digital voltmeter or potentiometer with standard cell; fume cupboard with 6 V d.c. power supply with meter 50 or 100 mA f.s.d.; stirrer; [cell vessel].

Solutions

0.1 M HCl, 0.1 M solution of ethanoic (acetic) acid, 0.1 M NaOH, plantinizing solution as described in Technical notes on p. 136.

References

[1] *Electrolyte solutions*. R. A. Robinson and R. H. Stokes. Butterworths, London, 2nd edn (rev) (1970), p. 198.

[2] *The physical chemistry of electrolytic solutions*. H. S. Harned and B. B. Owen. Reinhold, New York, 3rd edn. (1958), Ch 11.

[3] *Modern electrochemistry*. J. O'M. Bockris and A. K. N. Reddy, Macdonald, London (1970), vol. 2, p. 1121.

[4] *The determination of stability constants*. F. J. C. Rossotti and H. Rossotti. McGraw-Hill, New York (1961), p. 140.

[5] *The dissociation constant of acetic acid* from 0 to 60° Centigrade, H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.* **55**, 652 (1933).
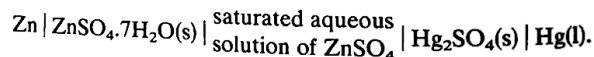
4.4 Thermodynamics of a chemical reaction from temperature coefficient of a cell e.m.f.

The measurement of the e.m.f.s of electrical cells under reversible conditions, and the variation of cell e.m.f. with temperature, are valuable and commonly used methods of obtaining thermodynamic quantities for chemical reactions.

In this experiment we obtain the free energy change ΔG, the enthalpy change ΔH and the entropy change ΔS for the reaction

$$Zn(s) + Hg_2SO_4(s) + 7H_2O(l) \rightleftharpoons ZnSO_4 \cdot 7H_2O(s) + 2Hg(l).$$
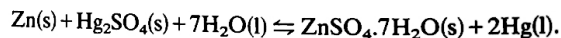
We do this by measuring the e.m.f. E, and the temperature coefficient at constant pressure $(\partial E/\partial T)_p$, of the Clark cell:

$$Zn \mid ZnSO_4 \cdot 7H_2O(s) \mid \begin{array}{c} \text{saturated aqueous} \\ \text{solution of } ZnSO_4 \end{array} \mid Hg_2SO_4(s) \mid Hg(l).$$

Theory[1]

The free energy change ΔG for one mole of the cell reaction is related to the cell e.m.f. E by the relation

$$\Delta G = -zFE, \tag{4.4.1}$$

where F is the Faraday constant, and z refers to the number of electrons transferred in the reaction (p. 121).

Since $(\partial \Delta G/\partial T)_p = -\Delta S$, it follows that

$$\Delta S = zF(\partial E/\partial T)_p. \tag{4.4.2}$$

By definition, $\Delta H = \Delta G + T\,\Delta S$, and therefore

$$\Delta H = -zFE + zFT(\partial E/\partial T)_p. \tag{4.4.3}$$

Apparatus[2]

The Zn amalgam will be thermodynamically equivalent to solid zinc when (and only when) it is saturated with zinc.

The Clark cell, shown in Fig. 4.4.1, is supplied ready-assembled. The zinc is in the form of a ~40 per cent w/v amalgam of zinc in mercury, which makes the electrode potential more reproducible. When the cell is being cooled down again after heating, hydrated zinc sulphate crystallizes out of solution. As it does so, there is a tendency for air bubbles to form, which, if they accumulate sufficiently, will prevent the cell developing an e.m.f. The insertion of glass wool into the side-arm minimizes this effect, but does not entirely prevent the development of air locks over a period of time.

A convenient way of maintaining the cell at a stable, known temperature is to mount it in a Dewar flask, and pour in water which has been heated or cooled to the required temperature.

The e.m.f. of the cell is measured with a potentiometer or digital voltmeter (DVM) (p. 131).
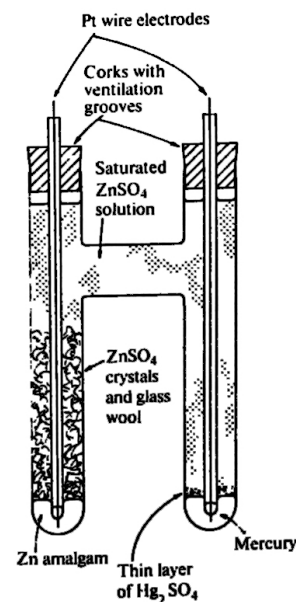

Fig. 4.4.1. A Clark cell

Procedure

If using a potentiometer, standardize it and connect it as instructed.*

Connect the potentiometer or DVM to the cell. It is important that the cell be kept *upright* at all times.

Measure the e.m.f. of the cell at room temperature. If using a potentiometer, confirm that the cell is functioning reversibly. Do this by checking that, in two consecutive measurements, the e.m.f. is independent of the side from which the balance point is approached.

Mount the Clark cell in the Dewar flask. Heat some water in a beaker to 41 °C, and pour it around the cell. Cover the cell, but keep the water well away from the corks and electrodes. Allow time for thermal equilibrium to be achieved.

Measure the e.m.f. of the cell at 40 °C. It should be within 15 mV of 1.400 V. If it is not, *gently* wiggle the electrode which dips into the amalgam. If this does not give the correct e.m.f., seek advice.

Repeat the procedure for nine temperatures spaced over the range 0 °C to 40 °C. Do not study the temperature variation sequentially, but instead change the order of temperature so as to randomize any systematic errors associated with increasing or decreasing the temperature.

At the end of the experiment, ensure that the wires are disconnected from the electrodes of the cell.

The criterion for judging whether thermodynamic equilibrium has occurred within the cell is the constancy of the cell e.m.f. Attainment of thermal equilibrium is not the only requirement for this; time must also be allowed for mass transport, especially when the temperature is increased.

Calculation

Plot the e.m.f. E in volts against the temperature T of the cell in kelvins.

Calculate or estimate graphically the best-fitting straight line through the points. Obtain the value of E at 298 K by interpolation. Measure the slope of the line $(\partial E/\partial T)_p$.

From your experimental observation of the polarity of the cell and your knowledge of the constitution of its electrodes, state the direction of the cell reaction given previously. Show that $z = 2$.

Calculate ΔG, ΔH and ΔS for the cell reaction (eqns (4.4.1), (4.4.2) and (4.4.3)).

Employ your knowledge of thermodynamics to answer the following questions:[1]

(a) Why is the sign of ΔG negative for the cell reaction?

(b) How can the value of ΔS be interpreted in terms of the physical changes occurring in the reaction?

(c) What is meant by reversible conditions in the context of this experiment, and why is it necessary to measure E under reversible conditions in order to evaluate ΔG and ΔS?

(d) When the cell is operating reversibly, what is the magnitude of the heat exchanged with the surroundings and the direction of its flow?

(e) Under what conditions would all the energy of the reaction appear as heat lost to the surroundings? What is the magnitude of this heat loss?

Results

Accuracy

The cell e.m.f. may alter if non-negligible currents have been drawn from it, or if air locks have formed after it has been in service for some time.

Comment

This experiment demonstrates a convenient way of measuring the thermodynamic changes accompanying a chemical reaction. The limitation on the method is that the reaction must occur in a reversible cell at the temperature of interest, and many electrodes are not reversible (p. 122). The questions provide an interesting exercise in the application of the First and Second Laws of thermodynamics.

Technical notes

Apparatus

Clark cell (Fig. 4.4.1), including Pt wire electrodes (p. 131), and Zn amalgam;*† potentiometer with galvanometer and standard cell, or DVM; [Dewar flask]; electrical leads; beaker, bunsen burner, gauze.

Preparation of Zn amalgam

Allow an excess quantity of fresh zinc shavings to dissolve in mercury in a stoppered flask for two or three days.

References

[1] *Basic chemical thermodynamics*. E. B. Smith. Clarendon Press, Oxford, 3rd edn (1982), p. 105.
[2] *A laboratory manual of experiments in physical chemistry*. D. Brennan and C. F. H. Tipper. McGraw-Hill, London (1967).

4.5 Redox potentials and equivalence points from potentiometric titrations

An *electrode potential* is the potential associated with the reduction of a species by electrons, relative to that of the reduction of protons by electrons. *Redox potentials* refer to reductions in