Understanding Electrochemical Cells

Technical Report 17

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Aim of this book

This simple pictorial treatment aims to give the non-chemist a ‘feel’ for what happens in an electrochemical cell.

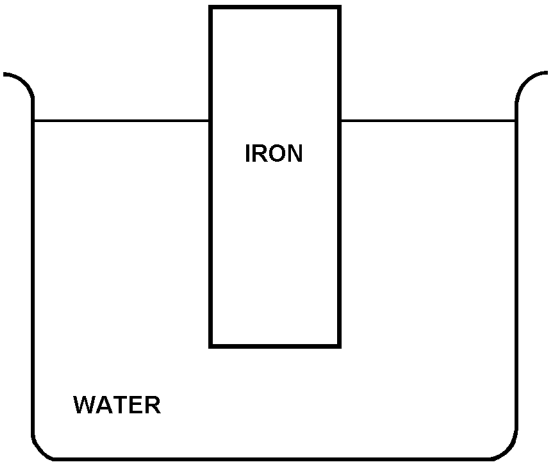
It uses unsophisticated models of the particles involved, and no mathematics, to account for the driving force behind some of the phenomena.

The book does not pretend to be comprehensive, and for simplicity’s sake strict factual accuracy is sacrificed where appropriate.

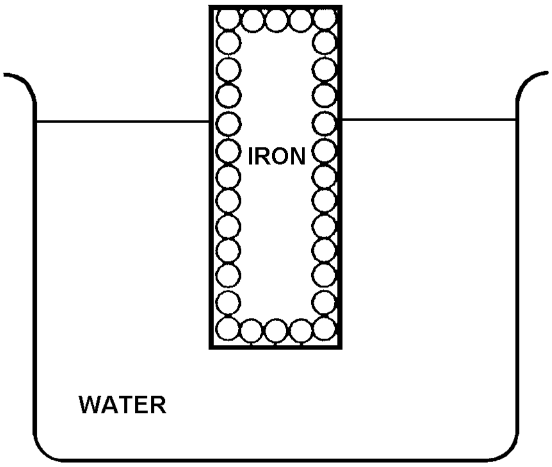
Metals in Water

1. A bar of iron is dipped into water.

   Contact with water causes certain changes to occur, where the water touches the iron:



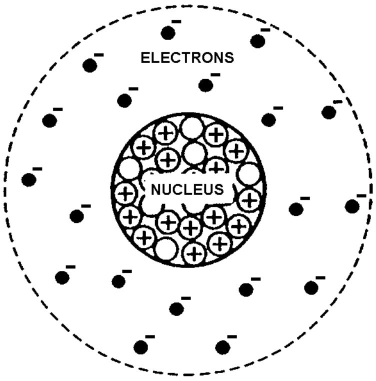
2. The water affects only the atoms on the surface of the iron:



Ionisation

3. Each atom consists of a positively charged nucleus, surrounded by negatively charged electrons.

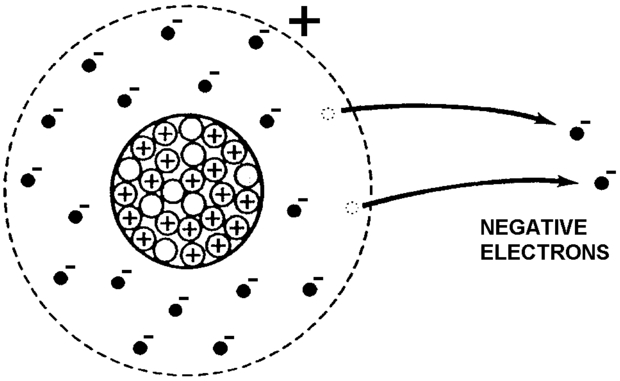
   In a complete atom, the positive and negative charges exactly balance each other. So the atom is electrically neutral:



NEUTRAL ATOM

4. It is possible for one or more electrons near the outside of the atom to be pulled away.

   This leaves an incomplete atom which has a nett positive charge called a positive **ION**:

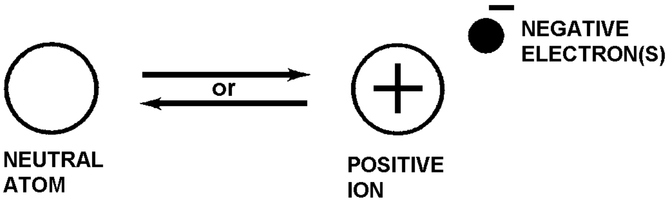


POSITIVE ION

5. This process is called **IONISATION**.

   Ionisation can also happen in reverse: electrons re-combine with positive ions to form neutral atoms.

   To make diagrams clearer, atoms and ions are drawn simply as circles.



IONISATION

6. Some metal atoms lose electrons to form ions much easier than others. It depends on how strongly the metal's positive ion attracts electrons. And this depends on the nature of the metal.

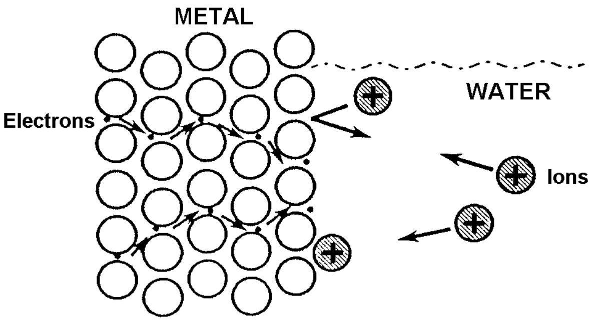
   Reactive metals, such as sodium, are those which ionise very easily. Unreactive metals, such as platinum, are those which ionise only with difficulty.

SODIUM atoms ionise	**dangerously easily**
ZINC	**easily**
IRON	**fairly easily**
COPPER	**with some difficulty**
GOLD	**with great difficulty**
PLATINUM	**hardly at all**

Electric Currents

7. Positive ions are thousands of times larger and heavier than the tiny electrons. The massive positive ions are too big to move around inside metals. But the tiny electrons move very easily in the spaces between the metal atoms. This is an electric current in a metal.

   On the other hand, electrons cannot survive in water; they quickly re-combine with positive ions. But ions can move through water. This is an electric current in a solution.



ELECTRIC CURRENTS

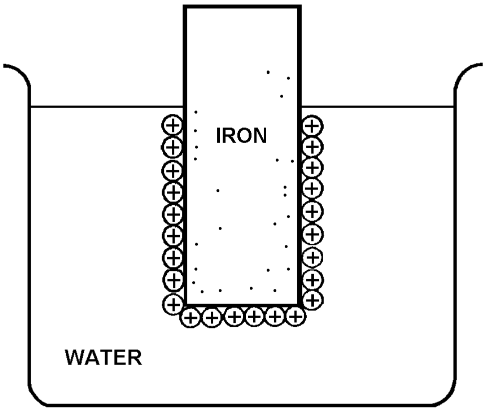
Adsorbed Ions

8. Back to the iron bar dipped in water.

   Some of the surface iron atoms, in contact with the water, ionise. The released electrons can move about freely in the metal, but the positive ions formed cannot. They remain on the surface of the metal bar.

   Now the bar has some extra electrons moving around inside it (from the ionisation). So it is more negative inside than it was before touching the water. The surface of the bar is now more positive than before; both charges balance exactly.

   The positive ions are held quite firmly on the bar’s surface, by electrostatic attraction. This is **ADSORPTION**. The ions are **ADSORBED** onto the surface of the metal. (They cannot penetrate right into the metal; this would be a**B**sorption).

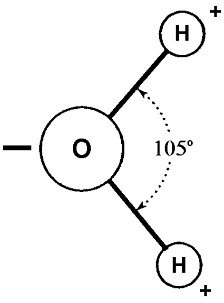


Water and Ionisation

9. But why should water affect the surface atoms like this?

   Water consists of banana-shaped **MOLECULES**. Each water molecule contains two hydrogen atoms (H) joined to a single oxygen atom **(O)**. The formula is **H_2O**. The bonds make an angle of 105°.

   The negative electrons from the atoms in the molecule tend to gather near the central oxygen atom, on the bulge of the 'banana'. So this part of the molecule is quite strongly negative, and the two ends are positive. The water molecule is **POLAR**. The negatively charged bulge strongly attracts positive ions.



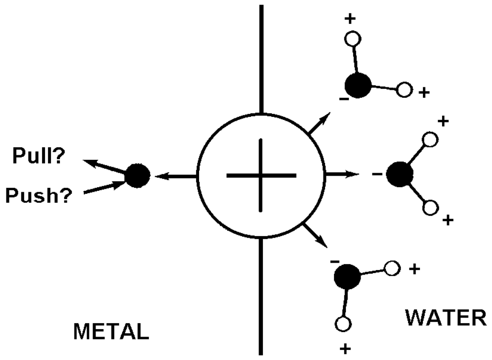
A WATER MOLECULE

10. How does this affect ionisation? Several forces act:

   - In the water, the polar banana-shaped water molecules strongly attract positive ions and try to pull them into the water, leaving the electrons behind in the metal. This encourages ionisation.
   - In the metal, electrons and ions attract each other and tend to re-combine. This discourages ionisation.
   - If the metal bar, already has an excess of electrons in it (i.e. is negatively charged), these extra electrons repel electrons trying to leave the surface atoms. This discourages ionisation.
   - On the other hand, if the bar is short of electrons (i.e. is positively charged), ionisation of the surface atoms is encouraged.

   The end result depends on how strong these forces are. And this depends on the nature of the metal used.

   For a neutral iron bar dipped into the water, a lot of ionisation occurs. So the metal becomes considerably negatively charged within.



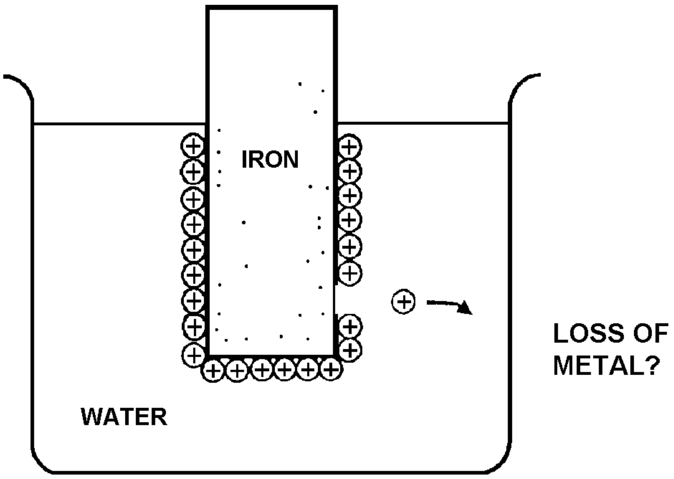
FORCES OF IONISATION

Desorption

11. Adsorbed ions may break away from the surface of the bar, and move off into the water. This is called **DESORPTION**.

    If this happens the bar loses mass. That is, it corrodes slightly, leaving tiny pits in the surface. Newly exposed atoms may then ionise to replace the desorbed ions. So the metal bar becomes even more negatively charged than before.

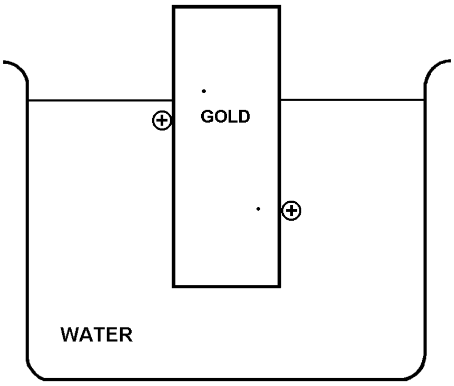
    But this desorption cannot happen to many ions, because the build-up of negative charge in the bar opposes desorption and ionisation more and more strongly. So further corrosion quickly stops, and the end result is an equilibrium state.

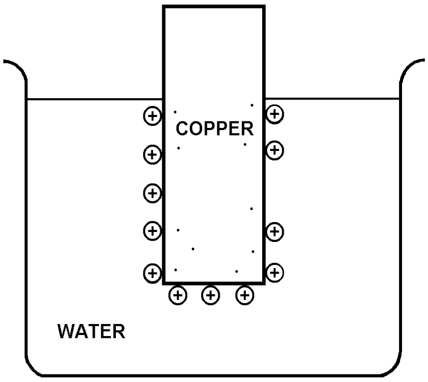


Different Metals

12. So when a bar of metal is dipped in water, the amount of negative charge it ends up with depends on the metal used.

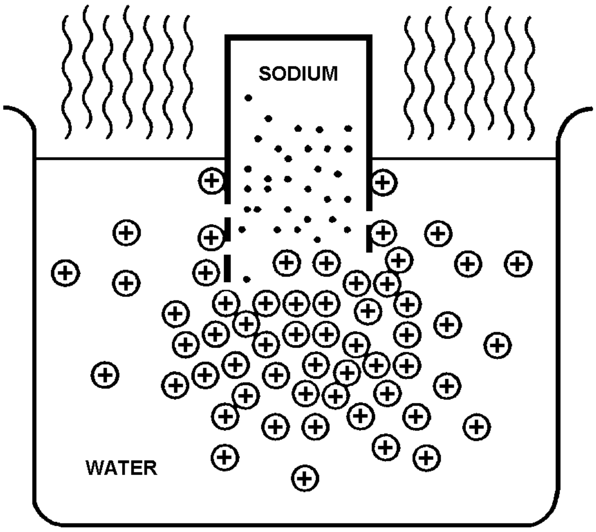
    Relatively unreactive metals like gold and copper become less negative than iron, because fewer extra electrons are released into the metal by ionisation.





13. Sodium metal is so reactive that on contact with water it rapidly ionises and dissolves away completely.

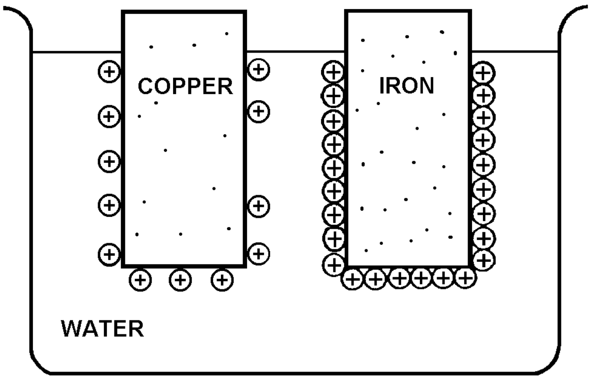
    What happens to all the electrons released as the sodium atoms ionise?



An Electrochemical Cell

14. A bar of iron builds up a greater concentration of electrons in it than a bar of copper, when dipped in water. In the iron, the electrons are crowded more closely together and so repel each other more strongly. That is, the 'electron pressure' in the iron is greater than in the copper.

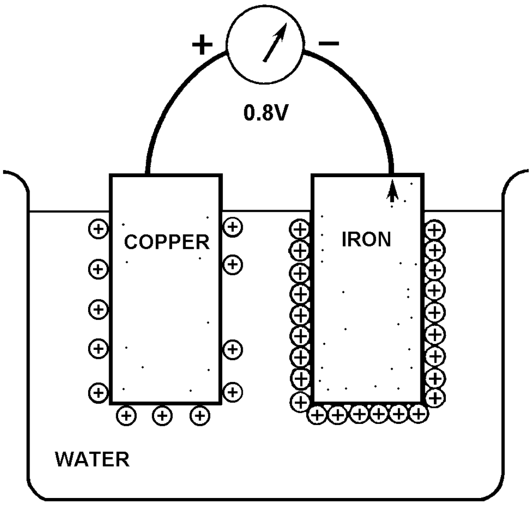
    The iron's **ELECTRIC POTENTIAL** is more negative (lower) than the copper's.



15. A voltmeter connected across the two bars shows this difference in 'electron pressures'. In fact the potential difference between these bars is nearly 0.8 volts.

    This arrangement is an **ELECTROCHEMICAL CELL**. The liquid in the cell is the **ELECTROLYTE**. The metal bars are the **ELECTRODES**. The potential difference between them is the **REST POTENTIAL** of this particular cell (copper/iron). It is called 'rest' potential because the cell settles at this value when left undisturbed on its own.

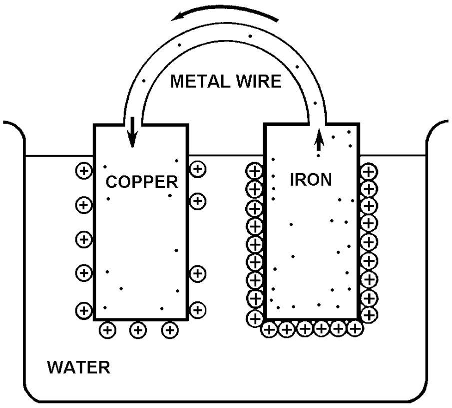
    Other pairs of dissimilar metals dipped in water have their own characteristic rest potentials.



16. If the copper and iron bars are connected by a conducting wire instead of by a voltmeter, there is a brief flow of electrons from high electron pressure to low electron pressure.

    The flow stops when the pressures are equal. That is, when both metals are at the same potential or 'voltage'.

    The iron bar now has fewer electrons than before the brief flow, and the copper bar now has more.



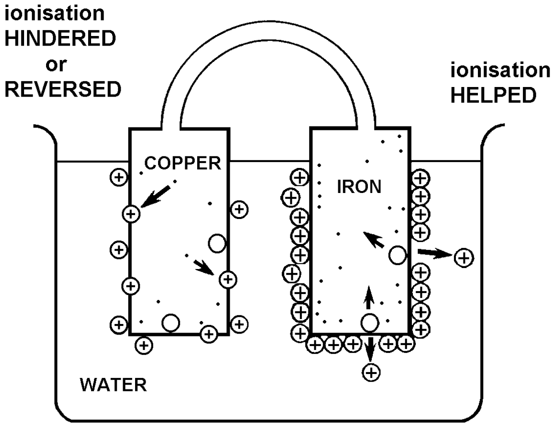
17. In the iron bar, the reduced negative charge means that the adsorbed positive ions are less strongly attached to the surface than before. Also, ionisation of surface atoms is encouraged.

    So some loosely adsorbed ions may detach, and be replaced by more ionisation. This releases extra electrons into the iron, which flow round to the copper bar.

    In the copper bar the opposite is true. The extra electrons attract adsorbed copper ions more strongly than before, and further ionisation is discouraged.

    Some tightly absorbed copper ions may re-combine with electrons to form neutral atoms again. But once all the adsorbed copper ions have re-combined with electrons, any more electrons flowing round from the iron bar have nowhere to go. They build up in the copper bar and inhibit further flow.

    So, very shortly after being connected, both bars end up at the same potential. All electron flow stops.



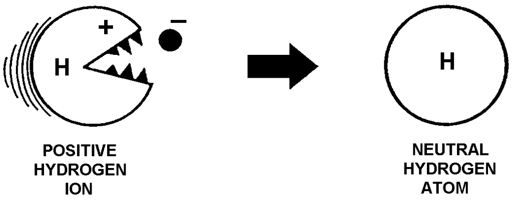
A Power Supply

18. What could get the electrons flowing again?

    Something is needed which consumes excess electrons and prevents them building up in the copper bar. **HYDROGEN IONS** will do the job.

    Positive hydrogen ions are hydrogen atoms short of one electron. They are strongly attracted to electrons, and combine with them to form neutral hydrogen atoms.

    In pure water there are very few hydrogen ions. But in **ACIDS** they are plentiful. So adding some acid to the water gets the electron flow going again.



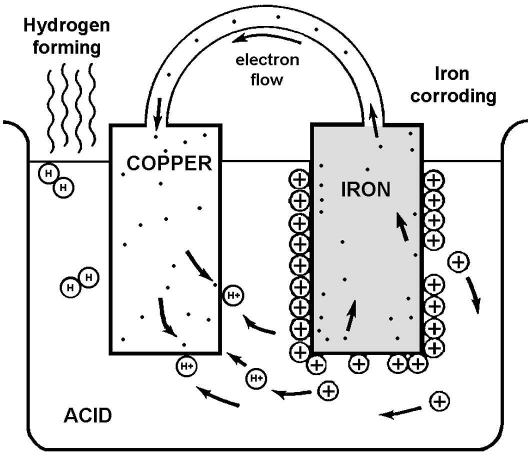
A HYDROGEN ION CONSUMING AN ELECTRON

19. At the iron bar, ions leave the surface and pass into the water. Fresh atoms ionise to replace the desorbed ions. The iron bar corrodes. The electrons released by the ionised iron atoms flow through the connecting wire to the copper bar.

    At the copper bar, the released electrons which have built up attract positive hydrogen ions. The hydrogen ions are adsorbed onto the bar's surface and then combine with the electrons to form hydrogen gas. The gas bubbles up and leaves the solution. The copper bar does not corrode. It simply provides a surface where hydrogen ions can meet and combine with electrons.

    Electrons keep on flowing round the wire until all the iron has corroded away. Or until all the hydrogen ions in the acid have been used up, and no other positive ions are left which can take over their job.

    In fact, the beaker of acid and the two electrodes make a single cell DC power supply.



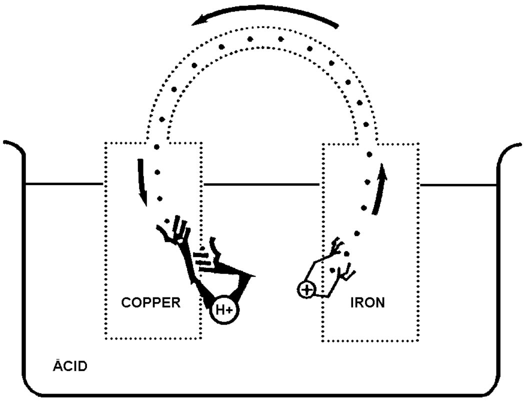
A POWER SUPPLY (CELL)

Current Flow Directions

20. In the cell there is a competition for electrons between the two different positive ions. Hydrogen ions (as well as copper ions) pull harder on the surface electrons than iron ions do. So in the copper bar, electron pressure gets lower than in the iron bar, causing the electron flow.

    It is like a 'tug-of-war' with electrons as the 'rope'. The hydrogen ions win. They succeed in pulling electrons away from the iron ions and round the wire.

    This is the driving force of the cell. This is why the electrons flow in the direction they do.



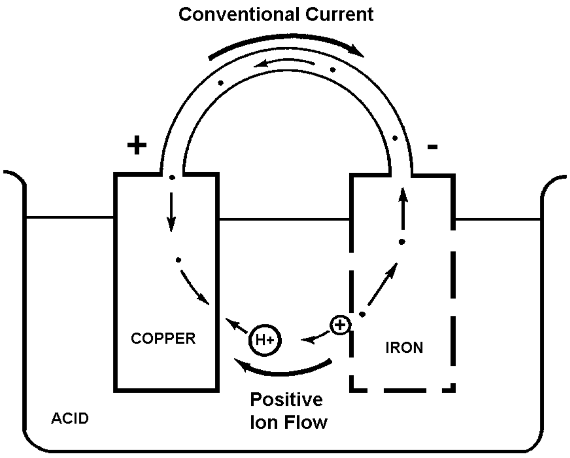
A TUG-OF-WAR

21. In the wire, electrons (negative charge) flow anti-clockwise. But for historical reasons we say that the **CONVENTIONAL ELECTRIC CURRENT** flows counter to the electron flow, that is, clockwise.

    In the solution, positive ions carry the current away from the iron and towards the copper. That is, also clockwise.

    So the conventional current in the wire, and the positive ions in the solution both flow round the circuit in the same sense.

    If this cell is used as a power supply, the copper electrode is called **positive**, and the iron electrode is called **negative**. The conventional current always flows out of the cell's positive terminal and back into the cell's negative terminal.



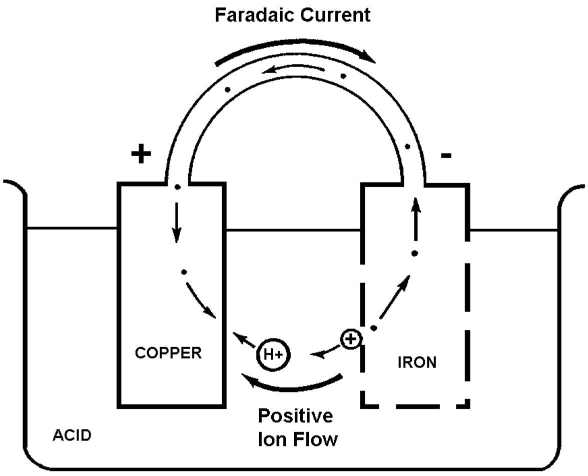
In WIRE, current carried by ELECTRONS
In WATER, current carried by IONS

Faradaic Current and Corrosion

22. The electrons in the electric current come from ionising iron atoms, that is, from corroding iron. This type of current is called a **FARADAIC** current (after the English scientist Michael Faraday).

    The more iron corrodes, the more the faradaic current flows, and vice versa. So the corrosion rate is proportional to the faradaic current. Anything that resists the flow of faradaic current slows down the corrosion.

    Finding out what resists the faradaic current is clearly important in the study of corrosion.

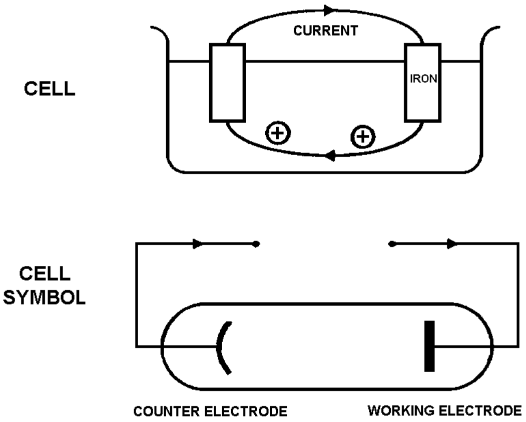


Corrosion rate proportional to Faradaic current

23. A **CELL SYMBOL** is often used to depict an electrochemical cell. The metal specimen being studied, in this case corroding iron, is the **WORKING ELECTRODE (WE)**.

    The other electrode, in this case copper, is the **COUNTER ELECTRODE (CE)**. The CE is there only to complete the circuit, and is of no interest. An unreactive metal, such as platinum, or other inert conductor, such as graphite, is often used as counter electrode.

    The cell shown is a **TWO-TERMINAL** cell. Three- and four-terminal cells also exist.



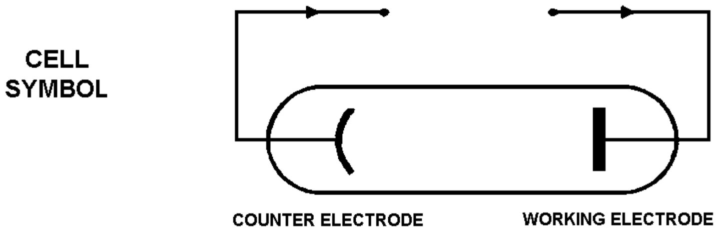
24. What things resist the flow of faradaic current, and so slow down corrosion?

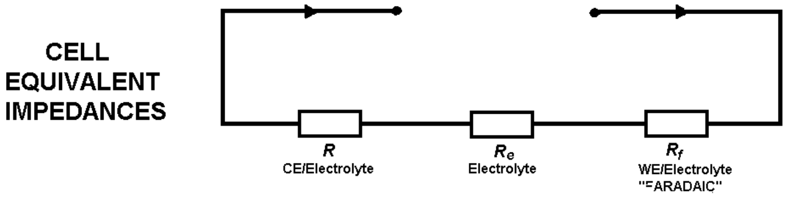
The metal bars and connecting wire usually have very little electrical resistance, and can be neglected. This leaves three main obstacles to the flow of faradaic current:

- At the surface of the iron bar, atoms must ionise. Then the ions must detach themselves and move into the solution. The restricting effect of these processes on the current is equivalent to a resistance, the **FARADAIC RESISTANCE***, $\boldsymbol{R_f}$. R_f is at the interface between the working electrode and the electrolyte.
- In the solution, positive ions (hydrogen and iron) must make their way across to the copper bar. This is hard for the bulky ions, compared to the flow of tiny electrons through metals. The equivalent resistance here is the **ELECTROLYTE RESISTANCE**, $\boldsymbol{R_e}$. R_e is spread between the two electrodes.
- At the surface of the copper bar, hydrogen ions must be adsorbed, and then combine with electrons. But this equivalent resistance, $\boldsymbol{R}$, can be made very low by using a large-area electrode made of a suitable conductor.

All three resistances affect corrosion rate. But the **faradaic resistance** is usually the most significant. It does not depend on the distance between the electrodes, which the electrolyte resistance does. And R_f is a property of the WE/electrolyte interface itself, that is, the corroding surface.

* Also called the **CHARGE TRANSFER RESISTANCE, $\boldsymbol{R_{ct}}$**





Corrosion of Metals in Contact

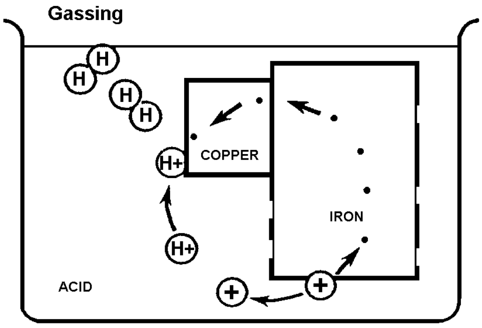
25. The two electrodes need not be connected by a wire outside the electrolyte for faradaic current to flow. The cell works perfectly well if the metals merely touch and make electrical contact.

    An example is a copper pipe fitted to an iron boiler. Or particles of copper (or other unreactive impurity metal), embedded in the surface of a piece of iron.

    The usual faradaic current flows, the iron corrodes, and hydrogen gas bubbles from the copper surfaces. The copper itself is not attacked by the electrolyte.

    The faradaic current flows entirely within the electrodes, instead of conveniently via an external wire. So it is hard to measure or control. The 'separated' electrode cell is used when measurements must be made.

    An isolated bar of very pure and homogeneous metal dipped in acid hardly corrodes at all. There is nowhere for faradaic current to flow, unless the bar can touch a less reactive conductor and form a cell.

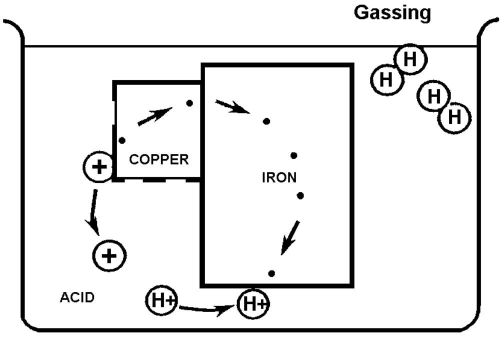


CORROSION OF IRON IN CONTACT WITH COPPER

26. Zinc is more reactive than iron. That is, zinc atoms ionise more easily than iron atoms (and hydrogen atoms). So in a zinc/iron cell, the zinc corrodes away, releasing electrons into the iron, where hydrogen gas forms. The iron is unattacked.

    By corroding itself, the zinc protects the iron that it touches. The zinc is a **SACRIFICIAL ANODE**.

    'Galvanising' (zinc plating) on steel dustbins, iron nails, etc., is a very effective form of sacrificial anode protection. It works even when large areas of zinc have gone. As long as some zinc is left in contact with the iron, the zinc corrodes preferentially. Mildly acidic rainwater is usually the electrolyte.

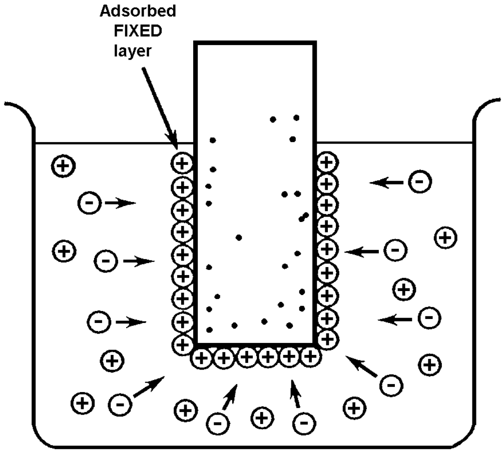


CORROSION OF ZINC IN CONTACT WITH IRON:
"SACRIFICIAL ANODE"

The Double Layer

27. A bar of metal immersed in a solution become negatively charged inside, and covered with a positive **ADSORBED FIXED LAYER** outside.

    Positive and negative ions drift around in the solution. The adsorbed layer of ions attracts nearby negative ions, which move towards the bar's surface. The negative ions form a **DIFFUSE MOBILE LAYER** near the bar's surface. It is loosely held there by electrostatic attraction.

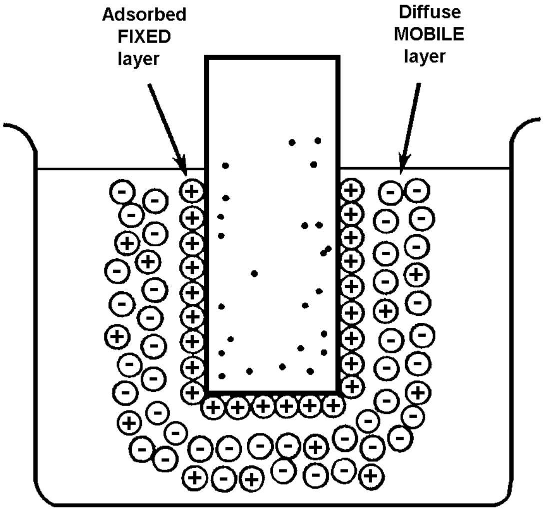


28. Ions are free to move around in this layer, and to enter or leave it. Some of the ions in the diffuse layer are positive, but the layer's nett charge is negative. It is balanced by the positive charge of the fixed layer.

    The diffuse mobile layer is repelled slightly by the excess of electrons inside the metal bar.

    The adsorbed fixed layer and the diffuse mobile layer together are the **ELECTRICAL DOUBLE LAYER**. The double layer acts as a capacitor, with a 'fixed plate' (the fixed layer) and a 'moveable plate' (the mobile layer). It is a kind of electrolytic capacitor.

    The **DOUBLE LAYER CAPACITOR, C_{dl}**, can be charged and discharged like any other capacitor.



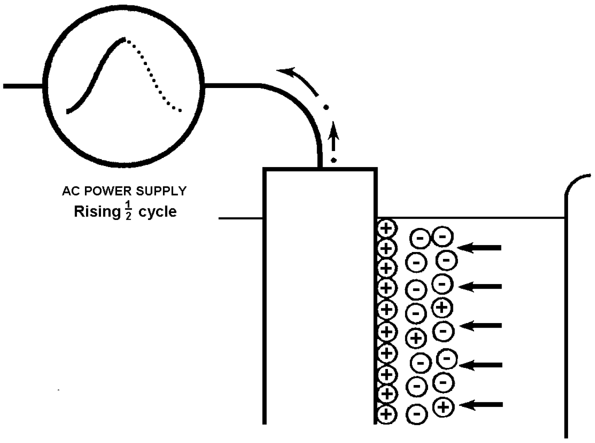
THE DOUBLE LAYER

AC and the Double Layer

29. An **alternating current** power supply pushes then pulls electrons in and out of the load, at the supply frequency. There is no nett current flow.

    During the rising half-cycle, conventional current flows into the electrode connected to the AC supply. That is, electrons are drawn out. The electrode is now less negatively charged (more positive) than before. So it attracts the diffuse mobile layer more strongly. The mobile layer moves closer.

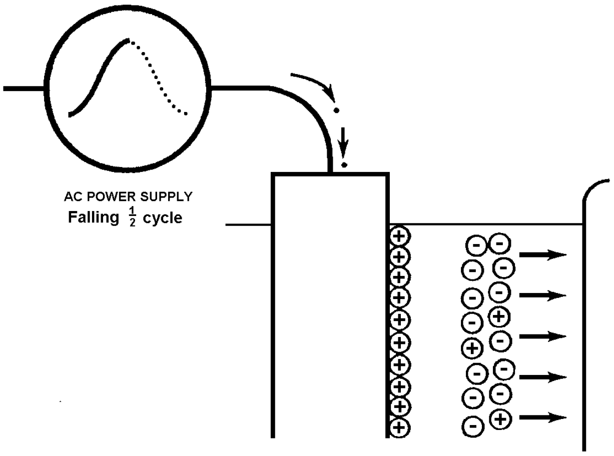
    The conventional current that has flowed into the electrode has **charged up** the double layer capacitor.



CHARGING THE DOUBLE LAYER

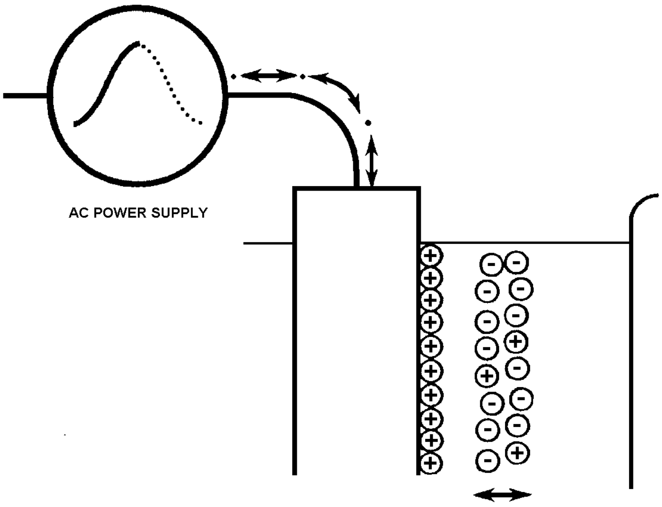
30. During the falling half-cycle, conventional current flows back out of the electrode. That is, electrons are pushed **in**. The electrode is now more negatively charged than before, and so repels the mobile layer more strongly. The mobile layer moves away.

    This is **discharging** the double layer capacitor.



DISCHARGING THE DOUBLE LAYER

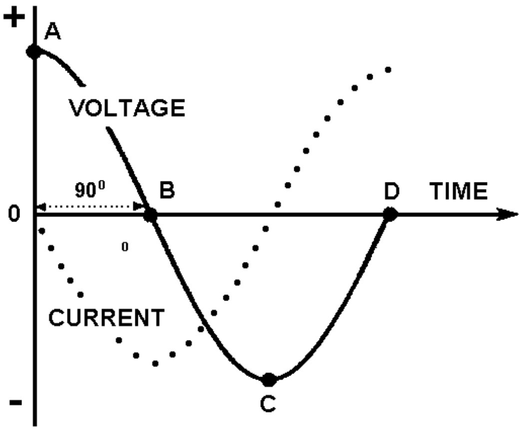
31. So an alternating voltage applied to the electrode makes the diffuse mobile layer oscillate at the AC frequency.



OSCILLATING MOBILE LAYER

32. And as usual with capacitors, the current waveform leads the voltage waveform by 90°.

- *When the voltage is at its maximum (**A**), the double layer is fully charged. The mobile layer is at its closest to the electrode, and no current flows.*
- *When the voltage is passing down through zero (**B**), the mobile layer is at its mid position, moving away at maximum speed. Here, the current flow **out** of the electrode is fastest.*
- *When the voltage is at its minimum (**C**), the double layer is fully discharged. The mobile layer is at its furthest from the electrode, and again no current flows.*
- *When the voltage is passing up through zero (**D**), the mobile layer is again at its mid position, moving in at maximum speed. Here, the current flow **into** the electrode is fastest.*



DOUBLE LAYER VOLTAGE & CURRENT WAVEFORMS

DC and the Double Layer

33. A **direct current** power supply pushes the electrons in a steady direction. Electrons flow out of the supply's negative terminal, and into its positive terminal. The conventional current flows counter to this.

    A steady flow of current into the electrode, that is, a steady withdrawal of electrons, makes the electrode positive enough to push away adsorbed ions into the solution (desorption). More surface atoms ionise to replace the desorbed ions. The electrons from this ionisation flow towards the DC power supply. This is the faradaic current in the metal.

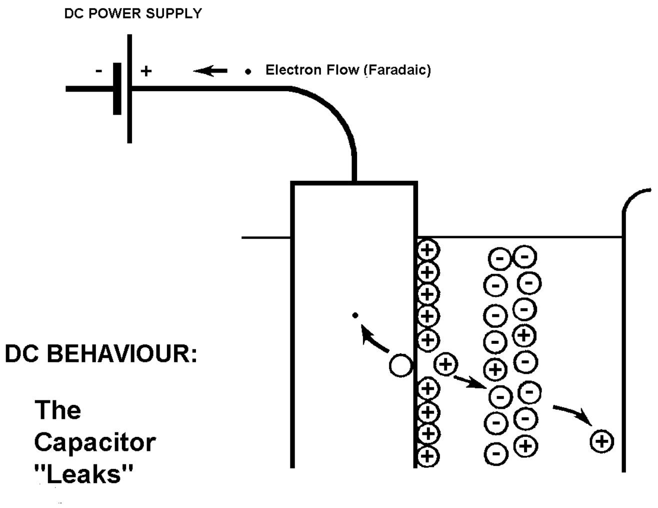
    The electrode loses mass (corrodes). A stream of desorbed ions passes into the diffuse mobile layer, and eventually out into the solution. This is the faradaic current in the electrolyte.

    During all this, the negative mobile layer stays at a constant distance from the electrode. This distance depends on what DC voltage is being applied. The more positive the electrode, the closer the mobile layer.

    Connecting the DC power supply in reverse forces all the above changes to happen in reverse. Instead of corroding, the electrode ***gains*** *material (****electroplating*** *or gassing). But the voltage used must be high enough to overcome the tendency of the electrode atoms to ionise in water.*

    Unlike AC voltage, DC voltage makes a **nett current** flow through the double layer, from one 'plate' to the other.

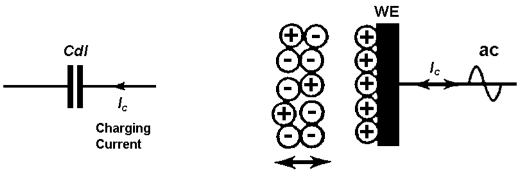
    The double layer capacitor '**leaks**'.



Behaviour of the Double Layer

34. So, with AC the double layer behaves ideally like a perfect capacitor (C_{di}).

    It charges and discharges (charging current I_c). There is no nett current flow, and no ‘leakage’. There is no chemical reaction (e.g. corrosion).

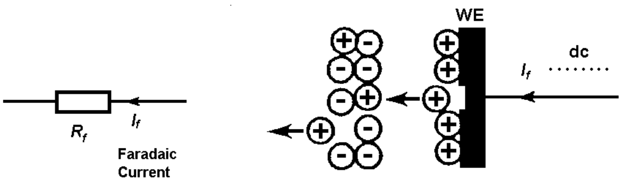


- No 'LEAKAGE':
  (Only Charge/Discharge of Double Layer)
- No Nett Current Flow
- No Chemical Reaction

AC BEHAVIOUR

35. With DC the double layer behaves like a resistor, the faradaic resistance R_f.

    A nett current flows, (I_f), and there is a chemical reaction.

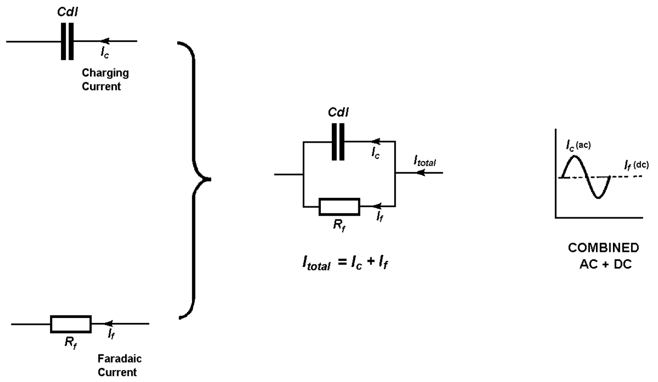


- No Nett Current Flow
- No Chemical Reaction (Corrosion)

DC BEHAVIOUR

36. Both AC and DC behaviour can happen together. The double layer is like a leaky capacitor, represented by a resistor in parallel with a capacitor.

- The AC component makes the diffuse mobile layer oscillate.
- The DC component (DC 'bias') causes faradaic current flow and chemical reaction. It also controls the mid position of the oscillating mobile layer.

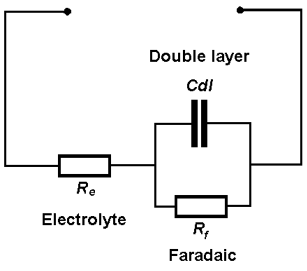


AC & DC BEHAVIOUR

Equivalent Impedances

37. Very low frequency AC is the same as slowly changing DC. So, at low frequencies, some chemical reaction can happen as well as slow oscillation of the mobile layer. But any chemical changes during the rising half-cycle are reversed during the falling half-cycle. That is, no nett changes occur with pure AC.

- With low frequency AC the impedance of capacitor C_{dl} is high. So most current flows through R_f and R_e, and DC behaviour rules.
- With high frequency AC the impedance of C_{dl} is low. *So* R_f is bypassed and most current flows through C_{dl} and R_e. This time AC behaviour rules.



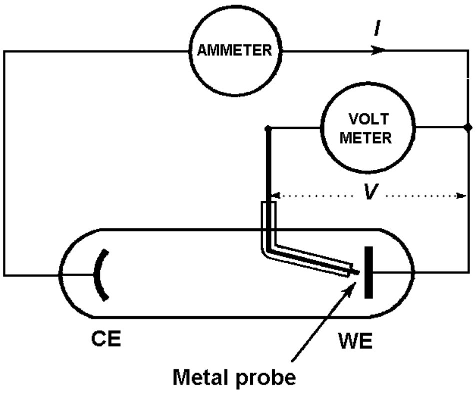
CELL EQUIVALENT IMPEDANCES

DC Measurements

38. In the study of corrosion, finding the value of the faradaic resistance is important. To do this, the potential difference ***V*** across the working electrode/electrolyte interface must be measured. The current I must also be measured.

    To measure the voltage, the tip of a sleeved metal wire probe could be positioned in the electrolyte as close as possible to the working electrode surface. Ideally it should just touch the double layer, so that none of the electrolyte resistance is included.

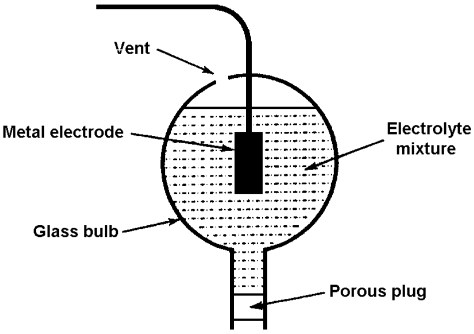
    The trouble with this idea is that, like all metals dipped in water, the probe builds up its own potential. This potential varies with the metal used, temperature, electrolyte concentration, and so on. It adds a vague extra voltage to the measured ***V***.



The Reference Electrode

39. The problem is solved by using a **REFERENCE ELECTRODE** assembly. This is a particular metal wire immersed in a specified electrolyte mixture. It has a steady and precisely known **REFERENCE POTENTIAL**.

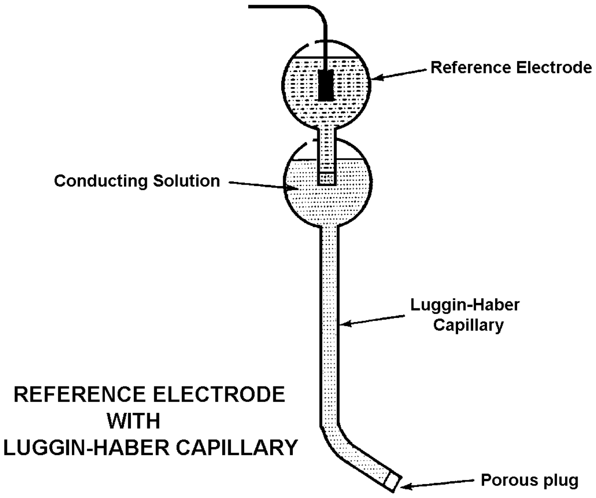
    - *Commonly used is the* ***CALOMEL ELECTRODE****. This contains a platinum wire in contact with mercury, water and compounds of mercury and potassium, at specified concentrations.*



REFERENCE ELECTRODE ASSEMBLY

40. The reference electrode assembly is too big to be positioned close to the working electrode. And in any case it should be kept out of the test cell environment.

    A probe made of a long fine tube filled with conducting solution can be used to electrically connect the reference electrode assembly to the measurement point. Special porous plugs allow good electrical contact but very little solution leakage. This is a **LUGGIN-HABER CAPILLARY**.



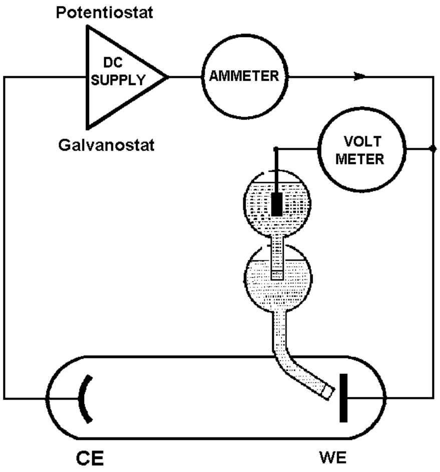
REFERENCE ELECTRODE
WITH
LUGGIN-HABER CAPILLARY

DC Measurement Set-up

41. So, a DC measurement set-up needs an ammeter to measure the current flow through the cell. A high impedance voltmeter measures (ideally) the potential difference across the double layer. For accuracy, the voltmeter connection to the electrolyte is via a reference electrode and Luggin-Haber probe.

    A variable DC power supply can force current through the cell, in either direction if needed. Using negative feedback, the power supply can automatically adjust current flow to keep the **voltage** constant, at a value selected by the user. This is a **POTENTIOSTAT**.

    Or, the voltage can be automatically adjusted by a feedback loop to keep the **current** at a constant selected value. This is a **GALVANOSTAT**. Both are useful.



DC MEASUREMENT SETUP

The 1287 Electrochemical Interface

42. The **1287 Electrochemical Interface** combines all these DC measuring features, and many more, in a single instrument.

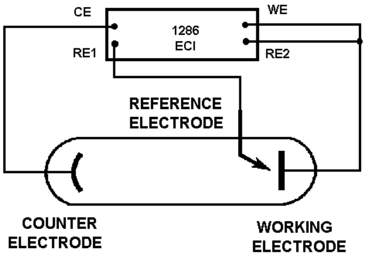
    Current is driven through the cell via the counter and working electrodes. These are connected to the **CE** and **WE** terminals in the 1287.

    The 1287 ECI measures the potential difference between terminals **RE1** and **RE2**. The reference electrode connects to the RE1 terminal and the working electrode connects to RE2. This is a **THREE-TERMINAL** cell.

    Sometimes an experiment needs **two** reference electrodes. Here the RE2 terminal connects directly to the second reference electrode, not to the working electrode. This is a **FOUR-TERMINAL** cell.

    Control of the cell can be **potentiostatic**. The user-set potential across RE1 and RE2 is called the **POLARISATION VOLTAGE**.

    Or control can be **galvanostatic**. The user-set current via CE and WE is called the **POLARISATION CURRENT**.

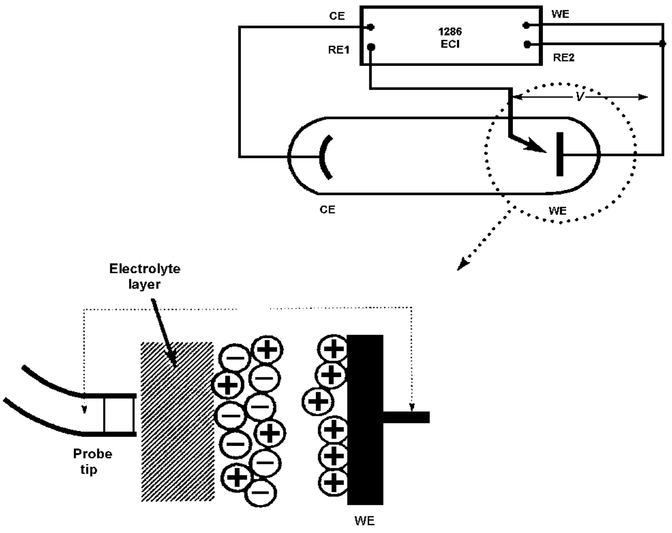


THE 1286 ELECTROCHEMICAL INTERFACE

Parasitic Electrolyte Resistance

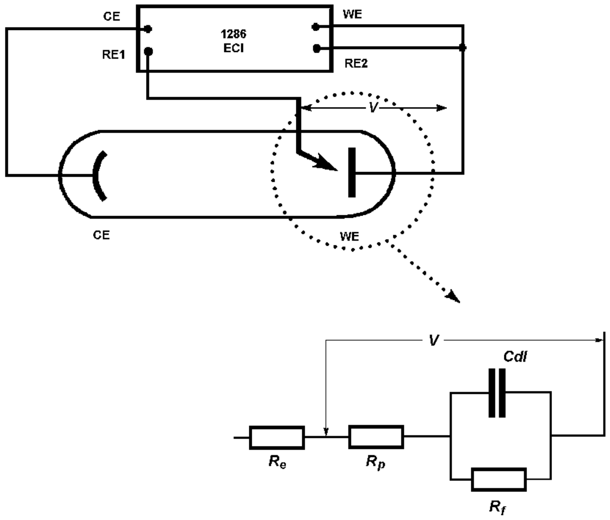
43. A problem with the three-terminal cell is getting the tip of the reference electrode probe close enough to the double layer to just touch its outer surface.

    In practice a thin layer of electrolyte always remains between the probe tip and the double layer.



44. This layer of electrolyte has an unwanted resistance which is in series with the double layer. It is the **PARASITIC ELECTROLYTE RESISTANCE R_p**. Voltage ***V*** includes the potential drop across Rp as well as the double layer.

    - *The **1287 Electrochemical Interface** can measure R_p, and then electronically eliminate its effects. This allows the voltage across the double layer itself to be measured and controlled.*



Measuring Corrosion Rate

45. An obvious way to measure corrosion rate is to:

    1. Weigh a bar of metal.
    2. Leave it in the corrosive liquid for a certain time.
    3. Re-weigh the corroded bar.

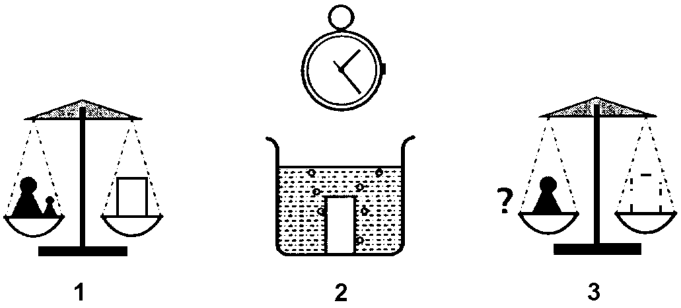
    From this the weight loss per minute is calculated. That is, the corrosion rate.

    But the weaknesses of this weight loss method are:

    - It can take a long time.
    - It can be inaccurate especially for slow corrosion rates.
    - It cannot be used if some of the corrosion products stick to the bar and upset the weight measurements.

    By using the 1287 Electrochemical Interface these disadvantages are avoided. The 1287 ECI performs DC measurements **quickly** and **reproducibly**, enabling faradaic resistance to be calculated and so corrosion rate.

    Other data about cell reaction mechanism, and electrolyte resistance, are also obtained at the same time.



WEIGHT LOSS METHOD

AC Measurement Set-up: 1287 ECI + 1250 FRA

46. There are no limitations in doing purely DC measurements:

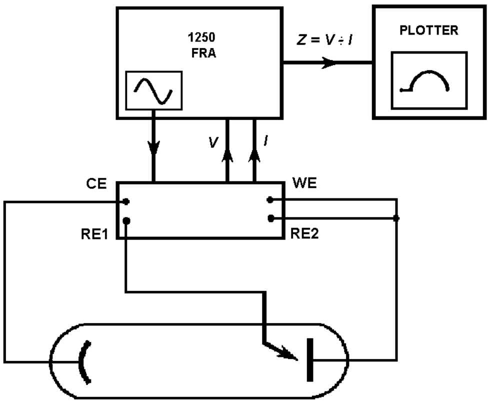
- They give no information about the double layer capacitance.
- Very low conductivity electrolytes can give inaccurate results (because so little DC current flows).
- Corrosion products sometimes build-up and change the nature of the system being measured.

These problems are solved by adding a small **AC signal** to the DC polarisation voltage being applied to the cell. Now both **AC behaviour** and **DC behaviour** can be measured at the same time.

This may be done by connecting a **1250 Frequency Response Analyser** to the 1287 ECI. Sine waves generated by the 1250 are fed to the 1287 where they add to the DC signal. The combined signal stimulates the cell.

To get maximum data from the cell a **FREQUENCY SWEEP** can be used. That is, the AC frequency is programmed to vary in small steps from practically DC through to many kilohertz. The AC amplitude is kept low to minimise the disturbance to the cell.

One very good way of recording the results is to program the 1250 to calculate the **AC IMPEDANCE** of the cell, from the voltage and current measurements being made by the 1287. This AC impedance can be plotted in real time, under control of the 1250, to show how it varies with frequency.

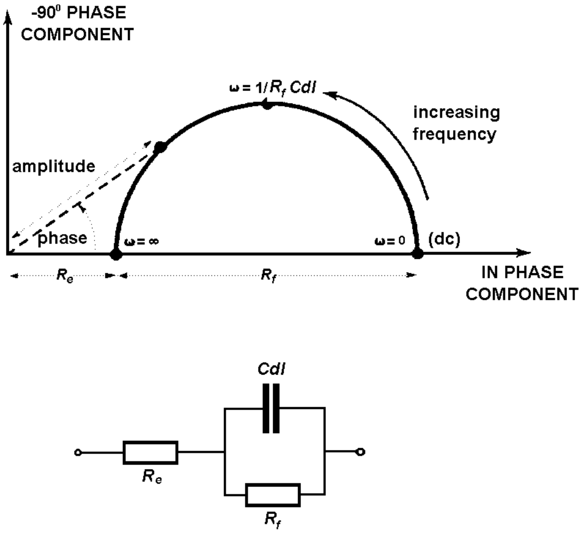


AC WORK: 1286 ECI + 1250 FRA

47. The resulting **IMPEDANCE PLOT** shows how the amplitude **and phase** of the cell's impedance change with frequency. From the plot, ideally, R_f, R_e and C_{dl} can be found as well as other data on the cell chemistry and kinetics.

    AC methods offer many advantages:

    - Data on several cell parameters are obtained quickly and simultaneously.
    - High electrolyte DC resistance is not a problem.
    - No reaction products build up because there is no nett current flow (if the DC component is made zero). This results in the least possible disturbance of the cell.
    - The AC impedance plot can change markedly for tiny otherwise undetectable changes in the specimen. This makes the method very sensitive. The plot can act as a finely detailed 'fingerprint' of an electrochemical system.



AC IMPEDANCE PLOT

Related Solartron Publications

	Part No.
Identification of Electrochemical Processes by Frequency Response Analysis (Prof. Claude Gabrielli)	BTR004
An Introduction of Electrochemical Impedance Measurement (Dr N D Cogger)	BTR006
Frequency Response Analysis (Dr P E Wellstead)	BTR010
The Measurement of Signals from Electrochemical Phenomena (Dr N D Cogger)	BTR014
Use & application of EIS Techniques (Prof. Claude Gabrielli)	BTR024

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