

SHORT COMMUNICATIONS

EXCESS ENTHALPY DURING ELECTROLYSIS OF D₂OK. S. V. SANTHANAM, J. RANGARAJAN,
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RECENTLY several reports¹⁻⁵ discussed the generation of excess enthalpy during the electrolysis of D₂O and suggested the possibility of either nuclear fusion^{1,2,6} or chemical reaction^{2,7} as the cause of this excess enthalpy. We wish to consider here the enthalpy estimates arising from the adsorption of D₂ ($-\Delta H = 120 \text{ kJ mol}^{-1}$) and the recombination of D₂ and O₂ in the electrolytic cell ($-\Delta H = 285 \text{ kJ mol}^{-1}$).

D₂O used in the experiments had a purity of 99.5% (as determined by NMR). The titanium cathode (4" × 4") was cleaned and etched to remove oxide films and impurities on the surface of the metal. Platinum sputtered on glass and of the same area as the Ti cathode was used as the anode. Sodium chloride (BDH, Analar grade; 1.16 g) was dissolved in 20 ml of D₂O and used for the electrolysis. The temperature of the electrolytic solution was measured continuously using either a Beckman or a Riege (DDR) thermometer. The cathode surface temperature was measured using a P 85 BIOA. 202 N thermistor (Thermometrics, N. J., USA; $R = 1.845 \text{ k}\Omega$). The electrolytic cell was a 50 ml beaker to which a Perspex plate was fitted to hold the electrodes in parallel configuration. The cell was placed in a Dewar during the experiment. Cooling correction to be applied to the measured temperature was obtained by independently running the electrolysis in the same cell to the steady state temperature and allowing it to cool to the initial temperature. The correction interval was kept the same as the temperature measuring interval, as Newton's law of cooling is valid only for short temperature intervals.

Figure 1 shows the current-voltage curve of D₂O at Ti working electrode. An interesting feature of this curve is the appearance of looping (hysteresis) during the anodic sweep following the cathodic potential sweep to -1.20 V vs SCE . Clearly there is no desorption peak observed during the anodic cycle, as is generally seen. The pronounced hysteresis resulting from adsorption sluggishness has been

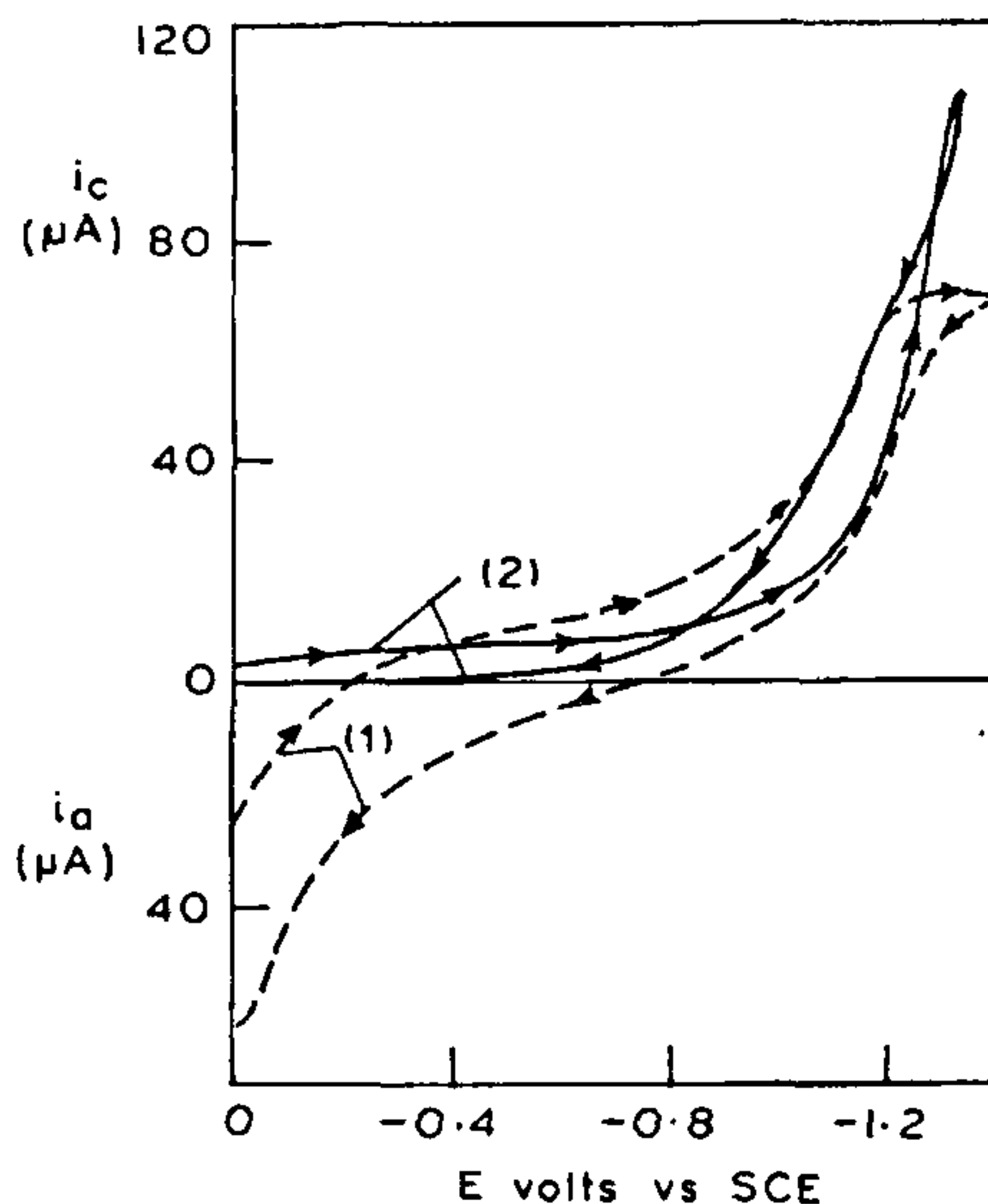


Figure 1. Current-voltage curves for D₂O (solid line) and H₂O (broken line) at Ti working electrode. Sweep rate 0.10 V s^{-1} . Arrows indicate sweep directions.

previously reported⁸ for some metals in the electrolysis of H₂O. The features of figure 1 are attributed to specific adsorption of the product of electrolysis^{9,10}. Kolotytkin and co-workers¹¹⁻¹⁴ and Parsons¹⁵ have examined this behaviour in detail. A particular point to be noted here is that the hysteresis onset is not observed before the cathodic background limit of D₂O is reached; it is likely to be caused by adsorption of D or D₂. The current-voltage curve for H₂O at Ti cathode has also been examined; here hysteresis is not observed (dotted line in figure 1). As predicted by the earlier theories^{15,16}, the desorption peak of H₂ is seen in the current-voltage curve. The peak shape is broad, indicating a slow desorption of the adsorbed species. This feature is interpreted on the basis of metal-gas physical adsorption based on the Lennard-Jones potential energy diagram^{17,18}. Physical adsorption is attributed to long-range forces and it does not involve dissociation of H₂; the heat of adsorption $-\Delta H_p$ is of the same order of

magnitude as the heat of liquefaction of gaseous H_2 (ref. 18). Chemisorption can also occur and this is discernible in the desorption peak as a shoulder (in the present case it is not observed). The distinction between weak and strong adsorption processes has been investigated previously¹⁸; these results suggest that strong adsorption occurs only on permitted sites and the sites involve surface atoms. Each surface atom may act as one such site. One half of the available sites may be used for strong adsorption from structural considerations.

Galvanostatic electrolysis of D_2O in a partially closed container containing 1 M NaCl was conducted at 33.0 mA cm^{-2} or 66.0 mA cm^{-2} . The temperature of the electrolytic solution was measured at regular times for a period of 8 h. Figure 2 summarizes the data obtained during the electrolysis. The experiment was repeated four times, using fresh D_2O and with newly prepared Ti cathode. The rise in temperature measured here is considered as the resultant temperature of heating and cooling of the electrolytic solution. At the current densities used for the electrolysis D_2 and O_2 are produced [$Cl_2(g) + 2e \rightleftharpoons 2Cl^-(aq)$, $E^0 = 1.358 \text{ V}$ (ref. 19), and $O_2 + 4D^+ + 4e \rightleftharpoons 2D_2O$, $E^0 = 0.815 \text{ V}$ (ref. 19)].

We now analyse the rate of temperature increase, considering it as arising from Joule heating or from a chemical reaction (table 1). A combination of the

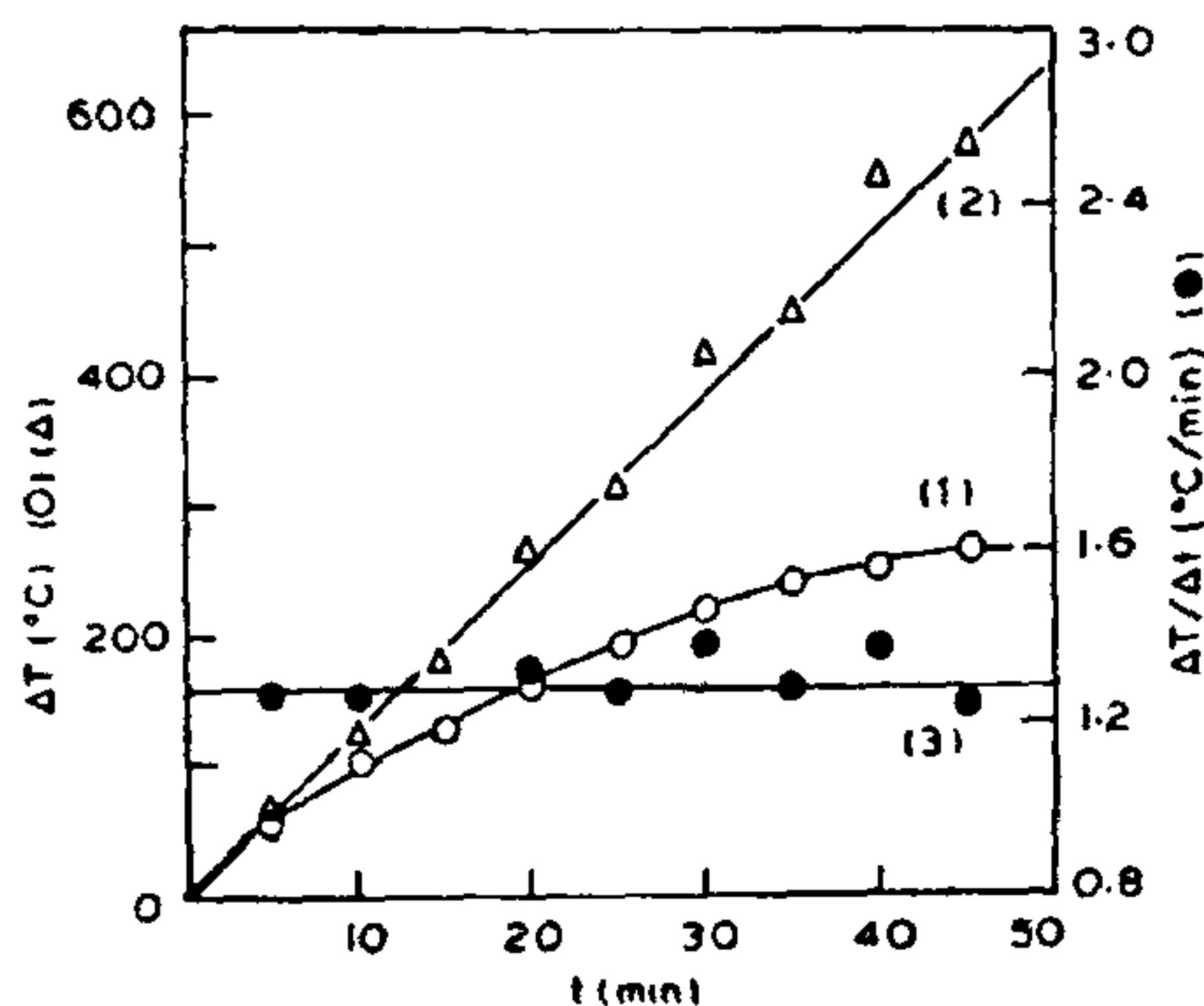


Figure 2. Plot of ΔT vs t during the electrolysis of D_2O at Ti cathode and Pt anode. Curve 1 is the ΔT vs t plot with no cooling correction applied to the measurement. Curve 2 is the ΔT vs t plot with the cooling correction as described in the text. Curve 3 is the $\Delta T/\Delta t$ vs t plot (after the cooling correction) for the electrolysis of D_2O .

Table 1 Rationalization of power balance in the electrolysis of D_2O

E_{app} 2.58 V, i_0 0.033 A cm^{-2} , cell current 0.50 A

Case I:

Power consumed in the electrolysis of D_2O	= 0.77 J s^{-1} (W)
Balance of power remaining	= 0.52 J s^{-1} (v_s)
Expected rate of temperature change	= $0.52/116.18$ $\text{J s}^{-1}/\text{J}^{\circ}\text{C}^{-1}$ = $0.0045^{\circ}\text{C s}^{-1}$ = $0.27^{\circ}\text{C min}^{-1}$

Experimentally measured rate of temperature change (after cooling correction)	= $1.30^{\circ}\text{C min}^{-1}$
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Case II:

a) Exothermic adsorption of D_2 on cathode

Heat produced by exothermic reaction*	= 120 kJ mol^{-1}
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Rate at which charge is passed (100% current efficiency for the electrolysis)	= 0.50 C s^{-1}
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Moles of D_2 produced by electrode reaction	= $2.59 \times 10^{-6} \text{ mol s}^{-1}$
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Expected power from the exothermic reaction	= 0.30 J s^{-1} (W)
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Expected rate of temperature change	= $0.15^{\circ}\text{C min}^{-1}$
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b) Exothermic reaction due to $2D_2 + O_2 \rightarrow 2D_2O$

Heat generated by recombination reaction	= $285.83 \text{ kJ mol}^{-1}$
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Expected power for the number of moles of D_2 produced in 1 sec	= 0.73 J s^{-1} (W)
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Expected rate of temperature change	= $0.38^{\circ}\text{C min}^{-1}$
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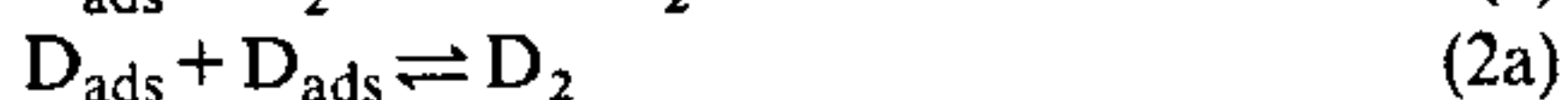
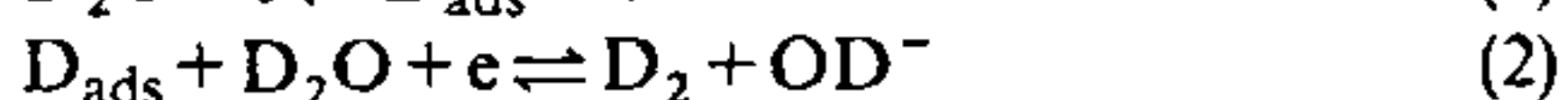
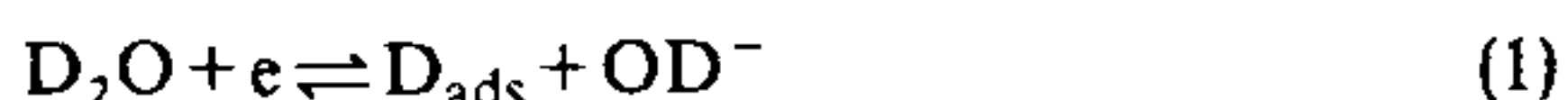
These calculations were done by accurately measuring the potential difference across the cell and the current through the cell. Rate of cooling was measured by raising the electrolytic solution to the same steady state temperature as during electrolysis, turning off the electrolysis and monitoring the temperature over time. Mass of $D_2O = 22.00 \text{ g}$, mass of Ti and Pt plates = 18.77 g , mass of glass beaker = 17.12 g . D_2 adsorption on Ti will increase the weight of the cathode very marginally (in mg) which is neglected in the calculation.

For a hypothetical situation in which all the input power is consumed for Joule heating, the expected rate of temperature change is $0.68^{\circ}\text{C min}^{-1}$ (no electrolysis occurring).

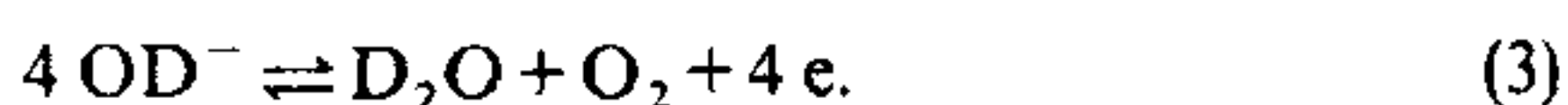
Experiments conducted with distilled water showed a rate of change of temperature of $0.26^{\circ}\text{C min}^{-1}$, which is substantially less than the value obtained with D_2O .

*This value is taken from Bailar, J. C., Emehus, H. J., Nyholm, R. and Trotman, A. F., (eds), *Comprehensive Inorganic Chemistry*, Pergamon Press, London, 1973, vol. 1, p. 51. The ΔH refers to the difference between metal-deuterium bond energy (E_{MD}) and the deuterium dissociation energy (E_{DD}).

two cases is also considered. For the Joule heating in the electrolysis of D_2O , first the power required to split D_2O into its constituents should be subtracted from the total power that is fed into the electrolytic cell. In other words, out of the total potential difference applied to the cell, E_{app} , one part will go to establish the thermoneutral potential of 1.54 V, caused by the heat of reaction and the heat of dissociation of deuterium and oxygen, i.e.:



and



The balance of power is considered as being utilized for Joule heating, which produces the temperature change in the cell. This scheme is shown in table 1. For the second case, two possible exothermic processes occurring in the cell are considered: (i) adsorption of D_2 on Ti, which is estimated to release 120 kJ mol^{-1} , and (ii) recombination of D_2 and O_2 in the electrolysis, which releases $285.83 \text{ kJ mol}^{-1}$ (this calculation assumes that D_2 is not adsorbed during electrolysis).

Pauling⁵ attributed the excess enthalpy in the Fleischmann and Pons experiment¹ to the formation of Pd deuteride and its subsequent decomposition. The decomposition of deuteride is explosive. As Ti has 0.72 orbital per atom of the orbitals vacant in the outer shell⁵, this could be used for deuteride formation. Our experiments do confirm, Ti lattice expansion and generation of a cracking noise² during the electrolysis due to adsorption of D_2 .

The data presented in table 1 allow an enthalpy estimate to be made of the exothermic chemical reaction. Subtraction of the expected excess temperature in case II from the measured excess temperature in case I yields $0.87^\circ\text{C min}^{-1}$ (a) or $0.65^\circ\text{C min}^{-1}$ (b). To obtain this temperature change we should expect an exothermic reaction of $0.32 \times 10^6 \text{ J mol}^{-1}$ with D_2 adsorbed on the metal, or $0.38 \times 10^6 \text{ J mol}^{-1}$ for the case when the difference in temperature is solely due to the chemical reaction with negligible adsorption of D_2 occurring. Under the experimental conditions used here this is inconceivable by ordinary processes.

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1. Fleischmann, M., Pons, S. and Hawkins, M., *J. Electroanal. Chem.*, 1989, **261**, 301; and erratum, *ibid.*, 1989, **263**, 187.
2. Santhanam, K. S. V., Rangarajan, J., O'Neil, Braganza, Haram, S. K., Limaye, N. M. and Mandal, K. C., *Indian. J. Technol.*, 1989, **27**, 175.
3. Rangarajan, S. K., *Curr. Sci.*, 1989, **58**, 598.
4. Gittus, J. and Bockris, J. O. M., *Nature (London)*, 1989, **339**, 105.
5. Walling, C. and Simons, J., *J. Phys. Chem.*, 1989, **93**, 4694.
6. Jones, S. E., Palmer, E. P., Czirr, J. B., Decker, D. L., Jensen, G. L., Thorne, J. M., Taylor, S. F. and Rafelski, J., *Nature (London)*, 1989, **338**, 737.
7. Pauling, L., *Nature (London)*, 1989, **339**, 105.
8. Frumkin, A. N., In: *Advances in Electrochemistry and Electrochemical Engineering*, (ed.) P. Delahay, Interscience, New York, 1961, vol. 1, pp. 65-122; 1963, vol. 3, p. 287.
9. Kolotyrkin, J. M. and Bune, N. Ya., *Zh. Fiz. Khim.*, 1947, **21**, 581.
10. Kolotyrkin, J. M. and Bune, N. Ya., *Zh. Fiz. Khim.*, 1955, **29**, 435.
11. Kolotyrkin, J. M., *Trans. Faraday Soc.*, 1959, **55**, 455.
12. Medvedeva, L. A. and Kolotyrkin, J. M., *Zh. Fiz. Khim.*, 1959, **31**, 2668.
13. Kolotyrkin, J. M. and Medvedeva, L. A., *Zh. Fiz. Khim.*, 1951, **25**, 1355.
14. Kolotyrkin, J. M. and Medvedeva, L. A., *Zh. Fiz. Khim.*, 1953, **27**, 1344.
15. Parsons, R., *Trans. Faraday Soc.*, 1958, **54**, 1053.
16. Breiter, M. W., *Ann. N. Y. Acad. Sci.*, 1963, **101**, 709.
17. Hayward, D. O. and Trapnell, B. M. W., *Chemisorption*, 2nd edition, Butterworths, London, 1964.
18. Bond, G. C., *Catalysis by Metals*, Academic Press, New York, 1962.
19. Bard, A. J., Parsons, R. and Jordon, J., *Standard Potentials in Aqueous Solution*, Dekker, New York, 1985.