

4.08 Introduction to Electrode Potentials

(5 points)

1 Outline

This experiment illustrates the first year lectures on equilibrium electrochemistry, although parts of it are relevant to material encountered throughout the Part I course. Its specific aims are:

To show how electrode potentials arise on a variety of different types of electrode.

To emphasize the use of the Nernst Equation in predicting cell potentials.

To illustrate the use of electrode potentials in determining thermodynamic data, notably entropy changes by the variation of electrode potentials with temperature.

To explore the non ideality of electrolyte solutions.

2 Safety

Most of the chemicals you will use in this experiment are not especially hazardous. However, lead acetate is very poisonous, as is potassium dicyanoargentate(I).

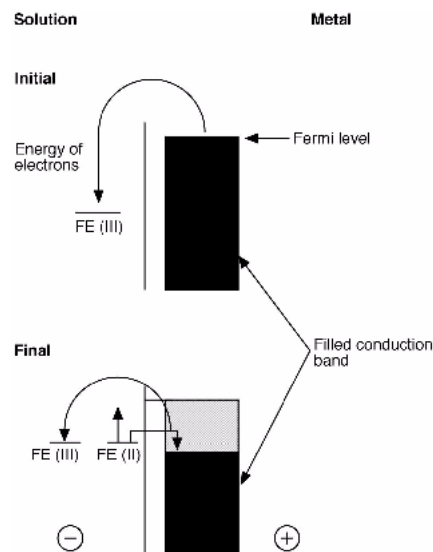
Some platinum compounds act as sensitizers – that is, skin contact may produce an allergic reaction which becomes more severe with each further contact. Chronic exposure may lead to susceptibility to anaphylactic shock. It is therefore essential that you use these compounds in a fume cupboard, and wear gloves when handling them, or solutions containing them. If any signs of allergy or irritation become evident, immediately cease work and contact a demonstrator.

Potassium ferricyanide and potassium ferrocyanide are poisonous; use gloves when weighing them out. You can obtain more detailed safety information through the web page for this experiment, <http://ptcl.chem.ox.ac.uk/~hmc/tlab/experiments/408.html>

3 Theory

This section provides a brief summary of the theoretical background relevant to this experiment. If you are familiar with the treatment in Atkins, "Physical Chemistry", or Compton and Sanders, "Electrode Potentials", you may want to move directly to the experimental section.

Fig. 1. Relationship of the Fermi level to ion potential.



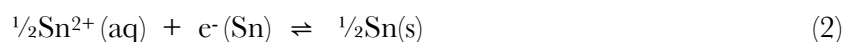
Introduction

Electrode potentials arise as a result of the transfer of electrons between a metal (electrode) and a solution (Fig. 1). Examples include:

* an inert platinum wire dipping into an aqueous solution of Fe^{2+} and Fe^{3+} :



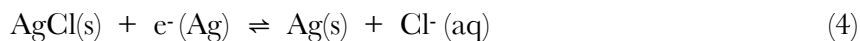
* a tin electrode dipping into an aqueous solution of Sn^{2+} :



* an inert platinum electrode dipping into a solution of chloride ions, over which chlorine bubbles:



* a silver wire coated with silver chloride dipping into an aqueous solution of chloride ions:

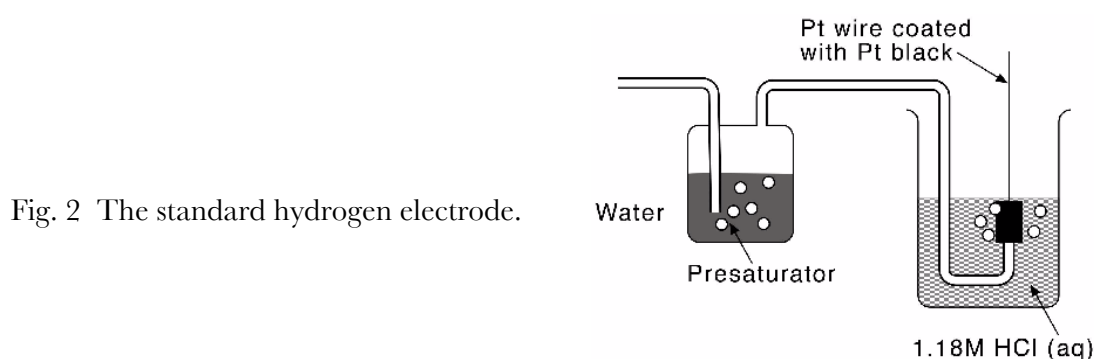


A transfer of charge (electrons) between metal and solution causes a potential difference (p.d.) to develop between the electrode and the solution. We cannot measure this directly, since any such measurement requires another electrode dipping into the solution. We therefore use a reference electrode against which all other electrodes are measured. Historically, this reference is the Standard Hydrogen Electrode (SHE), in which the potential determining equilibrium is:

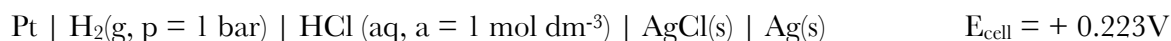


An inert platinum wire, over which hydrogen gas is bubbled, dips into hydrochloric acid solution and acts as the electrode (Fig. 2). The electrode potential of this half-cell is defined to be 0V. Note that because this electrode is taken to be the reference electrode, it must be reproducible, so its conditions need to be rigorously defined: partial pressure of $H_2 = 1$ atm (we will approximate this to 1 bar - see footnote 4); $[H^+] = 1.18M$ (corresponding to unit activity; note that the concentration of acid in the cell is 1.18M, *not* 18M!); $T = 298K$.

To ensure fast electrode kinetics, a platinum black catalyst is used. Pt-black coated surfaces provide a greater surface area for the adsorption of gas molecules than shiny surfaces, due to the presence of finely divided Pt on 'platinised Pt'. The greater rate of adsorption causes the true electrode potential to be attained more quickly for Pt-black electrodes than for bright Pt electrodes.



An electrochemical cell is made up of two electrodes and an electrolyte. A simple example is the Harned cell:



Each vertical line in the above 'cell diagram' refers to a phase boundary. Salt bridges are represented by a double vertical line ||.) Note that in quoting potential differences together with a cell diagram, the convention is to specify the potential, ϕ , of the right hand electrode relative to that of the left hand electrode. Thus for the above cell

$$+0.223 \text{ V} = \phi_{\text{Ag}} - \phi_{\text{Pt}}$$

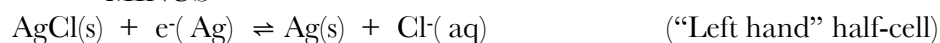
Alternatively for the cell written as



The value of E_{cell} reflects the difference in the potentials established by processes (4) at the Ag electrode and (5) at the Pt electrode. E_{cell} is related to the free energy change of the reaction:



MINUS



via the equation¹

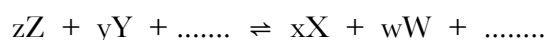
$$\Delta G = -FE_{\text{cell}}$$

If all chemical species participating in the potential determining equilibrium at the two electrodes are present under standard conditions, then $E_{\text{cell}} = E^\circ$ and $\Delta G^\circ = -FE^\circ$. The standard conditions are:

- * gases have unit pressure, and
- * solutes have unit activity. The extent to which the latter can be approximated by unit concentration is discussed below.

The conditions (temperature, gas pressure, solute activities,...) under which a cell is operating affect the electromotive force (emf) set up between its two electrodes. This emf is conventionally measured with a digital voltmeter. The Standard Electrode Potential (SEP) of any redox system is defined as the measured p.d. between the two electrodes of a cell in which the electrode of interest is measured relative to the SHE and in which all the chemical species contributing to the potential determining equilibria at each electrode are present at a concentration corresponding to unit activity in the case of a solution phase species, or to unit pressure in the case of a gas.

The Nernst Equation tells us how the cell emf's vary with temperature and activity of all species contributing to the potential determining equilibria at each electrode. For the cell reaction:



corresponding to a transfer of one mole of electrons per mole-equation at each electrode, the Nernst equation is:

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{F} \ln \left\{ \frac{a_X^x a_W^w \dots}{a_Z^z a_Y^y \dots} \right\}$$

In the equation above, $E_{\text{cell}}^\circ = E_{\text{right-hand electrode}}^\circ - E_{\text{left-hand electrode}}^\circ$ ('right' and 'left' are defined by the cell diagram)

¹This equation only applies to one electron transfers per mole-equation. If n electrons are transferred per mole-equation, then this expression becomes $\Delta G = -nFE_{\text{cell}}$.

- R = universal molar gas constant = $8.3145 \text{ JK}^{-1}\text{mol}^{-1}$
 T = absolute temperature
 F = Faraday constant = $96\,485 \text{ Cmol}^{-1}$
 a_i = activity of species i ;

$a_i = \gamma_i[i]$ where γ_i is the activity coefficient of i and $[i]$ is the molality of species i (in other words, the number of moles of i per kilogram of solvent. When water is the solvent, the molality and molarity are generally very similar.) The activity of a pure solid or a pure liquid is one; for gases, partial pressure replaces activity (for very high gas pressures, where non-ideal behaviour may be detectable, fugacity is used instead of partial pressure. However, for gases at temperatures well above their critical point, the partial pressure is usually entirely adequate.)

For example, the Nernst Equation for the Harned cell is given by²

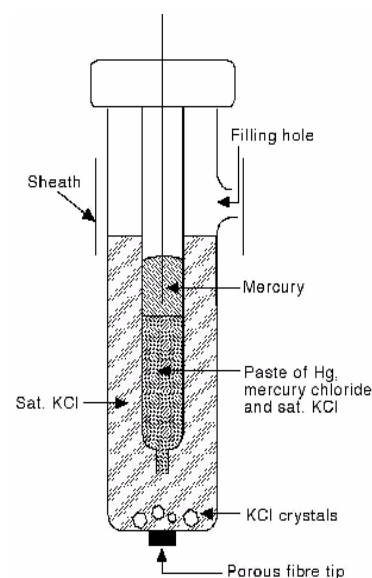
$$E_{\text{cell}} = 0.223 - \{RT/F\} \ln \{1/[a_{\text{H}^+} \cdot a_{\text{Cl}^-}]\}$$

Salt Bridges and Calomel Reference Electrodes

Salt bridges are vital electrical connections between two half-cells in which the electrolytes at each electrode are not identical. Mixing the two electrolytes would either cause a chemical reaction, or would change the concentration of the electrolyte.

Salt bridges are designed such that there is no 'liquid junction potential' (ELJP) between the solution/bridge interface. Any such potential would interfere with the measurement of the cell emf. The elimination of the liquid junction potential is neatly done by making the salt bridge out of a saturated solution of an electrolyte that has similar transport numbers for both cation and anion (e.g. KCl , KNO_3 , NH_4NO_3).

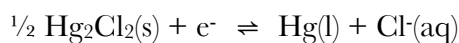
Fig. 3. The calomel electrode



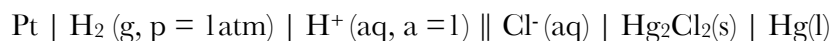
The use of SHEs in experimental procedure often dictates the use of a salt bridge. However the calomel electrode (Fig. 3) is a more convenient reference electrode to set up and to use, and often eliminates the need for a salt bridge. The potential determining

²Note that the partial pressure of hydrogen is one atmosphere, and that silver and silver chloride have unit activity. Also note that the activities of the hydroxonium and chloride ions are used, and not the "activity of hydrochloric acid", a_{HCl} . The inclusion of a_{H^+} and a_{Cl^-} rather than a_{HCl} reflects the true nature of the chemical species involved in the established potential determining equilibria as shown by equations (4) and (5).

equilibrium is:



The emf of the cell:



is +0.242V at 298K. Note the following.

* This value is not the SEP of the calomel electrode, since the activity of the saturated KCl(aq) (ca. 6M) is not unity. (the SEP = + 0.27V).

* The electrode has a salt bridge built in. This is a porous frit between the electrolyte and the saturated KCl solution in the electrode (see Fig. 4). This means there is no ELJP when the electrolyte dips into dilute aqueous solutions.

Electrode Potentials and Thermodynamics

Electrochemical (galvanic) cells can allow us to determine thermodynamic data, often with great precision and accuracy.

Since $dG = VdP - SdT$, $(\partial G/\partial T)_P = -S$, it follows that $(\partial \Delta G/\partial T)_P = -\Delta S$.

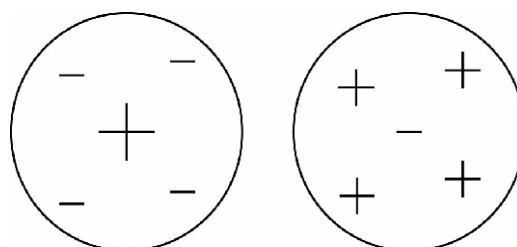
As $\Delta G^\circ = -FE^\circ$, $F(\partial E^\circ/\partial T)_P = \Delta S$, and $F(\partial E^\circ/\partial T)_P = \Delta S^\circ$.

Further $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, $\Delta H^\circ = -FE^\circ + TF(\partial E^\circ/\partial T)_P$

Debye-Hückel Theory

Electrolytic solutions are grossly non-ideal since charged species are present. In solution, ions interact with each other and so their movement is not entirely random. The ions set up ionic atmospheres in which each cation is surrounded by a diffuse charge cloud of anions, and vice-versa. These atmospheres on a time-average are spherically symmetrical (see Fig. 4).

Fig. 4. Clustering of counterions around anions and cations.



It is found experimentally that $\gamma < 1$ for dilute electrolytic solutions ($\gamma = 1$ for ideal solutions). The Debye-Hückel Limiting Law states that:

$$\log \gamma_i = -A z_i^2 I^{\frac{1}{2}}$$

where A is a solvent and temperature specific parameter (= 0.509 for water at 298K.)
 z_i is the charge on species i, I is the ionic strength of the solution, defined by

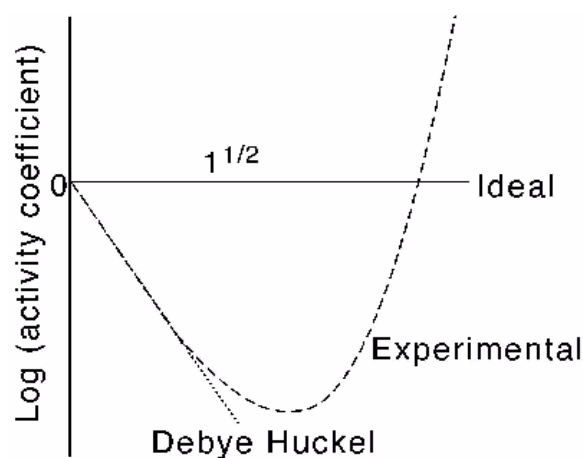
$$I = \frac{1}{2} \sum [i] z_i^2$$

Note that this expression is only valid at low ionic strengths ($< 10^{-2}m$), as it assumes:

- * solution non-ideality is only due to ion/ion interactions, and not at all due to ion/solvent interactions,
- * ions are point charges that obey Coulomb's Law, and
- * the electrolyte is fully dissociated, and there are no ion-pairs in the solution.

Figure 5 shows the experimentally determined relationship between γ and I, and that predicted by Debye-Hückel Theory. Note the axes show $\lg \gamma$ and \sqrt{I} . Evidently, Debye-Hückel Theory is only an approximation at high ionic strengths, as ion/solvent interactions become significant.

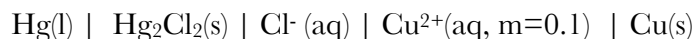
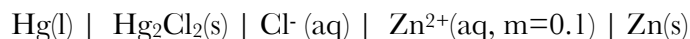
Fig. 5. Debye-Huckel, ideal and experimental variation of the activity coefficient with concentration.



Experimental procedure and calculations

Electrode Potentials

Prepare 100 cm³ of 1M zinc nitrate solution, starting from the solid (strictly you should be using molality throughout, but it is reasonable to replace molal solutions by molar solutions). Dilute a 10 cm³ portion to 0.1m. Prepare 100 cm³ of 0.1m copper sulfate solution from the stock supplied. Set up the following cells, using your 0.1 m solutions of zinc (II) nitrate and copper (II) sulfate and a calomel electrode.

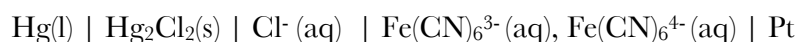


Measure the emf of each cell using a digital voltmeter (DVM). Make sure that your reading is steady, before you record it. Hence determine the standard electrode potentials of the Zn/Zn²⁺ and Cu/Cu²⁺ couples, measured on the hydrogen scale assuming that the 0.1 m solutions approximate to ideality

The Nernst Equation

For the Calomel/Zn cell that you prepared above, choose five concentrations of the zinc nitrate solution in the range $10^{-4} < [\text{Zn}^{2+}] < 1.0 \text{ mol dm}^{-3}$, and measure the cell emf for each concentration. Plot E_{cell} against $\lg[\text{Zn}^{2+}]$. Compare the slope of your graph with that predicted by the Nernst Equation.

Carefully (using gloves), prepare four solutions containing equimolar amounts of both potassium ferricyanide and potassium ferrocyanide³ in the range 0.0005 to 0.05 mol dm⁻³ (if any is spilt onto your skin wash thoroughly under a tap and report it to lab technician). Measure the emf between a bright platinum electrode placed into the solutions, and a calomel electrode:



Tabulate your results, and interpret them in terms of the Nernst Equation.

Set up the following cell, in which the left hand electrode is a standard hydrogen electrode (you may use 1M HCl for this electrode, even though strictly you should use 1.18M acid):



Prepare Pt-black electrodes (Appendix A) for this purpose. Note that the arrangement will be different to that in fig. 2, as the electrode that you will use has a hydrogen gas connection. Set the pressure of the hydrogen (see the appendix for the operation of gas cylinders) to 1 bar⁴. (DO NOT APPLY EXCESS PRESSURE as this will cause overly-vigorous bubbling which can lead to the spillage of hydrochloric acid.) The hydrogen should be bubbling at a rate of about one bubble per second through the acid. Measure the emf of the cell (E_1). This should be +0.242V. A steady reading may take some time to develop. Calculate the difference between your value and that expected where appropriate. This is the calomel correction. If there is a difference, you must apply the following equation and correct all of your results.

$$E_{\text{corrected}} = E_{\text{measured}} + (0.242 - E_1)$$

³Using IUPAC nomenclature, ferricyanide is hexacyanoferrate(III), $[\text{Fe(CN)}_6]^{3-}$, and ferrocyanide is hexacyanoferrate(II), $[\text{Fe(CN)}_6]^{4-}$.

⁴One bar is defined as being equal to 10⁵ Pascals. One atmosphere pressure is strictly equal to 1.01325 bar.

Temperature Dependence of Cells

Silver/Silver Chloride - Calomel

Set up the following cell in a water bath, using a 1M solution of HCl..



Use the commercial calomel and the silver/silver chloride reference electrodes provided. You will need to replat the silver/silver chloride electrode with a thin layer of fresh silver chloride in order to get good data.

Measure the emf of the cell at six temperatures between 310 and 340K, allowing time to reach thermal equilibrium. Plot E_{cell} against T and hence determine $\Delta S_r(298\text{K})$ and $\Delta H_r(298\text{K})$ for the relevant cell reaction. Comment on the sign of $\Delta S_r(298\text{K})$ in the light of the latter.

Zinc-Ferricyanide/Ferrocyanide

This experiment involves use of a salt bridge (Fig. 6); instructions on preparing a salt bridge are available from the technician. If in doubt as to the need for a salt bridge in this experiment, try mixing a small amount of the two solutions.

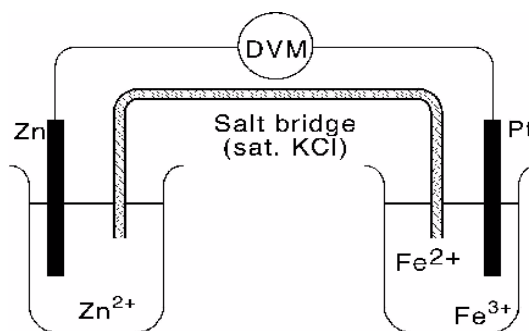
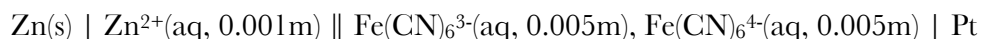


Fig. 6. A cell with a salt bridge.

Set up the following cell in a water bath.

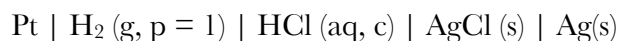


Vary the temperature of the water bath from 300 to 330K. Record the cell emf at six temperatures within this range.

Explain why it is difficult to determine thermodynamic quantities for the reaction taking place in this cell, although you could do this for the previous cell. What conclusions can you draw from your data? (Hint: Under what conditions do your readings not depend upon knowing the activities?)

Harned Cell and Non-Ideality

Prepare a silver/silver chloride electrode (Appendix A). Prepare six solutions of hydrochloric acid with concentrations, c , in the range of 1.0M to 0.005M. Set up the Harned Cell:



Measure the emf of the cell, varying the concentrations of HCl. Plot a suitable graph to determine the standard electrode potential of the silver/silver chloride electrode. See Atkins's chapter ten, page 321, or Compton and Sanders, chapter four, page 65, if in doubt. Calculate the mean activity coefficient (γ_{\pm}) of the H^+ and Cl^- ions at 1.0M HCl(aq). Comment.

Appendix A Preparation of Electrodes

Carry out all electroplating operations and handling of concentrated acids in fume cupboard number one. Wear eye protection at ALL times and gloves when handling strong acids and where advised below.

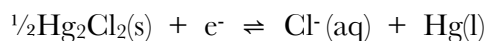
Metal Electrodes

Metal electrodes are usually made from a wire, gauze or a spade of metal, sealed through a glass tube. The metal may be joined by soldering, or by a drop of mercury to a second wire within the tube but not exposed to the solution. The electrical characteristics of metal electrodes can depend on the state of their surfaces; care must be taken in preparing them.

To make copper or zinc electrodes, clean wire or rod electrodes gently with fine sandpaper⁵ before use. Freshly cleaned surfaces are reactive, so should not be exposed to air for long. Store metal electrodes in demineralized water until you need them.

Calomel Electrodes

A saturated calomel electrode is supplied. The potential determining equilibrium of this electrode is:



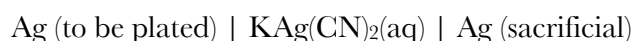
The electrode potential relative to the standard hydrogen electrode is +0.242V at 298K, provided that the solution inside the calomel electrode is saturated with KCl (ca 6M). Calomel electrodes must be stored in a KCl solution of the same strength as the filling solution.

⁵For metals we use "wet and dry"; for wood, we use ordinary sandpaper.

Silver/ Silver chloride Electrodes

Ask a demonstrator or technician to supervise you whilst you prepare silver/silver chloride electrodes. You must use a fume cupboard that is turned on. Wear gloves and safety goggles at all times.

Clean the silver wire provided first with 'wet and dry' sandpaper, and then by dipping the wire into 3M nitric acid. Wash the wire thoroughly with demineralized water. Next, to roughly 75ml of demineralized water, dissolve about an eighth of a (small) spatula of potassium dicyanoargentate(I) [KAg(CN)₂]. This solution (and fumes from it) are toxic, so TAKE CARE. Set up the following cell:



Connect the cell to a power pack (this is on the end of fume cupboard number one) and pass a current of about 10mA for about 10 minutes. Note that the silver electrode to be plated is the cathode. This becomes plated with a fine layer of metallic silver. The other electrode is an anode, and dissolves during the experiment to form Ag⁺. You may however get a white solid on the anode, and a cream solid on the cathode. These should be removed by thoroughly washing the electrodes in demineralized water. There should NOT be any white solid on either electrode when you continue with the preparation.

Wash the electrodes before chloridizing the electrodes by passing a 10mA current through a cell containing a platinum cathode, with a 25% (by volume) hydrochloric acid solution, for about 10 mins. In this cell, the anode should be the cathode that was plated with silver above. The Ag/AgCl electrode will vary in colour from plum to brown. Wash the electrodes with water, and store the Ag/AgCl electrode under saturated KCl in a darkened bottle. You must use this electrode on the same day as its preparation, since it is light sensitive.

Platinum-black Electrodes

You must wear safety goggles, rubber gloves and a safety mask at all times during this preparation. The solution is TOXIC. If it is spilt, dilute with demineralized water and clean it up immediately, and report the incident to the technician. Ensure that the fume cupboard is turned on. Platinum compounds may act as sensitizers, and for susceptible individuals, chronic exposure may lead to debilitating long-term and irreversible harm. Use of gloves when handling platinum compounds is therefore essential. (Platinum metal, however, may be regarded as safe to handle.)

Do not attempt to clean platinum electrodes with sandpaper. Instead, dip them into 3M nitric acid, and wash with demineralized water. Take the platinum containing solution from the bottle covered in silver foil in the fume cupboard (number one). This will be the electrolyte, and contains both chloroplatinic acid (H₂PtCl₆) and a small quantity of lead acetate. Use the platinum electrode to be coated as the cathode, and as anode, use a bright Pt electrode. Pass a current of ca 150mA for one to three minutes.

You should obtain an electrode that is black and evenly coated. Wash your Pt-black electrode with demineralized water, under which it must be stored. Return the platinum-containing electrolyte to the bottle, ensuring that you do not contaminate this solution.

Appendix B Use of the hydrogen cylinder

1. Check that all taps for the hydrogen supply leading into the laboratory are off.
2. Check that the handle in the middle of the front face (3) is turned fully anticlockwise - do NOT turn it hard against the stop, but turn gently anticlockwise until slight resistance is felt.
3. Using the spanner supplied, open the main valve (2, at the top of the cylinder itself).
4. Slowly screw the handle on the front face clockwise until the low pressure gauge is slightly above its zero reading.
5. Twist the red screw (4) through one full rotation anticlockwise (looking down onto the screw).
6. To close the cylinder, carry out steps 2-5 in reverse order.

