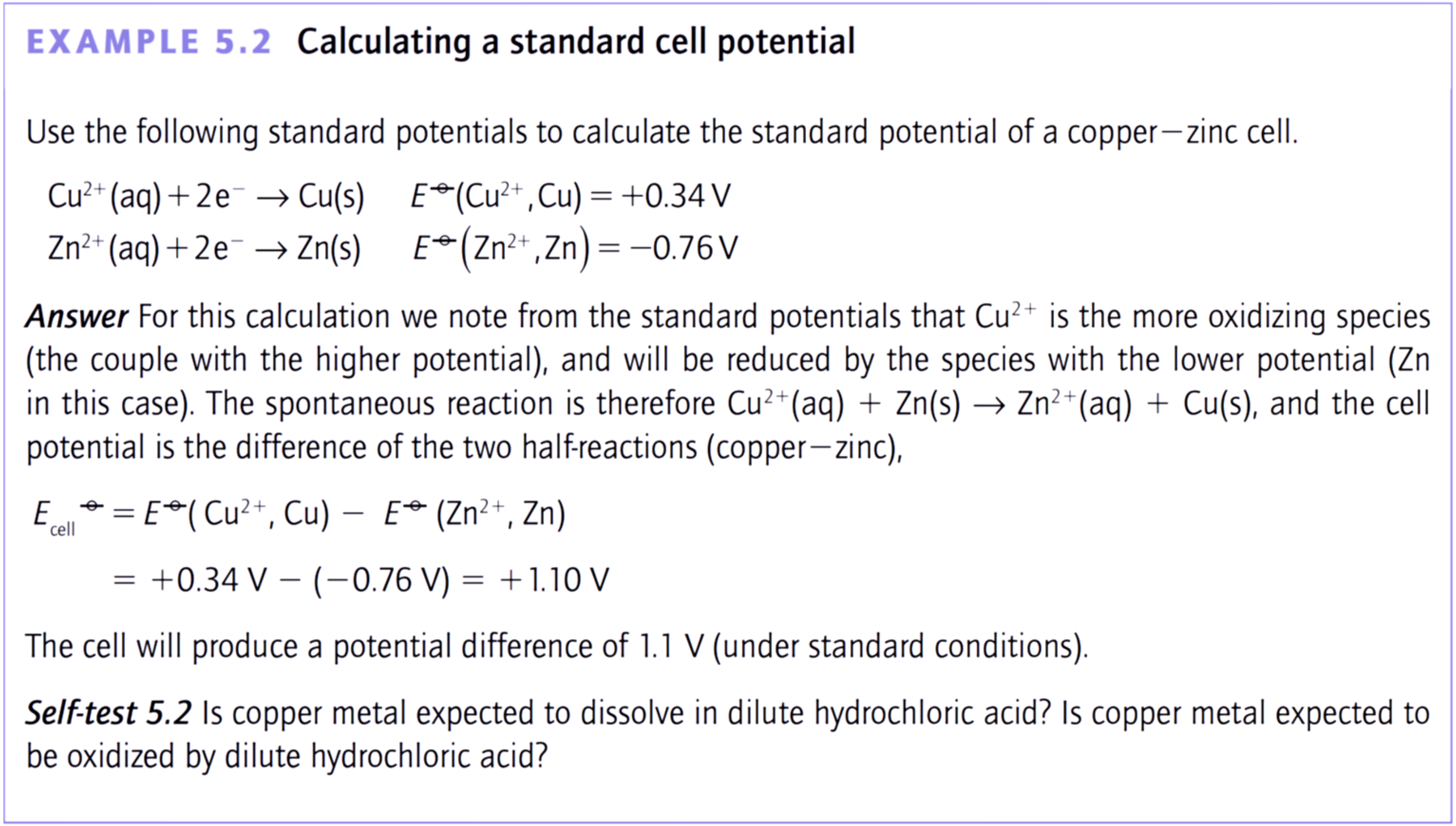
(where ν is the stoichiometric coefficient of the electrons transferred when the half-reactions are combined and F is Faraday’s constant (F 96.48 kC mol1).

- ✓ The potential that corresponds to the ΔrG° of a half-reaction is written E° , with

$$\Delta_r G^{\ominus} = -\nu F E^{\ominus}$$

- ✓ The potential E° is called the **standard potential** (or ‘**standard reduction potential**’)
- ✓ Because the standard reaction Gibbs energy is the difference of the $\Delta_r G°$ values for the two contributing half-reactions, $E_{cell}°$ (**standard cell potential**) for an overall reaction is also the difference of the two E°’s of the reduction half-reactions.
- ✓ A reaction is favourable if the corresponding **standard cell potential** is **positive**.

Combining half-reactions



EXAMPLE 5.2 Calculating a standard cell potential

Use the following standard potentials to calculate the standard potential of a copper–zinc cell.

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \quad E^{\ominus}(Cu^{2+},Cu) = +0.34\,V$

$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s) \quad E^{\ominus}(Zn^{2+},Zn) = -0.76\,V$

Answer For this calculation we note from the standard potentials that Cu^{2+} is the more oxidizing species (the couple with the higher potential), and will be reduced by the species with the lower potential (Zn in this case). The spontaneous reaction is therefore $Cu^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Cu(s)$, and the cell potential is the difference of the two half-reactions (copper–zinc),

$$E_{cell}^{\ominus} = E^{\ominus}(Cu^{2+}, Cu) - E^{\ominus}(Zn^{2+}, Zn)$$

$$= +0.34\ V - (-0.76\ V) = +1.10\ V$$

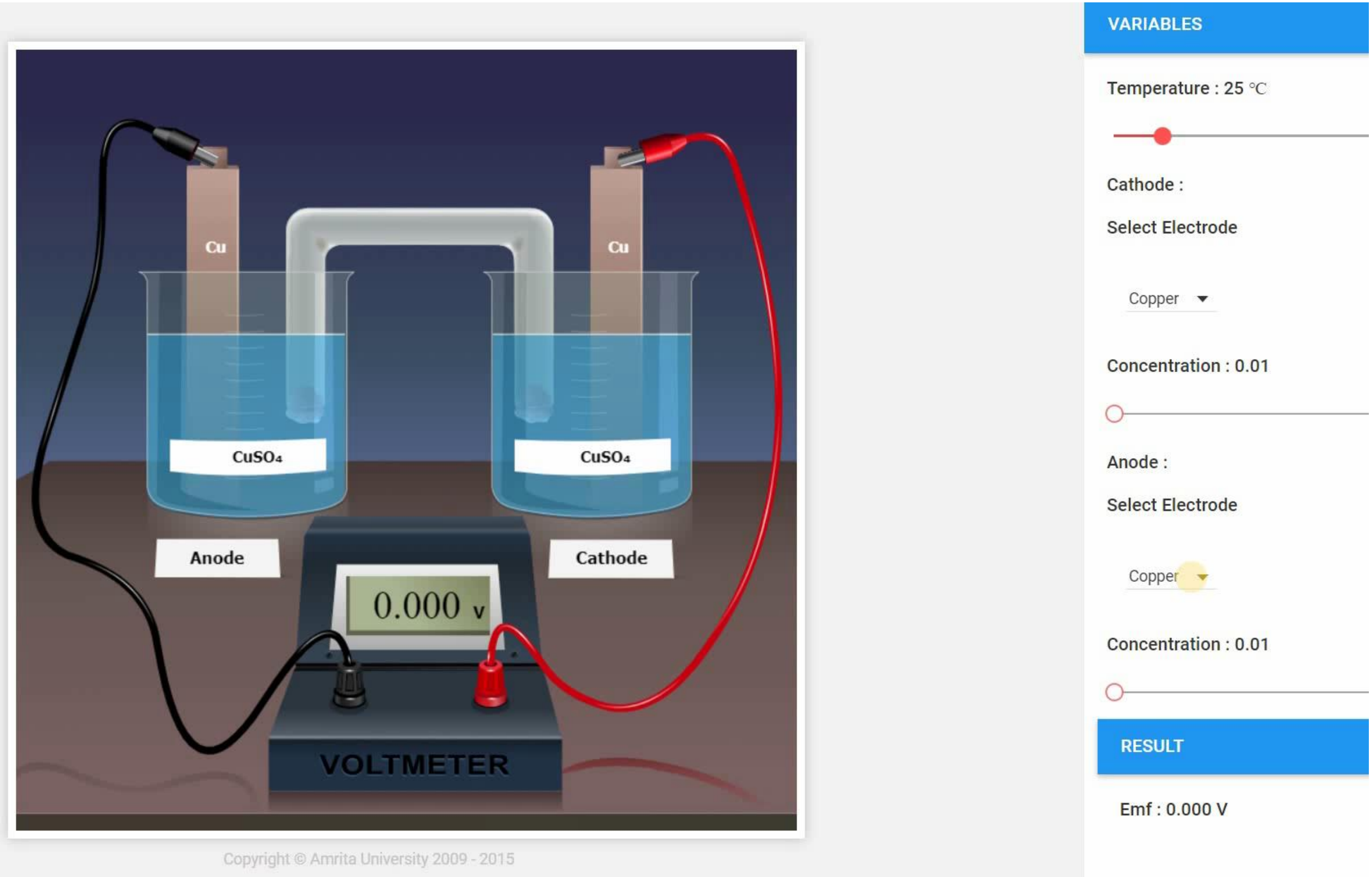
The cell will produce a potential difference of 1.1 V (under standard conditions).

Self-test 5.2 Is copper metal expected to dissolve in dilute hydrochloric acid? Is copper metal expected to be oxidized by dilute hydrochloric acid?

Spontaneity or Feasibility of Reaction

ΔG	K	E_{cell}^{o}	Reaction
Negative	> 1	Positive	Spontaneous
Zero	= 1	Zero	Equilibrium
Positive	< 1	Negative	Non-spontaneous

Combining half-reactions



VARIABLES

Temperature : 25 °C

Cathode :

Select Electrode

Copper

Concentration : 0.01

Anode :

Select Electrode

Copper

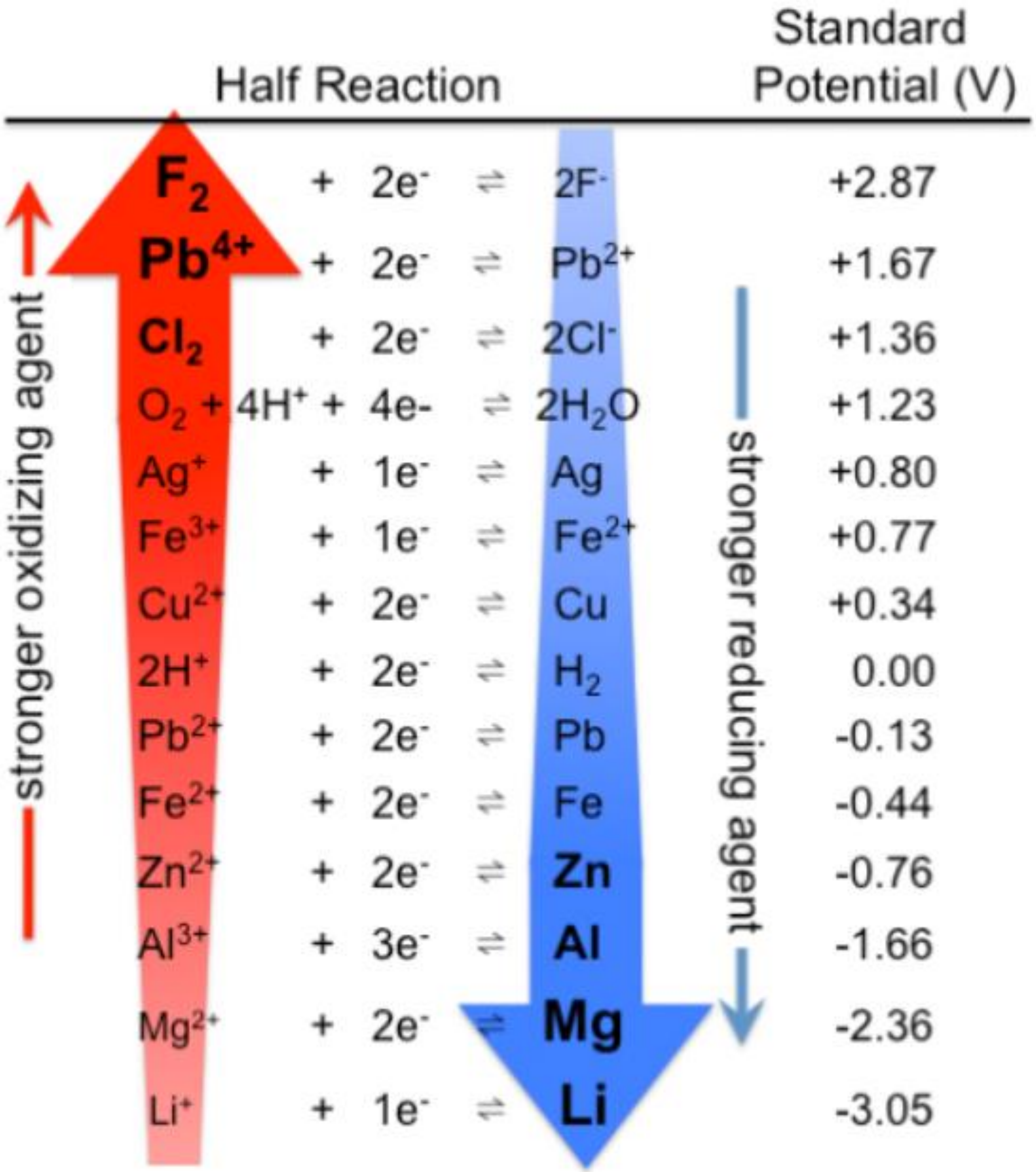
Concentration : 0.01

RESULT

Emf : 0.000 V

The electrochemical series

- *An important feature of the* ***electrochemical series*** *is that the reduced member of a couple has a thermodynamic tendency to reduce the oxidized member of any couple that lies above it in the series.*



Half Reaction	Standard Potential (V)
$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87
$Pb^{4+} + 2e^- \rightleftharpoons Pb^{2+}$	+1.67
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23
$Ag^+ + 1e^- \rightleftharpoons Ag$	+0.80
$Fe^{3+} + 1e^- \rightleftharpoons Fe^{2+}$	+0.77
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	-0.13
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	-0.44
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	-0.76
$Al^{3+} + 3e^- \rightleftharpoons Al$	-1.66
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	-2.36
$Li^+ + 1e^- \rightleftharpoons Li$	-3.05

The Nernst Equation

- ☐ To know the sign and value of $\Delta_r G$ at an arbitrary composition let us consider the following thermodynamic result

$$\Delta_r G = \Delta_r G^{\ominus} + RT \ln Q$$

where Q is the reaction quotient

$$a\,\mathrm{Ox}_A + b\,\mathrm{Red}_B \rightarrow a'\,\mathrm{Red}_A + b'\,\mathrm{Ox}_B \qquad Q = \frac{[\mathrm{Red}_A]^{a'}[\mathrm{Ox}_B]^{b'}}{[\mathrm{Ox}_A]^{a}[\mathrm{Red}_B]^{b}}$$

- ☐ The reaction quotient has the same form as the equilibrium constant K but the concentrations refer to an arbitrary stage of the reaction; at equilibrium, $Q = K$.
- ☐ The reaction is spontaneous at an arbitrary stage if $\Delta_r G < 0$.
- ☐ In terms of the potential of the corresponding cell the **Nernst equation** is

$$E_{\mathrm{cell}} = E_{\mathrm{cell}}^{\ominus} - \frac{RT}{\nu F} \ln Q$$

where $E_{cell} = -\Delta_r G/\nu F$ and $E_{cell}° = -\Delta_r G°/\nu F$

- ☐ A reaction is spontaneous if, under the prevailing conditions, $E_{cell} > 0$, for then $\Delta_r G < 0$.

The Nernst Equation

- At equilibrium $E_{\mathrm{cell}} = 0$ and $Q = K$,

$$\ln K = \frac{\nu F E_{\mathrm{cell}}^{\ominus}}{RT}$$

- The values of K that correspond to cell potentials in the range -2 to +2 V, with $\nu = 1$ and at 25˚C

$E^{\ominus}/\mathrm{V}$	K
$+2$	10^{34}
$+1$	10^{17}
0	1
-1	10^{-17}
-2	10^{-34}

Disproportionation

- Standard potentials can be used to define the inherent stability and instability of different oxidation states.
- Redox reaction in which the oxidation number of an element is simultaneously raised and lowered are termed **disproportionation**.
- ***The element undergoing disproportionation serves as its own oxidizing and reducing agent.***
- *Consider the following example*

$$2\,\mathrm{Cu^{+}(aq)} \rightarrow \mathrm{Cu^{2+}(aq)} + \mathrm{Cu(s)}$$

This reaction is the difference of the following two half-reactions:

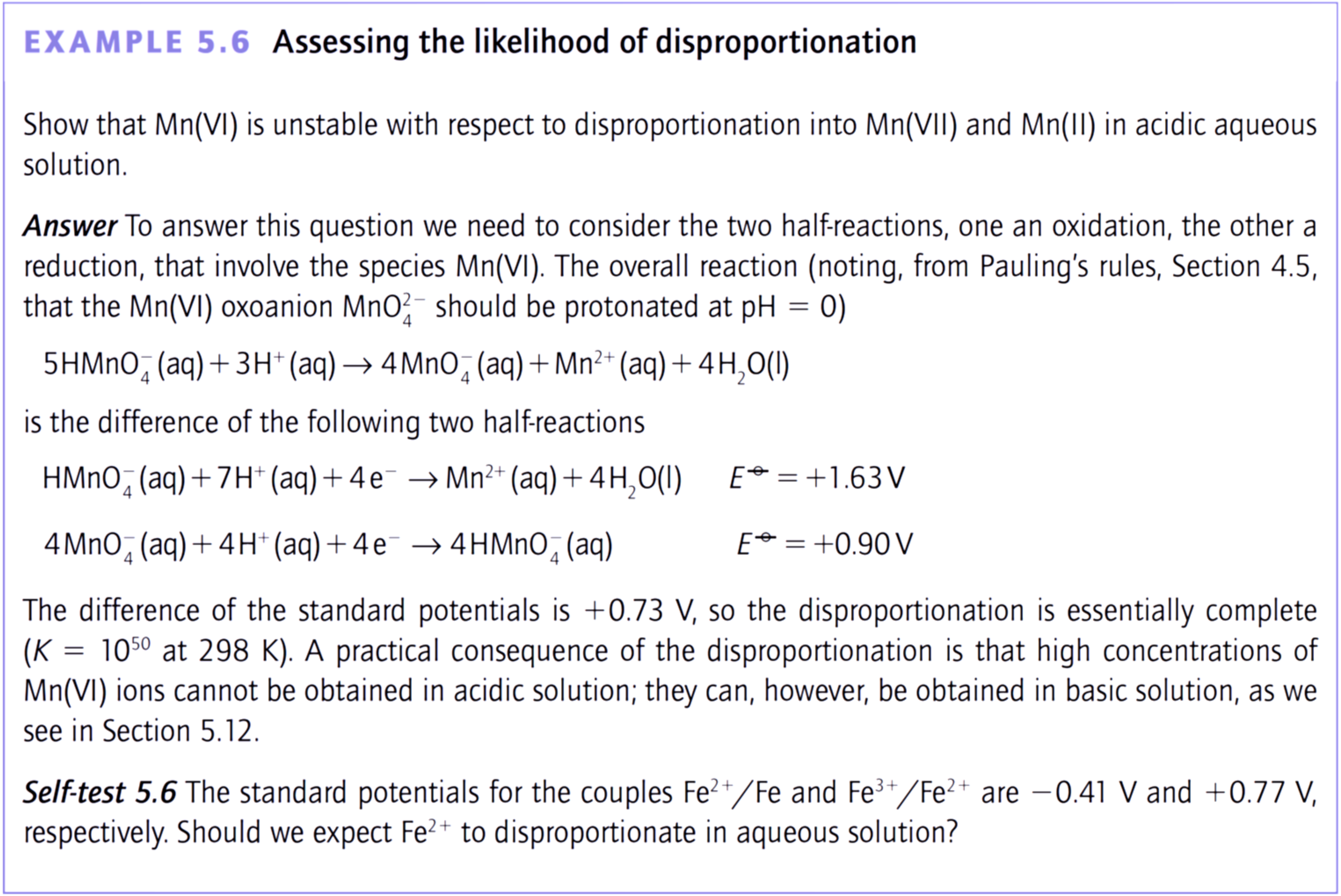
$$\mathrm{Cu^{+}(aq)} + \mathrm{e^{-}} \rightarrow \mathrm{Cu(s)} \qquad E^{\ominus} = +0.52\ \mathrm{V}$$

$$\mathrm{Cu^{2+}(aq)} + \mathrm{e^{-}} \rightarrow \mathrm{Cu^{+}(aq)} \qquad E^{\ominus} = +0.16\ \mathrm{V}$$

Because $E_{\mathrm{cell}}^{\ominus} = 0.52\ \mathrm{V} - 0.16\ \mathrm{V} = +0.36\ \mathrm{V}$ for the disproportionation reaction

- *Since, $E_{cell}° = +\ 0.36\ V\ (K = 1.3 \times 10_6$ at 298 K) so the reaction is highly favorable.*

Disproportionation



EXAMPLE 5.6 Assessing the likelihood of disproportionation

Show that Mn(VI) is unstable with respect to disproportionation into Mn(VII) and Mn(II) in acidic aqueous solution.

Answer To answer this question we need to consider the two half-reactions, one an oxidation, the other a reduction, that involve the species Mn(VI). The overall reaction (noting, from Pauling's rules, Section 4.5, that the Mn(VI) oxoanion MnO_4^{2-} should be protonated at pH = 0)

$$5HMnO_4^-(aq) + 3H^+(aq) \rightarrow 4MnO_4^-(aq) + Mn^{2+}(aq) + 4H_2O(l)$$

is the difference of the following two half-reactions

$$HMnO_4^-(aq) + 7H^+(aq) + 4e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l) \qquad E^\ominus = +1.63\,V$$

$$4MnO_4^-(aq) + 4H^+(aq) + 4e^- \rightarrow 4HMnO_4^-(aq) \qquad E^\ominus = +0.90\,V$$

The difference of the standard potentials is +0.73 V, so the disproportionation is essentially complete ($K = 10^{50}$ at 298 K). A practical consequence of the disproportionation is that high concentrations of Mn(VI) ions cannot be obtained in acidic solution; they can, however, be obtained in basic solution, as we see in Section 5.12.

Self-test 5.6 The standard potentials for the couples Fe^{2+}/Fe and Fe^{3+}/Fe^{2+} are −0.41 V and +0.77 V, respectively. Should we expect Fe^{2+} to disproportionate in aqueous solution?

Comproportionation

- In **comproportionation**, the *reverse of disproportionation*, two species with the same element in different oxidation states form a product in which the element is in an intermediate oxidation state.
- *An example is*

$$\mathrm{Ag^{2+}(aq) + Ag(s) \rightarrow 2\,Ag^{+}(aq)} \qquad E_{\mathrm{cell}}^{\ominus} = +1.18\,\mathrm{V}$$

The large positive potential indicates that Ag(II) and Ag(0) are completely converted to Ag(I) in aqueous solution ($K = 1 \times 10^{20}$ at 298 K).

The diagrammatic presentation of potential data

Latimer diagrams

- **Latimer diagrams** are useful for summarizing quantitative data for individual elements.
- In a **Latimer diagram** (also known as a *reduction potential diagram*) for an element, the *numerical value of the standard potential* (in volts) is *written over a horizontal line* (or arrow) connecting species with the element in different oxidation states.
- The most highly oxidized form of the element is on the left, and in species to the right the element is in successively lower oxidation states.
- A Latimer diagram summarizes a great deal of information in a compact form and shows the relationships between the various species in a particularly clear manner.
- The Latimer diagram for chlorine in acidic solution is

$$\underset{+7}{\mathrm{ClO_4^-}} \xrightarrow{+1.20} \underset{+5}{\mathrm{ClO_3^-}} \xrightarrow{+1.18} \underset{+3}{\mathrm{HClO_2}} \xrightarrow{+1.65} \underset{+1}{\mathrm{HClO}} \xrightarrow{+1.67} \underset{0}{\mathrm{Cl_2}} \xrightarrow{+1.36} \underset{-1}{\mathrm{Cl^-}}$$

- Oxidation numbers are sometimes written under (or over) the species.
- Conversion of a Latimer diagram to a half-reaction often involves balancing elements by including the predominant species present in acidic aqueous solution (H^+ and H_2O).

Latimer diagrams

- The standard state for a couple includes the condition that pH = 0. For example

$$\mathrm{HClO} \xrightarrow{+1.67} \mathrm{Cl_2}$$

denotes

$$2\,\mathrm{HClO(aq)} + 2\,\mathrm{H^+(aq)} + 2\,\mathrm{e^-} \rightarrow \mathrm{Cl_2(g)} + 2\,\mathrm{H_2O(l)} \qquad E^{\ominus} = +1.67\ \mathrm{V}$$

Similarly,

$$\mathrm{ClO_4^-} \xrightarrow{+1.20} \mathrm{ClO_3^-}$$

denotes

$$\mathrm{ClO_4^-(aq)} + 2\,\mathrm{H^+(aq)} + 2\,\mathrm{e^-} \rightarrow \mathrm{ClO_3^-(aq)} + \mathrm{H_2O(l)} \qquad E^{\ominus} = +1.20\ \mathrm{V}$$

- In basic aqueous solution (corresponding to pOH = 0 and therefore pH = 14), the Latimer diagram for chlorine is

$$\underset{+7}{\mathrm{ClO_4^-}} \xrightarrow{+0.37} \underset{+5}{\mathrm{ClO_3^-}} \xrightarrow{+0.30} \underset{+3}{\mathrm{ClO_2^-}} \xrightarrow{+0.68} \underset{+1}{\mathrm{ClO^-}} \xrightarrow{+0.42} \underset{0}{\mathrm{Cl_2}} \xrightarrow{+1.36} \underset{-1}{\mathrm{Cl^-}}$$

- Note that the value for the Cl_2/Cl^- couple is the same as in acidic solution because its half reaction does not involve the transfer of protons.

Latimer diagrams: Nonadjacent species

- ☐ The standard potential of a nonadjacent couple in the Latimer diagram can be obtained as follows:

$$E^{\ominus}(a+b) = \frac{\nu(a)E^{\ominus}(a) + \nu(b)E^{\ominus}(b)}{\nu(a) + \nu(b)}$$

■ **A brief example.** To use the Latimer diagram to calculate the value of $E^{\ominus}$ for the ClO_2^-/Cl_2 couple in basic aqueous solution we note the following two standard potentials:

$$ClO_2^-(aq) + 2H^+(aq) + 2e^- \rightarrow ClO^-(aq) + H_2O(l) \qquad E^{\ominus}(a) = +0.68\,V$$

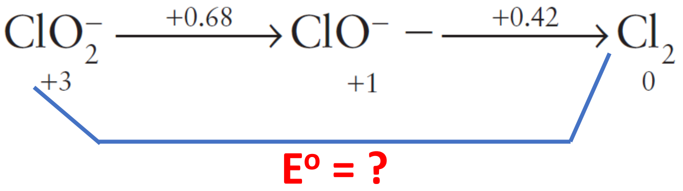
$$ClO^-(aq) + e^- \rightarrow \tfrac{1}{2}Cl_2(aq) \qquad E^{\ominus}(b) = +0.42\,V$$

Their sum,

$$ClO_2^-(aq) + 2\,H^+(aq) + 3\,e^- \rightarrow \tfrac{1}{2}\,Cl_2(g) + H_2O(l)$$

is the half-reaction for the couple we require. We see that $\nu(a) = 2$ and $\nu(b) = 1$. It follows from eqn 5.15 that the standard potential of the ClO/Cl^- couple is

$$E^{\ominus} = \frac{(2)(0.68\,V) + (1)(0.42\,V)}{3} = +0.59\,V$$ ■



$$\underset{+3}{ClO_2^-} \xrightarrow{+0.68} \underset{+1}{ClO^-} \xrightarrow{+0.42} \underset{0}{Cl_2}$$

E° = ?

Latimer diagrams: Disproportionation

- A species has a tendency to disproportionate into its two neighbours if the potential on the right of the species in a Latimer diagram is higher than that on the left.

Consider the disproportionation

$$2\,\mathrm{M}^{+}(\mathrm{aq}) \rightarrow \mathrm{M}(\mathrm{s}) + \mathrm{M}^{2+}(\mathrm{aq})$$

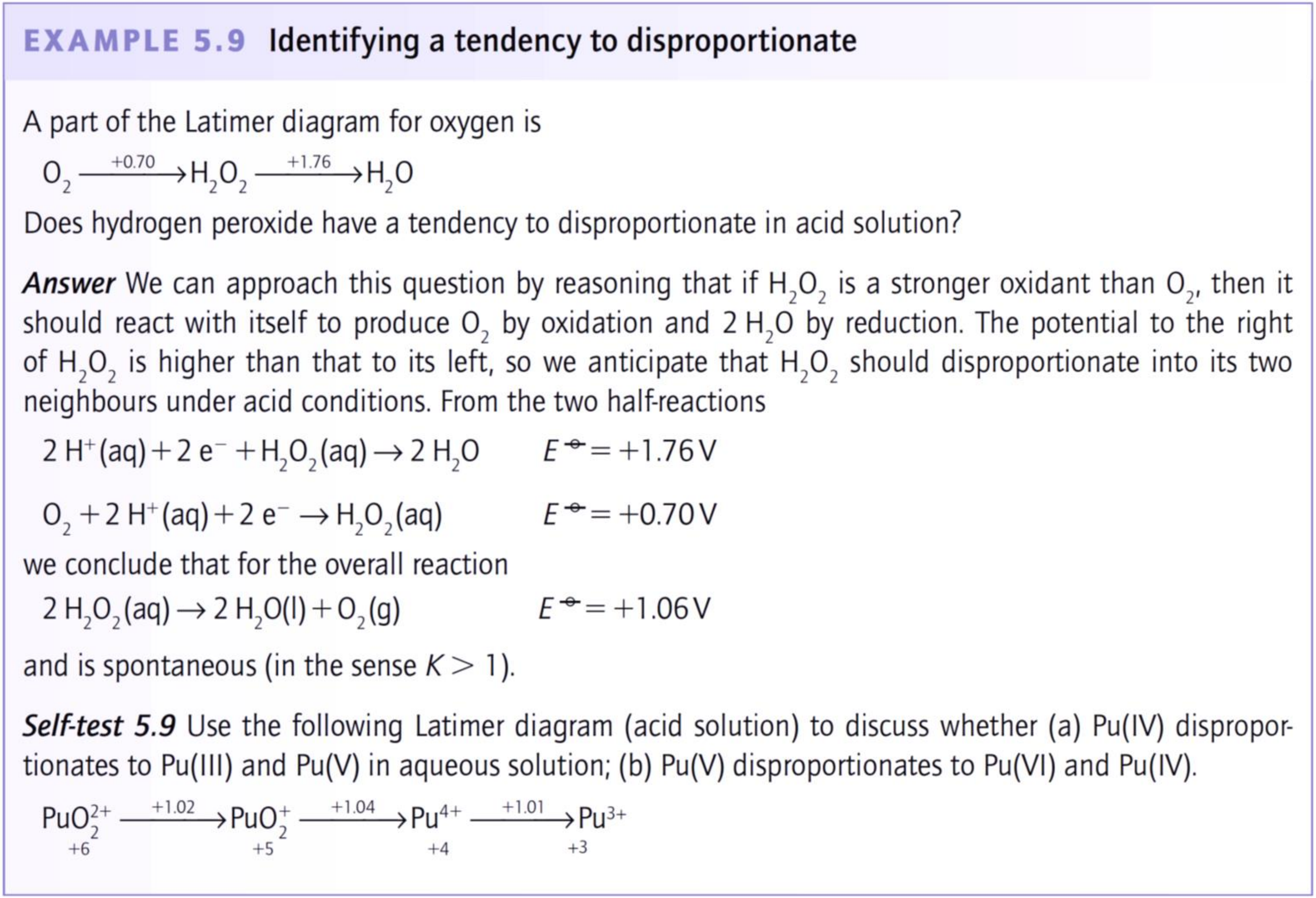
This reaction has $K > 1$ if $E^{\ominus} > 0$. To analyse this criterion in terms of a Latimer diagram, we express the overall reaction as the difference of two half-reactions:

$$\mathrm{M}^{+}(\mathrm{aq}) + \mathrm{e}^{-} \rightarrow \mathrm{M}(\mathrm{s}) \qquad E^{\ominus}(\mathrm{R})$$

$$\mathrm{M}^{2+}(\mathrm{aq}) + \mathrm{e}^{-} \rightarrow \mathrm{M}^{+}(\mathrm{aq}) \qquad E^{\ominus}(\mathrm{L})$$

- The standard potential for the overall reaction is E° = E°(R) - E°(L), which is positive if E°(R) > E°(L).
- A species is inherently unstable (that is, it has a tendency to disproportionate into its two neighbours) if the potential on the right of the species is higher than the potential on the left.

Latimer diagrams: Disproportionation



EXAMPLE 5.9 Identifying a tendency to disproportionate

A part of the Latimer diagram for oxygen is

$$O_2 \xrightarrow{+0.70} H_2O_2 \xrightarrow{+1.76} H_2O$$

Does hydrogen peroxide have a tendency to disproportionate in acid solution?

Answer We can approach this question by reasoning that if H_2O_2 is a stronger oxidant than O_2, then it should react with itself to produce O_2 by oxidation and 2 H_2O by reduction. The potential to the right of H_2O_2 is higher than that to its left, so we anticipate that H_2O_2 should disproportionate into its two neighbours under acid conditions. From the two half-reactions

$$2\,H^+(aq) + 2\,e^- + H_2O_2(aq) \rightarrow 2\,H_2O \qquad E^\ominus = +1.76\,V$$

$$O_2 + 2\,H^+(aq) + 2\,e^- \rightarrow H_2O_2(aq) \qquad E^\ominus = +0.70\,V$$

we conclude that for the overall reaction

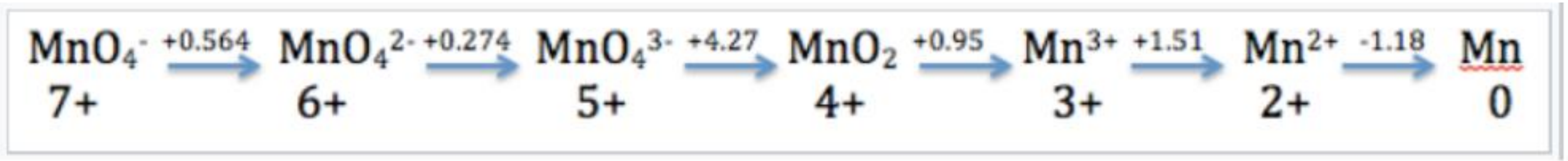
$$2\,H_2O_2(aq) \rightarrow 2\,H_2O(l) + O_2(g) \qquad E^\ominus = +1.06\,V$$

and is spontaneous (in the sense $K > 1$).

Self-test 5.9 Use the following Latimer diagram (acid solution) to discuss whether (a) Pu(IV) disproportionates to Pu(III) and Pu(V) in aqueous solution; (b) Pu(V) disproportionates to Pu(VI) and Pu(IV).

$$\underset{+6}{PuO_2^{2+}} \xrightarrow{+1.02} \underset{+5}{PuO_2^{+}} \xrightarrow{+1.04} \underset{+4}{Pu^{4+}} \xrightarrow{+1.01} \underset{+3}{Pu^{3+}}$$

Latimer diagram for manganese in acidic solution (pH = 0)



The Latimer diagram for Mn illustrates its standard reduction potentials (in 1 M acid) in oxidation states from +7 to 0.

The Latimer diagram compresses into shorthand notation all the standard potentials for redox reactions of the element Mn. For example, the entry that connects Mn^{2+} and Mn gives the potential for the half-cell reaction:

$Mn^{2+}_{(aq)} + 2\,e^- \longrightarrow Mn_{(s)}$ $E_{1/2}° = -1.18V$

and the entry connecting Mn^{4+} and Mn^{3+} represents the reaction:

$MnO_{2(s)} + 4\,H^+_{(aq)} + e^- \longrightarrow Mn^{3+}_{(aq)} + 2\,H_2O_{(l)}$, :$E_{1/2}° = +0.95V$

We can also calculate values for **multi-electron reactions** by first adding ΔG°(=-nFE°) values and then dividing by the total number of electrons

For example, for the 5-electron reduction of MnO_4^- to Mn^{2+}, we write

$$E^o = \frac{1(0.564)+1(0.274)+1(4.27)+1(0.95)+1(1.51)}{5} = +1.51V$$

and for the three-electron reduction of MnO_4^-(aq) to MnO_2(s),

$$E^o = \frac{1(0.564)+1(0.274)+1(4.27)}{3} = +1.70V$$

Remember to divide by the number of electrons involved in the oxidation number change (5 and 3 for the above equations).

Latimer diagram: Application

$$\begin{array}{cccccc} 0 & & -1 & & -2 & \\ O_2 & \xrightarrow{0.695} & H_2O_2 & \xrightarrow{1.763} & H_2O & \text{in acid} \\ 0 & & -1 & & -2 & \\ O_2 & \xrightarrow{-0.0649} & HO_2^- & \xrightarrow{0.867} & OH^- & \text{in base} \end{array}$$

EXAMPLE 8.1

Determine the standard reduction potential for the O_2/H_2O redox couple in acid:

$$O_2 + 4\ H^+ + 4e^- \longrightarrow 2\ H_2O \qquad E_3^o = ?$$

These species share H_2O_2 in their corresponding reduction half-reactions; addition of these half-reactions provides the O_2/H_2O half-reaction:

$$\begin{array}{llll} (1) & O_2 + 2H^+ + 2e^- & \longrightarrow\ H_2O_2 & E_1^o = 0.695\ V \\ \underline{(2)} & \underline{H_2O_2 + 2H^+ + 2e^-} & \underline{\longrightarrow\ 2H_2O} & \underline{E_2^o = 1.763\ \mathrm{V}} \\ (3) & O_2 + 4H^+ + 4e^- & \longrightarrow\ 2H_2O & E_3^o = ? \end{array}$$

Because voltage is not a state function, we obtain E_3^o by adding the ΔG^o values, noting that $\Delta G^o = -nFE^o$:

$$\Delta G_3^o = \Delta G_1^o + \Delta G_2^o$$

$$-nFE_3^o = (-nFE_1^o) + (-nFE_2^o) \qquad (F = 96485\ C/mol)$$

$$(-4\ mol)F(E_3^o) = (-2\ mol)F(0.695\ \mathrm{V}) + (-2\ mol)F(1.763\ \mathrm{V})$$

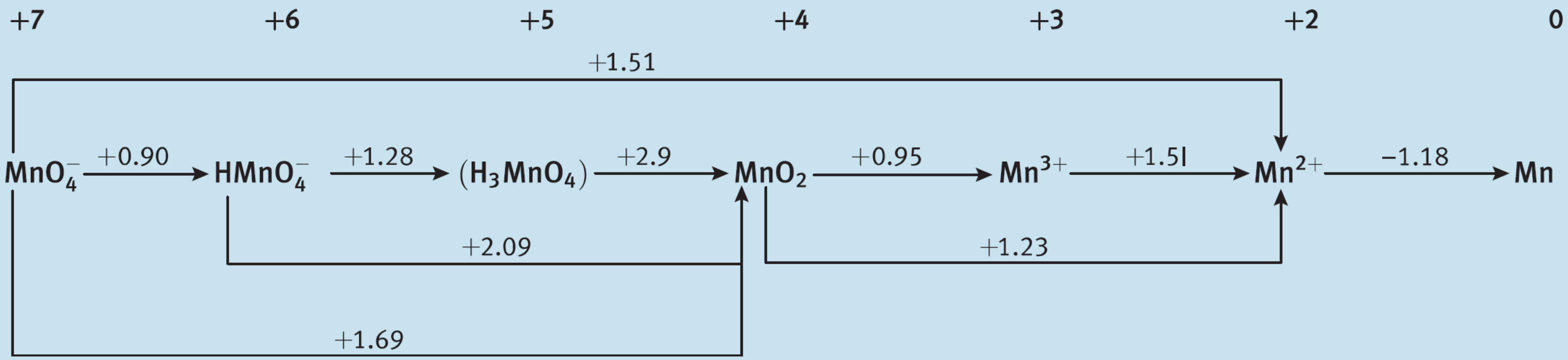
$$E_3^o = 1.23\ \mathrm{V}$$

(E_3^o is the average of E_1^o and E_2^o in this case only because the summed half-reactions each require the same number of moles of electrons.)

EXERCISE 8.1 Determine the standard reduction potential for $H_2O + 2e^- \longrightarrow OH^- + H^-$ in basic solution.

Latimer diagram for Mn

Acidic solution



+7 +6 +5 +4 +3 +2 0

$$MnO_4^- \xrightarrow{+0.90} HMnO_4^- \xrightarrow{+1.28} (H_3MnO_4) \xrightarrow{+2.9} MnO_2 \xrightarrow{+0.95} Mn^{3+} \xrightarrow{+1.5\mathrm{l}} Mn^{2+} \xrightarrow{-1.18} Mn$$

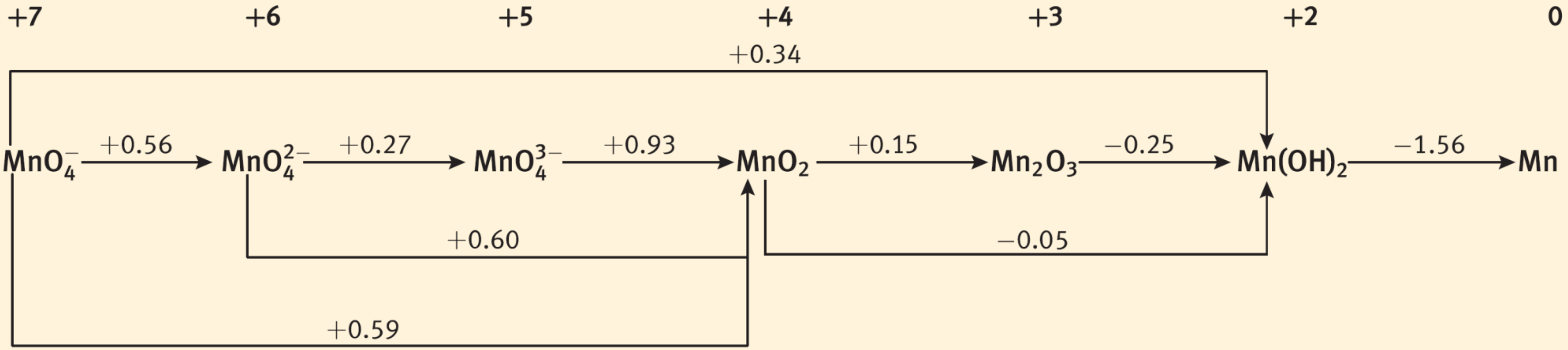
$$MnO_4^- \xrightarrow{+1.51} Mn^{2+}$$

$$HMnO_4^- \xrightarrow{+2.09} MnO_2$$

$$MnO_2 \xrightarrow{+1.23} Mn^{2+}$$

$$MnO_4^- \xrightarrow{+1.69} MnO_2$$

Basic solution



+7 +6 +5 +4 +3 +2 0

$$MnO_4^- \xrightarrow{+0.56} MnO_4^{2-} \xrightarrow{+0.27} MnO_4^{3-} \xrightarrow{+0.93} MnO_2 \xrightarrow{+0.15} Mn_2O_3 \xrightarrow{-0.25} Mn(OH)_2 \xrightarrow{-1.56} Mn$$

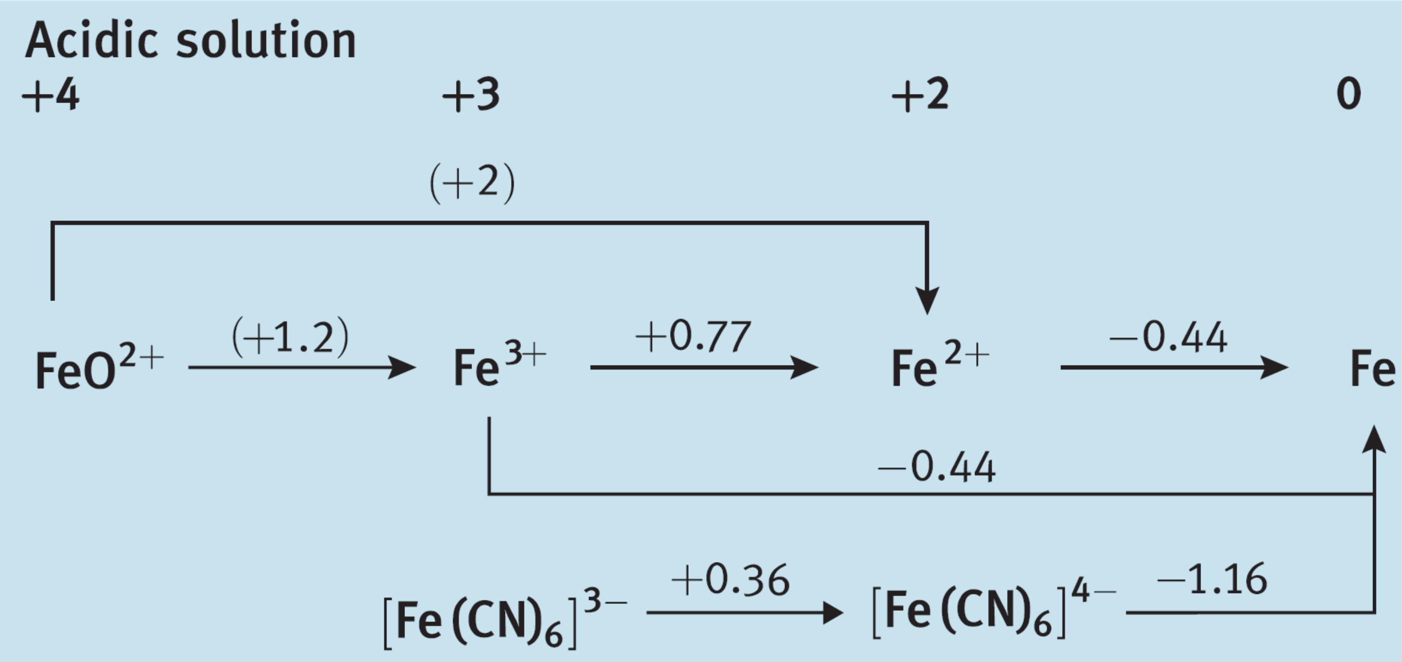
$$MnO_4^- \xrightarrow{+0.34} Mn(OH)_2$$

$$MnO_4^{2-} \xrightarrow{+0.60} MnO_2$$

$$MnO_2 \xrightarrow{-0.05} Mn(OH)_2$$

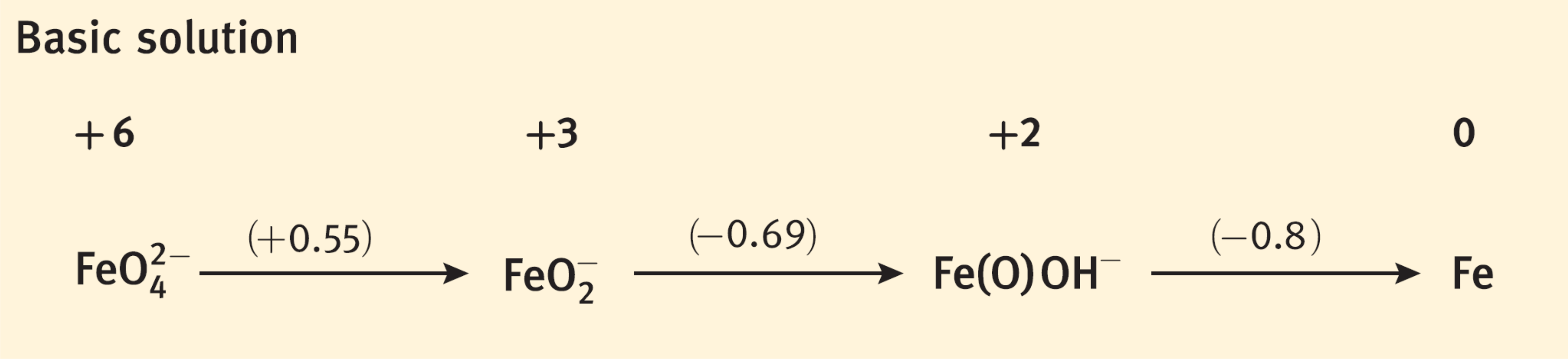
$$MnO_4^- \xrightarrow{+0.59} MnO_2$$

Latimer diagram for Fe



Acidic solution

$$\begin{tikzcd}
+4 & +3 & +2 & 0 \\
FeO^{2+} \arrow[r, "(+1.2)"] \arrow[rr, bend left, "(+2)"] & Fe^{3+} \arrow[r, "+0.77"] \arrow[rr, bend right, "-0.44"'] & Fe^{2+} \arrow[r, "-0.44"] & Fe \\
 & {[Fe(CN)_6]^{3-}} \arrow[r, "+0.36"] & {[Fe(CN)_6]^{4-}} \arrow[ur, "-1.16"] &
\end{tikzcd}$$



Basic solution

$$\begin{tikzcd}
+6 & +3 & +2 & 0 \\
FeO_4^{2-} \arrow[r, "(+0.55)"] & FeO_2^{-} \arrow[r, "(-0.69)"] & Fe(O)OH^{-} \arrow[r, "(-0.8)"] & Fe
\end{tikzcd}$$

Latimer diagram for Cu

Acidic solution

+2 **+1** **0**

$$\begin{tikzcd}
Cu^{2+} \arrow[r, "+0.159"] \arrow[rr, bend right, "+0.340"'] & Cu^{+} \arrow[r, "+0.520"] & Cu
\end{tikzcd}$$

$$\begin{tikzcd}
{[Cu(NH_3)_4]^{2+}} \arrow[r, "+0.10"] & {[Cu(NH_3)_2]^{+}} \arrow[r, "-0.10"] & Cu
\end{tikzcd}$$

$$\begin{tikzcd}
Cu^{2+} \arrow[r, "+1.12"] & {[Cu(CN)_2]^{+}} \arrow[r, "-0.44"] & Cu
\end{tikzcd}$$

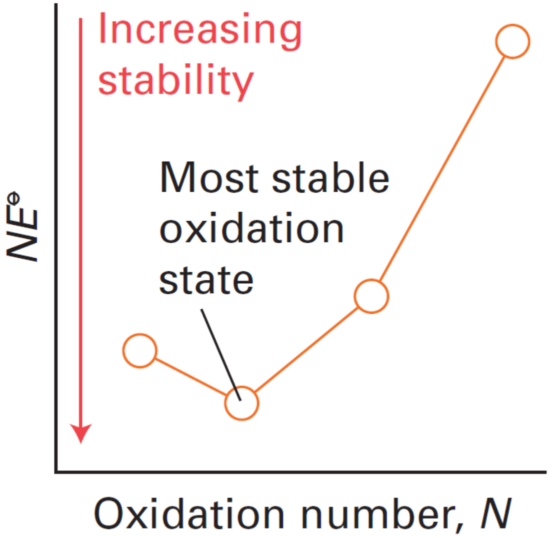
Basic solution

$$\begin{tikzcd}
Cu(OH)_2 \arrow[r, "-1.22"] & Cu_2O \arrow[r, "-1.37"] & Cu
\end{tikzcd}$$

The diagrammatic presentation of potential data

Frost diagrams

- ☐ A **Frost diagram** (also known as ***an oxidation state diagram***) of an element X is a plot of NE° for the couple X(N)/X(0) against the oxidation number, N, of the element.
- ☐ The general form of a Frost diagram is shown below:



- ☐ Frost diagrams depict whether a particular species X(N) is a good oxidizing agent or reducing agent.
- ☐ They also provide an important guide for identifying the oxidation states of an element that are inherently stable or unstable.

Frost diagram: Gibbs energies of formation for different oxidation states

- Let us consider the following reduction half-reaction

$$\mathrm{X}(N) + N\mathrm{e}^{-} \rightarrow \mathrm{X}(0)$$

- Since $NE° = -\Delta_rG° /F$, where $\Delta_rG°$ is the standard reaction Gibbs energy so, a Frost diagram can also be regarded as a plot of standard reaction Gibbs energy against oxidation number.

- Consequently, the most stable states of an element in aqueous solution correspond to species that lie lowest in its Frost diagram.

Frost diagram from *Latimer diagram*

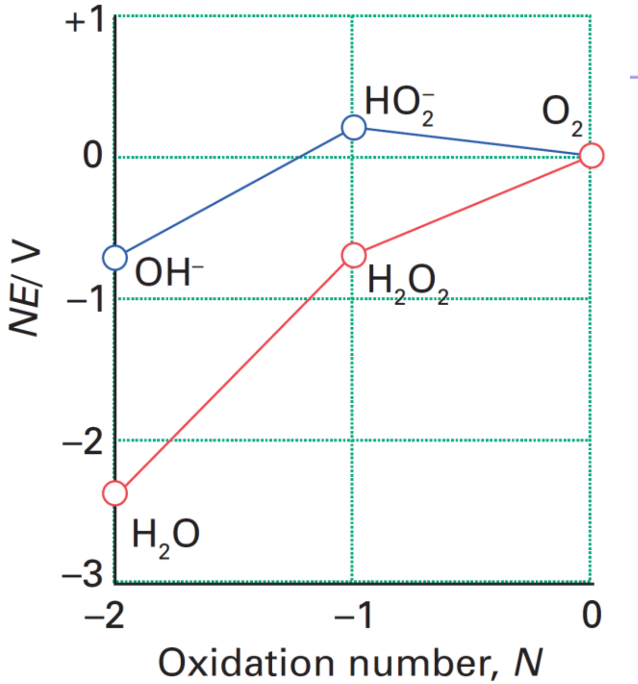
EXAMPLE 5.10 Constructing a Frost diagram

Construct a Frost diagram for oxygen from the Latimer diagram in Example 5.9.

Answer We begin by placing the element in its zero oxidation state (O_2) at the origin for the $NE^\ominus$ and N axes. For the reduction of O_2 to H_2O_2 (for which $N = -1$), $E^\ominus = +0.70$ V, so $NE^\ominus = -0.70$ V. Because the oxidation number of O in H_2O is -2 and $E^\ominus$ for the O_2/H_2O couple is $+1.23$ V, $NE^\ominus$ at $N = -2$ $E^\ominus = -2.46$ V. These results are plotted in Fig. 5.7.

Self-test 5.10 Construct a Frost diagram from the Latimer diagram for Tl:

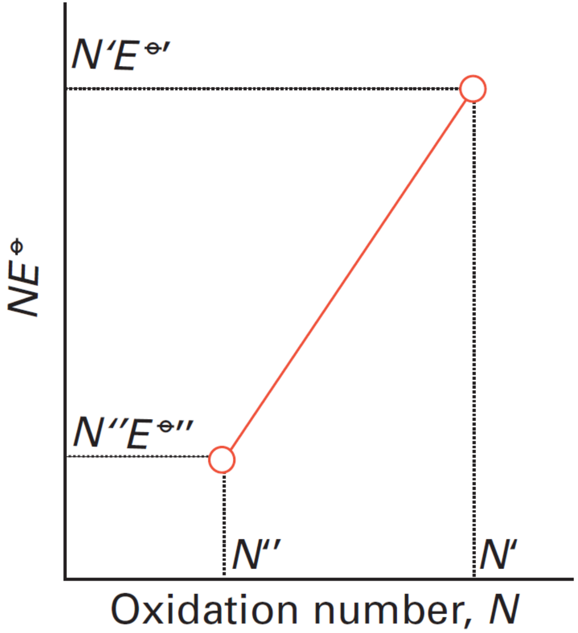
$$Tl^{3+} \xrightarrow{+1.25} Tl^{+} \xrightarrow{-0.34} Tl$$



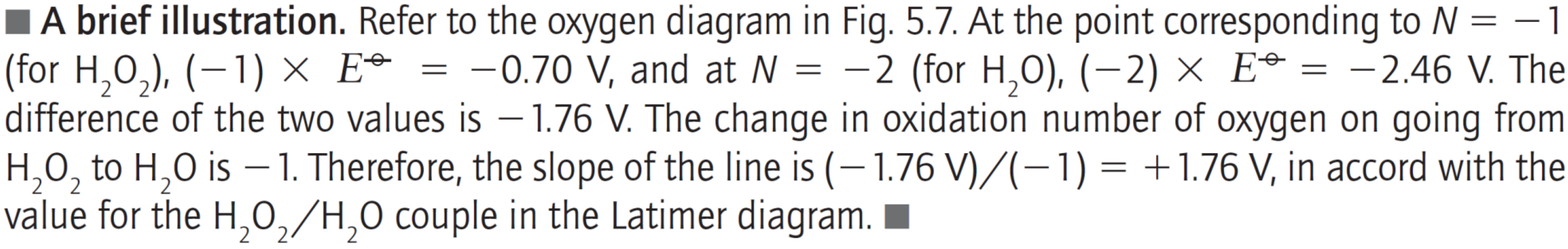
The Frost diagram for oxygen in acidic solution (red line, pH = 0) and alkaline solution (blue line, pH = 14).

Frost diagram: Interpretation

Let us consider the general structure of a region of a Frost diagram



1. The slope of the line joining any two points in a Frost diagram is equal to the standard potential of the couple formed by the two species that the points represent. (*The steeper the line joining two points (left to right) in a Frost diagram, the higher the standard potential*).



■ **A brief illustration.** Refer to the oxygen diagram in Fig. 5.7. At the point corresponding to $N = -1$ (for H_2O_2), $(-1) \times E^{\ominus} = -0.70$ V, and at $N = -2$ (for H_2O), $(-2) \times E^{\ominus} = -2.46$ V. The difference of the two values is -1.76 V. The change in oxidation number of oxygen on going from H_2O_2 to H_2O is -1. Therefore, the slope of the line is $(-1.76\text{ V})/(-1) = +1.76$ V, in accord with the value for the H_2O_2/H_2O couple in the Latimer diagram. ■

Frost diagram: Interpretation

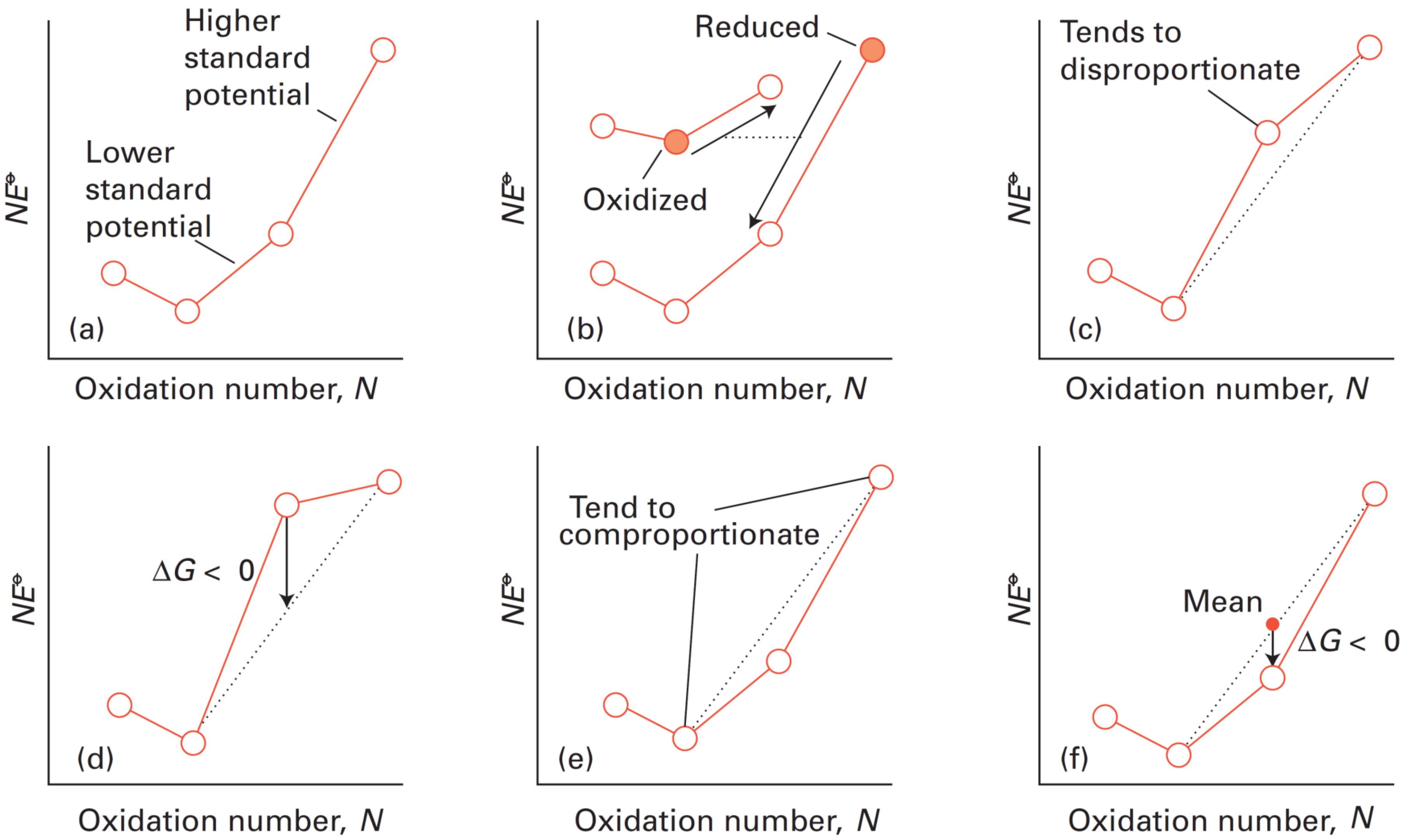


Figure A. *The interpretation of a Frost diagram to gauge (a) reduction potential, (b) tendency towards oxidation and reduction, (c, d) disproportionation, and (e, f) comproportionation.*

Frost diagram: Interpretation

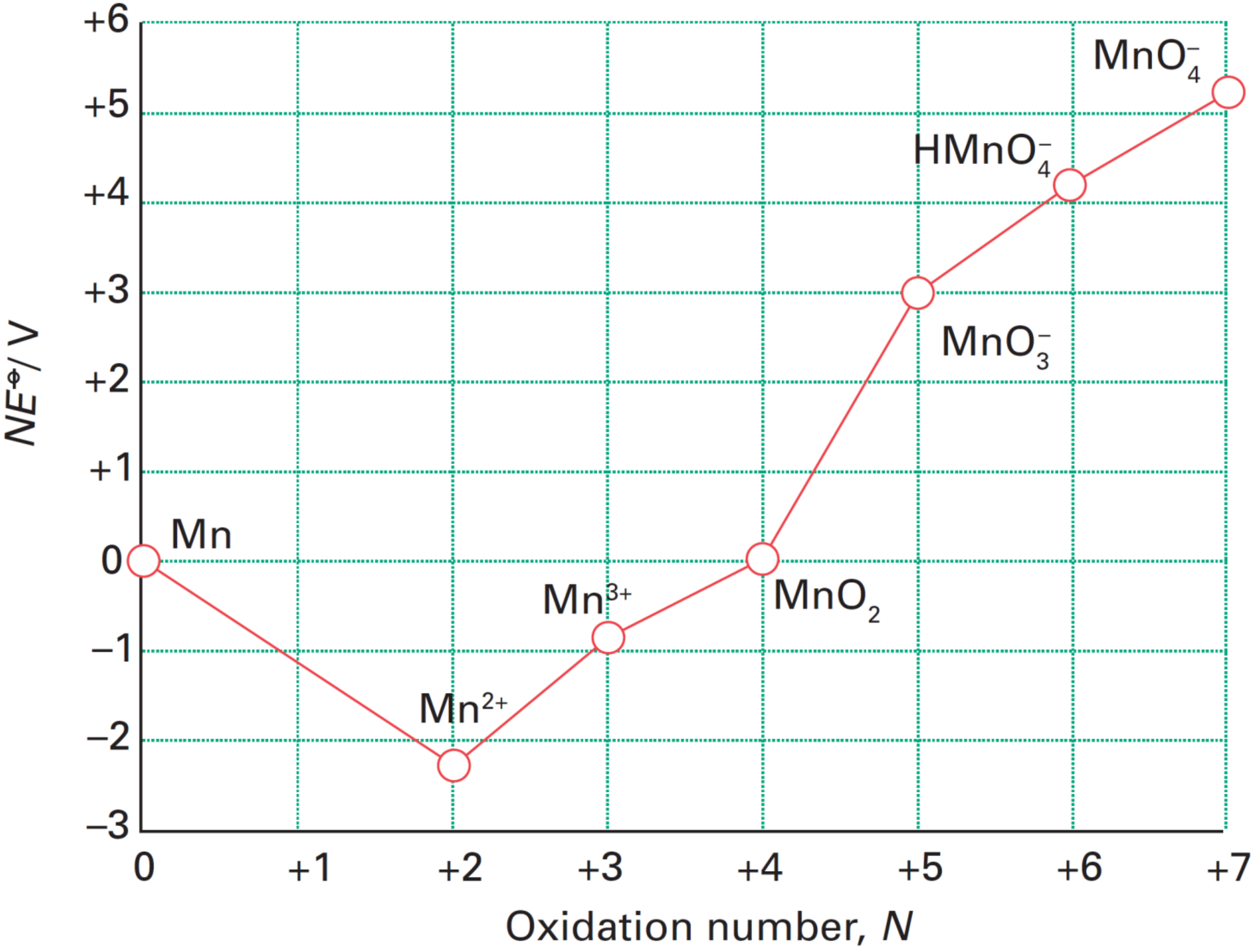
2. The oxidizing agent in the couple with the more positive slope (the more positive E°) is liable to undergo reduction (***Fig. A(b)***).

3. The reducing agent of the couple with the less positive slope (the most negative E°) is liable to undergo oxidation (***Fig. A(b)***).

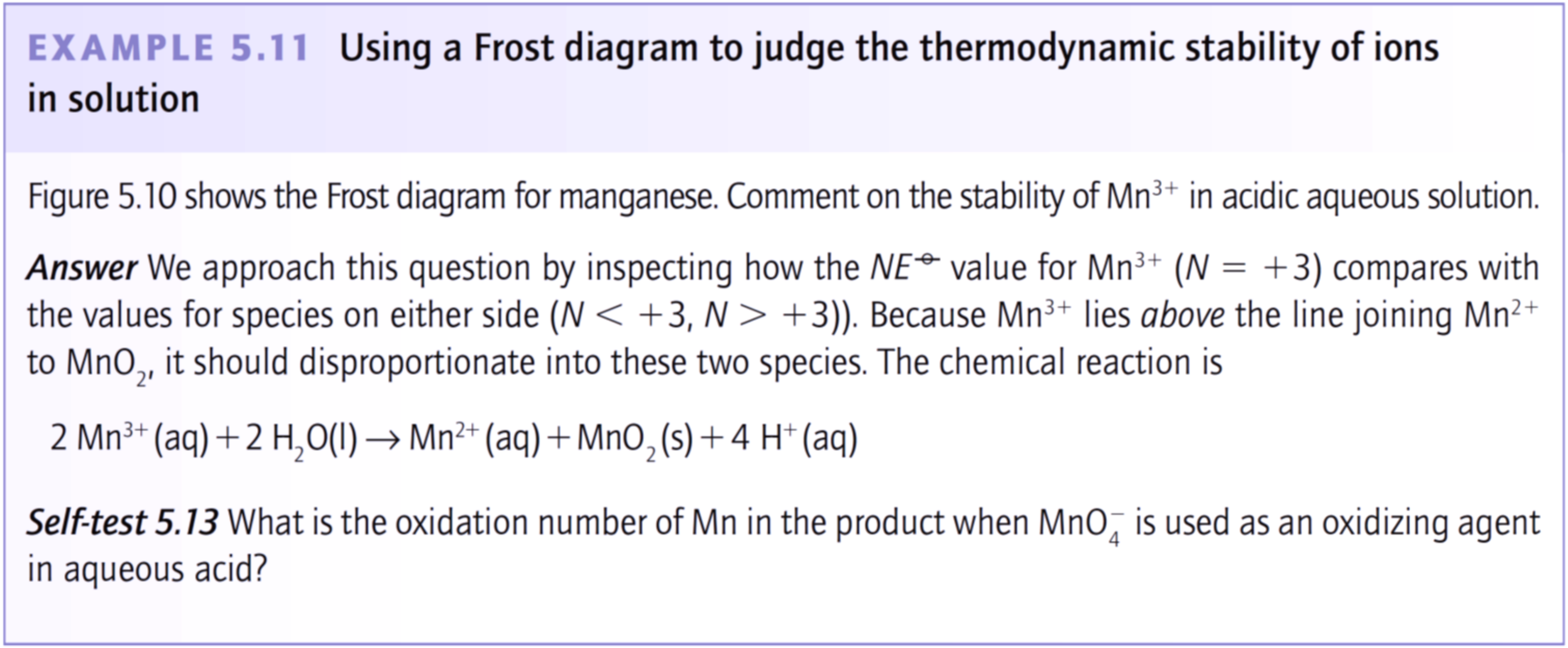
4. A species in a Frost diagram is unstable with respect to disproportionation if its point lies above the line connecting the two adjacent species (on a convex curve) (***Fig. A(c & d)***).

5. Two species will tend to comproportionate into an intermediate species that lies below the straight line joining the terminal species (on a concave curve) (***Fig. A(e & f)***).

Frost diagram for manganese in acidic solution (pH = 0)



Frost diagram for manganese in acidic solution (pH = 0)



EXAMPLE 5.11 Using a Frost diagram to judge the thermodynamic stability of ions in solution

Figure 5.10 shows the Frost diagram for manganese. Comment on the stability of Mn^{3+} in acidic aqueous solution.

Answer We approach this question by inspecting how the $NE^{\ominus}$ value for Mn^{3+} ($N = +3$) compares with the values for species on either side ($N < +3$, $N > +3$)). Because Mn^{3+} lies *above* the line joining Mn^{2+} to MnO_2, it should disproportionate into these two species. The chemical reaction is

$$2\,Mn^{3+}(aq) + 2\,H_2O(l) \rightarrow Mn^{2+}(aq) + MnO_2(s) + 4\,H^+(aq)$$

Self-test 5.13 What is the oxidation number of Mn in the product when MnO_4^- is used as an oxidizing agent in aqueous acid?