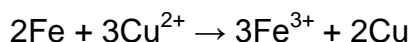


## Chemistry Olympiad Electrochemistry Additional Notes

### Reversibility

In all redox reactions, at least one species undergo reduction and at least one species undergo oxidation.

Example:



Due to the presence of both the reactant and product in the cells during the measurement of the electrode potentials, all reactions in electrochemistry are said to be at a state of equilibrium, at the moment the circuit is connected, in which the reactions are reversible.

### Types of Cells

However, due to the overall cell potential, the reactions can be classified into electrochemical or electrolytic cell:

1. positive  $E^\ominus_{\text{cell}}$ : electrochemical cell, chemical energy is converted to electrical energy. Process is spontaneous
2. negative  $E^\ominus_{\text{cell}}$ : electrolytic cell, electrical energy is required to convert to chemical energy. Process is non-spontaneous.

The relationship between  $E^\ominus_{\text{cell}}$  and  $\Delta G$  is given in the following equation

$$\Delta G = -nFE^\ominus_{\text{cell}}$$

Thus, a positive  $E^\ominus_{\text{cell}}$  will result in a negative  $\Delta G$ .

A cell with a positive  $E^\ominus_{\text{cell}}$  is energetically feasible and spontaneous.

A cell with  $E^\ominus_{\text{cell}} = 0$  is at equilibrium.

A cell with a negative  $E^\ominus_{\text{cell}}$  is not energetically feasible and spontaneous.

To determine what reaction takes place, the following steps are taken, given when  $\text{I}_2$ ,  $\text{Fe}^{3+}$ ,  $\text{H}^+$  and  $\text{Cl}^-$  mixed together:

1. determine the reactants and write out the half-equation

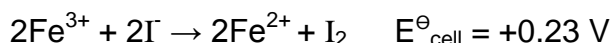
#### reduction



#### oxidation



2. choose the reduction reaction with the most positive  $E^\ominus_{\text{red}}$  and the oxidation reaction with the most positive  $E^\ominus_{\text{ox}}$  and add the equations and  $E^\ominus$  together



3. comment on feasibility and spontaneity
4. determine if reaction takes place and give observations

### **Electrochemical Cell**

An electrochemical cell is identified by:

1. presence of voltmeter
2. lack of electrical source
3. positive  $E^\ominus_{\text{cell}}$
4. presence of salt bridge

There are two main types of electrochemical half-cells:

1. conductive solid / ion
2. nonconductive solid, ion / ion

For the 2<sup>nd</sup> type of half-cell, an inert electrode is required but the former is able to use the conductive solid as the electrode.

### **Determination of Equation**

Given two electrochemical half-cells, ie  $\text{Cu}^{2+}/\text{Cu}$ ,  $\text{Zn}^{2+}/\text{Zn}$ , the following steps are done to determine the equation and calculate the  $E^\ominus_{\text{cell}}$ .

1. Write down both the reduction equation with  $E^\ominus_{\text{red}}$  values from the data booklet



2. The equation with the more positive  $E^{\ominus}_{\text{red}}$  will undergo reduction and the other species will undergo oxidation. Rewrite the oxidation equation and flip the sign of the  $E^{\ominus}$



3. Add the equations and  $E^{\ominus}$  values



### Equilibrium Effects on $E^{\ominus}_{\text{cell}}$

The half-cells are setup with the following parameters:

1. concentration of ions:  $1 \text{ mol dm}^{-3}$
2. pressure of gas: 1 atm
3. temperature: 298 K

A change which favours the forward reaction will make the  $E_{\text{cell}}$  more positive, also known as overpotential, and vice versa for a change which favours the backwards reaction, ie when  $\text{Zn}^{2+}$  is precipitated out of the Daniell cell, more Zn will undergo oxidation to produce more  $\text{Zn}^{2+}$ . This increases the flow of electrons,  $E_{\text{cell}}$  become more positive than +1.10 V.

This also means that by changing the conditions, one is able to make a spontaneous reaction non-spontaneous or vice versa. Take note of the following conditions:

1. conditions not at  $1 \text{ mol dm}^{-3}$ , 1 atm, 298 K
2. formation of a precipitate as a product
3. addition of a compound which precipitates a species

### Limitations of $E^{\ominus}_{\text{cell}}$

$E^{\ominus}_{\text{cell}}$  predicts the feasibility of a reaction but a reaction may be reacting extremely slowly that a change is not immediately observed. Such a reaction can be said to be kinetically not feasible. This limitation can be avoided by heating the reaction or adding a catalyst to increase the rate of reaction.

### Electrolytic Cell

An electrolytic cell is identified by:

1. presence of electrical source
2. presence of variable resistor
3. negative  $E^{\ominus}_{\text{cell}}$
4. absence of salt bridge

There are two main types of electrolytic cells:

1. aqueous
2. molten

In aqueous electrolytic cells, the cell is not heated but the presence of water can interfere with the reaction and be preferably reduced or oxidised. Molten electrolytic cells are usually heated and pose a problem of the electrode melting or reacting with products.

### Determination of Equation

Given two electrochemical half-cells, ie  $\text{Cu}^{2+}/\text{Cu}$ ,  $\text{Zn}^{2+}/\text{Zn}$ , the following steps are done to determine the equation and calculate the  $E^\ominus_{\text{cell}}$ .

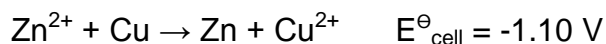
1. Write down both the reduction equation with  $E^\ominus_{\text{red}}$  values from the data booklet



2. The equation with the more positive  $E^\ominus_{\text{red}}$  will undergo oxidation and the other species will undergo reduction. Rewrite the oxidation equation and flip the sign of the  $E^\ominus$



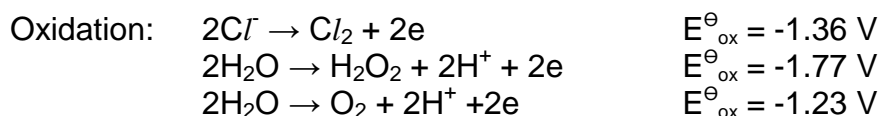
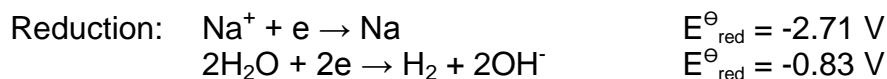
3. Add the equations and  $E^\ominus$  values



### Competing Reactions

Electrolytic cells containing aqueous solutions generally have to consider the reduction or oxidation of water due to its abundance.

Take the example of  $\text{NaCl}(\text{aq})$ . There are three possible species that can undergo redox reactions.



For reduction, Na is not produced as the  $E^\ominus_{\text{red}}$  of  $\text{Na}^+$  is too negative and  $\text{H}_2\text{O}$  will be preferably reduced.

For oxidation, the same explanation is given for  $\text{H}_2\text{O}$ , and  $\text{H}_2\text{O}_2$  is not formed. For  $\text{Cl}^-$ , the  $E^\ominus_{\text{ox}}$  is extremely close to that of the 2<sup>nd</sup>  $\text{H}_2\text{O}$  reaction and abundance of the reactant becomes the determining factor.

In dilute solutions, the abundance of  $\text{H}_2\text{O}$  coupled with the more negative  $E^\ominus_{\text{ox}}$  value of  $\text{Cl}^-$  mean that  $\text{H}_2\text{O}$  is oxidised to form  $\text{O}_2$ . However, as concentration increases, the increasing concentration of  $\text{Cl}^-$  leads to the overpotential effect, described the equilibrium effects, and  $\text{Cl}^-$  is oxidised instead.

Other methods that can lead to a species being preferably discharge include the cell setup and the nature of the electrode used. These properties are utilised in the purification of copper.

### **Drawing of Cells**

By convention, cells are drawn, left to right, from oxidation to reduction. Hence, the anode is on the left and the cathode is on the right.

The following steps are followed for the drawing of both electrochemical and electrolytic cells:

1. determine the oxidation and reduction processes
2. if the oxidation equation contains a conductive solid, draw it as the anode on the left. In the absence of a conductive solid, draw an inert electrode
3. repeat step 2 for the cathode
4. draw 2 separate cells for an electrochemical cell. For electrolytic cell, draw the electrodes in the same cell
5. connect the electrodes with a line, representing the wire. For the electrochemical cell, add a salt bridge between the 2 cells
6. draw a voltmeter on a length of the line for the electrochemical cell. For the electrolytic cell, draw a power source and a variable resistor
7. determine the flow of electrons. Electrons always flow from the anode to the cathode
8. determine the source of electrons. The anode is the source of electrons for the electrochemical cell and is labelled (-), the cathode is then labelled (+). For the electrolytic cell, the source of electrons is the negative end of the power source which is linked to the cathode and thus the cathode is labelled (-) and the anode (+)
9. label the diagram

### **Choice of Electrolyte**

The following are the factors when selecting electrolyte solution for cells:

1. the electrolyte must allow the movement of ions when a potential difference is applied. Aqueous solution, molten salt or graphite paste are commonly used
2. the electrolyte must preferably be inert. Usually an electrolyte  $E^\ominus$  values more negative than the reducing/oxidising species or the same ions are used
3. the electrolyte should be able to be handled with relative ease

## **Choice of Electrodes**

The following factors are used during the selection of electrodes:

1. Electrodes must be electrically conductive
2. Electrodes should be inert unless they are part of the redox reaction to avoid competing reactions as well as to ensure the circuit is closed at all times
3. In reactions where the  $E^\ominus$  are relatively similar, the electrode used should preferably be the same as the reacting species, ie use a Cu electrode for  $\text{Cu}^{2+}/\text{Cu}$  cell, due to overpotential effect. However, in such a situation, the electrode may be oxidised
4. Electrodes used must be of sufficiently high melting point for cells with molten electrolyte or they would melt
5. Electrodes must be easily replaced

## **Faraday's Laws of Electrolysis**

$$Q = It = nF$$

where:

Q = quantity of electricity in coulombs, C

I = current in amperes, A

t = time in seconds, s

n = moles of electrons passing in circuit per mol of reactant

F = Faraday constant,  $96500 \text{ C mol}^{-1}$

$$F = Le$$

where:

L = Avogadro constant,  $6.02 \times 10^{23} \text{ mol}^{-1}$

e = electronic charge,  $1.60 \times 10^{-19} \text{ C}$

Note:

In situation where multiple electrodes are placed in series in an electrolytic setup, the current at any point of the circuit is the same