Chem Factsheet

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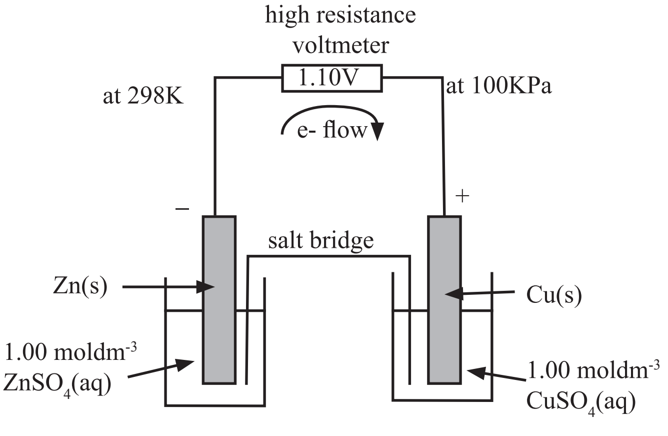
Electrochemical Cells : Concentration Effects

Figure 1 represents a Daniell cell, a typical electrochemical cell encountered at A-level.

Fig. 1 A Standard Daniell Cell



$Zn(s)|Zn^{2+}(aq) \,||\, Cu^{2+}(aq)|Cu(s)$; $E^{\ominus}_{cell} = +1.10V$

Notice that the conditions are standardised – temperature is set at 298K, pressure at 100kPa and the concentrations of solutions at 1.00 moldm^{-3}. Under these conditions, a potential difference of 1.10V is recorded with zinc as the negative electrode and copper as the positive electrode.

This voltage can be seen as the difference between the independent standard electrode potentials of $Zn(s)/Zn^{2+}(aq)$ and $Cu(s)/Cu^{2+}(aq)$ measured relative to a standard hydrogen electrode.

$|| Zn^{2+}(aq)|Zn(s)$; $E^{\ominus}_{Zn} = -0.76V$

$|| Cu^{2+}(aq)|Cu(s)$; $E^{\ominus}_{Cu} = +0.34V$

$E^{\ominus}_{cell} = 0.34 - (-0.76) = +1.10V$

But what about voltages under non-standard conditions?

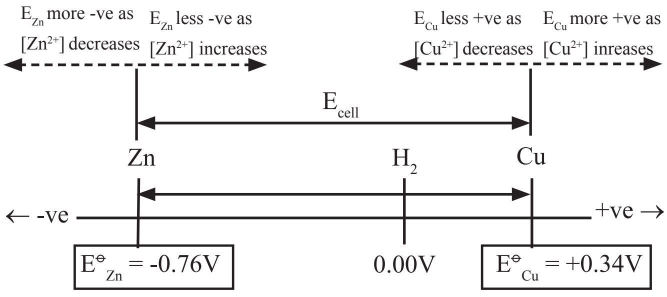
See ChemFact sheets 199 and 205

Increasing concentrations of oxidants causes the related E value to become more positive / less negative.

Increasing concentrations of reductants causes the related E value to become more negative / less positive.

The answer to this question can be summarised by the line number diagram in figure 2.

Fig. 2 E_{cell} variations with concentration



The difference in potential (E_{cell}) can be seen to decrease as $[Zn^{2+}]$ increases and / or $[Cu^{2+}]$ decreases. Conversely, the difference in potential (E_{cell}) will increase as $[Zn^{2+}]$ decreases and / or $[Cu^{2+}]$ increases.

Also, what happens to the cell voltage during discharge of the cell? Zinc atoms, being *more* reactive (more reducing because $E^{\ominus}_{Zn}$ more negative) than copper atoms, tend to release electrons and form zinc ions (Zn^{2+}).

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ ---------------(1)

If the high resistance voltmeter is replaced by a conducting wire, this reaction (oxidation) occurs to zinc atoms at the surface of the zinc electrode resulting in a loss of mass by the zinc electrode and an increase in the concentration of Zn^{2+} ions in solution.

The electrons released move round the circuit as shown in fig 1. Copper ions, being *more* reactive (more oxidising because $E^{\ominus}_{Cu}$ more positive) than zinc ions, tend to take these electrons from the electrode and form copper atoms.

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

This reaction (reduction) occurs at the surface of the copper electrode resulting in an increase in mass by the copper electrode and a decrease in the concentration of Cu^{2+} ions in solution.

Adding together half-equations (1) and (2), the overall cell reaction is

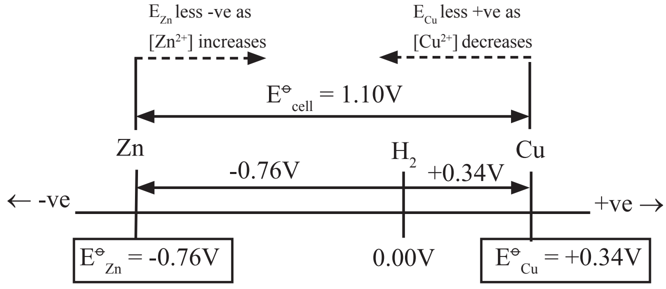
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$,

exactly the same reaction that occurs if zinc metal is added to aqueous copper(II) sulphate solution.

As half-equation (1) proceeds to the right, the concentration of the oxidising agent (Zn^{2+}) increases causing its potential relative to a standard hydrogen electrode to become less negative (i.e. more positive) as shown in figure 3.

As half-equation (2) proceeds to the right, the concentration of the oxidising agent (Cu^{2+}) decreases causing its potential relative to a standard hydrogen electrode to become less positive (i.e. more negative) as shown in figure 3.

Fig. 3 Changes during cell discharge



Hence the net effect of the cell reaction being allowed to proceed as a result of connecting the two electrodes by a conducting wire is for the cell voltage to decrease, until it eventually reaches zero volts. The reaction has then reached equilibrium with the ion concentration values satisfying the equilibrium constant (K_c) value at 298K.

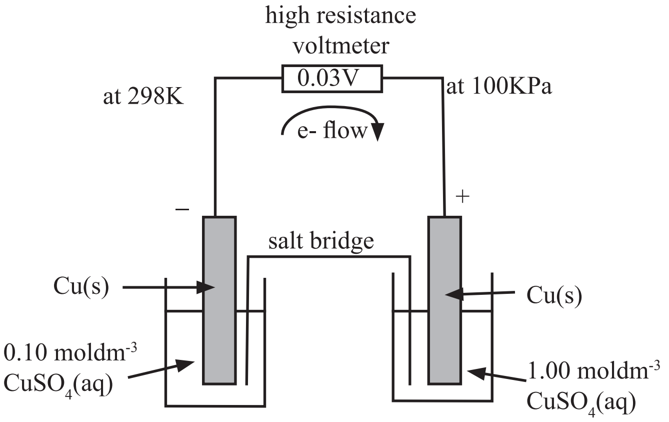
$$K_c = \frac{[Zn^{2+}(aq)]}{[Cu^{2+}(aq)]}$$

Concentrations cells

A *concentration cell* is an electrochemical cell which uses the same components for both electrodes but different concentrations of solutes.

A simple example of a concentration cell is that using two copper electrodes with different concentrations of $Cu^{2+}(aq)$, as shown in figure 4.

Fig. 4 A Simple Concentration Cell



$Cu(s)|Cu^{2+}(aq,0.1M)\ ||\ Cu^{2+}(aq,1.0M)|Cu(s)\ ;\ E^{\ominus}_{cell} = +0.03V$

Note the very small voltage produced by such cells. This means they are not viable power sources.

The half equation which applies to both electrodes of this concentration cell is $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$.

The oxidising agent is the Cu^{2+} ion and the reducing agent is the copper atom. Since the concentration of Cu^{2+} is lower in the left-hand half-cell, this electrode is less oxidising / more reducing. Hence, this is the negative electrode of the cell and oxidation will occur.

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

If the voltmeter is replaced by a conducting wire, the electrons released at the left-hand electrode will flow as shown and cause reduction at the right-hand electrode.

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$.

Hence, the overall effect is for the concentration of copper ions to increase in the left-hand half-cell, the concentration of copper ions to decrease in the right-hand half-cell and the cell voltage to progressively fall to zero, at which point the copper ion concentrations will become equal at 0.55 mol dm^{-3}.

This finishing concentration can be deduced as follows.
LH concentration increase by x to 0.1 + ×
RH concentration decrease by x to 1.0 – ×
At zero voltage, 0.1 + x = 1.0 – ×
→ × = 0.45 → Concn = 0.1 + 0.45 or 1.0 – 0.45 = 0.55 mol dm^{-3}.

Extension work

The qualitative treatment applied so far can be quantified using the *Nernst equation*. This allows an E value to be calculated for different concentrations rather than merely predicting a general change to "more positive" or "more negative" etc.

For the general half-equation: $M^{z+}(aq) + ze^- \rightleftharpoons M(s)$

$$E_M = E^{\ominus}_M + \frac{RT}{zF}\ln[M^{z+}]$$

where E_M = the non-standard electrode potential
$E^{\ominus}_M$ = the standard electrode potential
R = the universal gas constant = 8.31 JK^{-1}mol^{-1}
T = absolute temperature in K
z = number of electrons transferred in the half equation
F = Faraday's constant = 9.65×10^4 C mol^{-1}.

If RT/F is calculated at 298K the equation becomes

$$E_M = E^{\ominus}_M + \frac{0.026}{z}\ln[M^{Z+}]$$

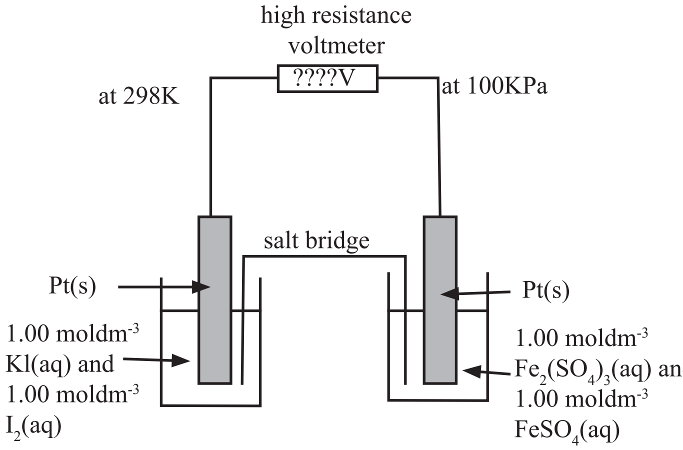
This Nernst equation accounts for the E_{cell} value of 0.03V shown in figure 4. See below.

For the left-hand half-cell in the copper concentration cell shown in figure 4, z = 2, $E^{\ominus}_{Cu} = +0.34V$ and $[Cu^{2+}] = 0.1$ moldm^{-3}. Substitution into the equation shown above gives $E_{Cu} = 0.31V$. Try it!

Hence the potential difference of the concentration cell is 0.34 – 0.31 = 0.03V.

Questions

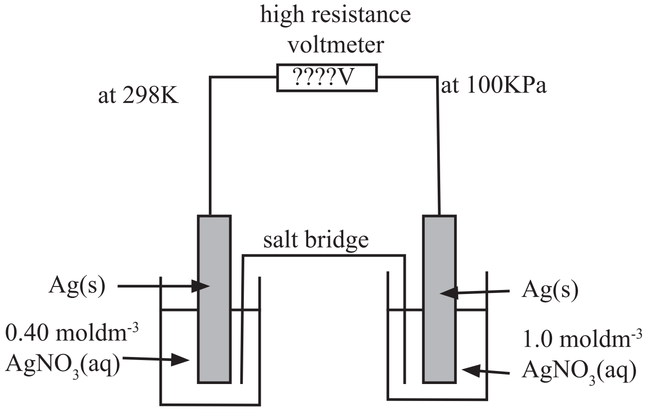
1. Consider the cell shown below.



The relevant half-equations here are : $I_2 + 2e^- \rightleftharpoons 2I^-$; $E^{\ominus} = +0.54V$ and $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$; $E^{\ominus} = +0.77V$.

(a) Calculate the voltage of this standard cell (i.e. the value of ??? in the diagram).
(b) Which component of the cell is the strongest oxidising agent?
(c) Which component of the cell is the strongest reducing agent?
(d) Which electrode in the cell will form the positive electrode. Explain your answer.
(e) Will the cell voltage increase or decrease if $[Fe^{2+}]$ is increased? Explain your answer.
(f) Will the cell voltage increase or decrease if $[I_2]$ is decreased? Explain your answer.
(g) Deduce the cell reaction that will occur if the voltmeter is replaced by a conducting wire.
(h) Will (i) $[Fe^{2+}]$ (ii) $[Fe^{3+}]$ (iii) $[I^-]$ (iv) $[I_2]$ increase or decrease during the course of the reaction?
(i) State in which direction electrons will flow in the external circuit.
(j) What will happen to the cell voltage as the cell reaction proceeds?

2. Consider the concentration cell shown below.



The relevant half-equation here is : $Ag^+ + e^- \rightleftharpoons Ag$: $E^{\ominus}_{Ag} = +0.80V$.

(a) Which electrode will be the positive electrode in this concentration cell. Explain your answer.
(b) Describe and explain what will happen to the cell voltage, the silver electrodes and the $[Ag^+]$ values if the voltmeter is replaced by a conducting wire.
(c) EXTENSION Calculate the value of the cell voltage of the cell as shown (i.e. the value of ??? in the diagram).

Answers to questions

1. (a) $E^{\ominus}_{cell} = (+0.77) - (+0.54) = 0.23V$.
   (b) Fe^{3+} (oxidant and has most positive E^{Θ} value).
   (c) I^- (reductant and has most negative E^{Θ} value).
   (d) Fe^{3+} / Fe^{2+} because it has the stronger oxidant, making it more likely to take electrons from the electrode and give it a positive potential.
   (e) Increasing $[Fe^{2+}]$ pushes the $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ equilibrium to the left resulting in more electrons being deposited on the electrode. This causes its potential to become less positive than +0.77V. Hence the difference in potential (cell voltage) will decrease.
   (f) Decreasing $[I_2]$ pulls the $I_2 + 2e^- \rightleftharpoons 2I^-$ equilibrium to the left resulting in more electrons being deposited on the electrode. This causes its potential to become less positive than +0.54V. Hence the difference in potential (cell voltage) will increase.
   (g) Most oxidising species is reduced : $Fe^{3+} + e^- \rightarrow Fe^{2+}$ -------(1)
   Most reducing species is oxidised : $2I^- \rightarrow I_2 + 2e^-$ ---------(2)
   (1) × 2 + (2) gives $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$
   (h) $[Fe^{2+}]$ increases (ii) $[Fe^{3+}]$ decreases (iii) $[I^-]$ decreases (iv) $[I_2]$ increases
   (i) From $I_2 / 2I^-$ electrode to Fe^{3+} / Fe^{2+} electrode.
   (j) Falls to zero when cell reaction reaches equilibrium.

2. (a) The Ag^+ ion is the oxidant. The higher the concentration of the oxidant the more positive is the potential. Hence, the right hand electrode is the positive electrode.
   (b) The cell voltage will fall to 0V. The $[Ag^+]$ will increase to 0.70 mol dm^{-3} on the left hand half-cell and decrease to 0.70 mol dm^{-3} on the right hand half-cell. The left hand silver electrode will lose mass as atoms are converted to ions. The right hand silver electrode will gain mass as ions are converted to atoms.
   (c) $z = 1$, $E^{\ominus}_{Ag} = +0.80V$ and $[Ag^+] = 0.40$ mol dm^{-3}
   → Potential of LH half-cell, $E_{Ag} = +0.80 + (0.026/1)\ln(0.40) = 0.776V$
   → Cell voltage = 0.80 – 0.776 = 0.024V.

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