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Hydrogen half-cells in molten salts. A potentiometric investigation of the systems (Pt or Au) H_2O/H_2, OH^- in fused alkali nitrates

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The potentiometric behaviour of the 'hydrogen electrodes' (Pt or Au) H_2O/H_2, OH^- has been investigated in molten $(Na_{0.5}, K_{0.5})NO_3$ at 503 K. In both cases the potential of the 'indifferent electrode' could be expressed by the general equation

$$E = K + \frac{RT}{F} \ln \frac{[H_2O]}{[H_2][OH^-]}$$

which is different from the one expected on the basis of a Nernstian behaviour of the theoretical overall system

$$2\,H_2O + 2\,e = H_2 + 2\,OH^-.$$

The experimental findings are discussed in terms of mechanistic models involving the actual electrode surface and the standard potential for the theoretical (reversible) hydrogen electrode is calculated: $E^0_{H_2O/H_2,OH^-} = -2{\cdot}0$ V (versus Ag/Ag$^+$ 0·07 M).

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1. Introduction

The literature on the behaviour of hydrogen electrodes in molten salts is very scanty. Studies on these electrodes are limited to a little work performed on alkali chlorides [1] at 700 K and on alkali carbonates at 800–1000 K, where the working conditions for high-temperature fuel electrodes were tested [2–4].

Carbonate solvents can be considered the most suitable to maintain a constant electrolyte composition for cell reactions involving carbonaceous fuels. However, when non-carbonaceous fuels (such as hydrogen, ammonia, hydrazine etc.) are employed, other molten solvents can become, in theory, more appropriate. For example, the use of medium temperature solvents can perhaps provide a convenient compromise between the necessity of sufficiently rapid kinetics, the advantage of lower heating energies and the possibility of employing a wider range of technologically interesting materials: teflon (PTFE), for example, can work quite indefinitely in the presence of the most corrosive species at temperatures up to 550 K.

The present paper deals with the potentiometric behaviour of gold and platinum electrodes, immersed in a solution of hydrogen in the (Na, K)NO_3 equimolar melt in the presence of known concentrations of water and hydroxide ions. The choice of this solvent for the first approach to the problem is more related to the fact that it is the most studied and known of the medium-temperature melts (which means knowledge of wellproven *in situ* analytical methods and easier interpretation of side effects) rather than to the possibility of its practical application.

Very recently, [5–7] the interesting performances of oxygen electrodes in (Na, K)NO_3 have been investigated. In particular the standard potential for the electrode process

$$\tfrac{1}{2}O_2 + H_2O + 2e = 2OH^- \qquad (1)$$

was calculated to be

$$E^0_{H_2O,O_2/OH^-} = -0{\cdot}405 \text{ V} \quad \text{(versus Ag/Ag}^+\text{ 0·07 M).} \qquad (1a)$$

Furthermore, from the results of a series of solubility experiments, the standard free energy variations for the dissolution processes of water [8], oxygen [9] and hydrogen [10] can be obtained. Then, for the solvent under study, an *a priori* estimation of the standard potential for the electrode reaction in alkaline solution

$$2\,H_2O + 2e = H_2 + 2\,OH^- \qquad (2)$$

was possible (see Appendix):

$$E^0_{H_2O/H_2,OH^-} = -2{\cdot}0\,V$$

$$\text{(versus Ag/Ag}^+\ 0{\cdot}07\ \text{M).} \qquad (2a)$$

This permitted a direct comparison of experimental and theoretical (reversible) electrodes' behaviour.

2. Experimental

2.1. *Apparatus*

The experimental work was carried out by using the cell and the potentiometric–voltammetric set-up described previously [6]. The direct contact of large glass surfaces with the molten solution was avoided by using teflon containers and devices. The electrodes were spirals or foils of gold and platinum (area 0·5–3 cm^2) polished with fine 'Wetordry paper' and washed with diluted acidic solutions, water and organic solvents.

All the experiments with platinum electrodes and some with gold electrodes were performed under vigorous stirring maintained in the cell by a magnetic bar (3 cm long and 0·7 cm diameter) rotated by a synchronous motor. The temperature of the melt was maintained at 503 ± 0·5 K in an insulated aluminium-block thermostat with the aid of a VECO thermistemp temperature controller (Mod. 71, Y.S.I., Yellow Spring, Ohio).

All the results were referred to a Ag/Ag$^+$ (0·07 M) reference half-cell.

2.2. *Chemicals*

The fused solvent (about 200 g) was a reagent-grade equimolar mixture of (Na, K)NO$_3$, pure or containing NO_2^- 0·5 M. Increasing hydroxide concentrations were obtained by adding small drops of suitable [6] solid solutions of carbonate-free NaOH in the specified solvent. The measurements at very low hydroxide concentrations required a drastic purification of the flowing gas in terms of carbon dioxide and other acidic impurities. Satisfactory results were obtained by using a series of traps containing concentrated aqueous solutions of sodium hydroxide.

Controlled partial pressures of water vapour could be maintained for long periods of time with the aid of thermostated water saturators. Variable hydrogen and water partial pressures were obtained by combining fluxes of H_2/N_2 and H_2/H_2O mixtures. The actual hydroxide [9] concentration in the melt was determined by RDE voltammetry; the concentrations of hydrogen and water were calculated from the relevant [8, 10] Henry's constants.

3. Results and discussion

3.1. *Hydroxide additions to a melt maintained under constant partial pressures of hydrogen and water*

Representative plots of potential versus log [OH$^-$] for gold and platinum indicator electrodes, immersed in melts maintained under constant partial pressures of hydrogen and water, are shown in Figs. 1 and 2. Almost all the experiments with platinum electrodes were performed in the presence of nitrite (0·5 M) in order to maintain the concentration of this species constant in the course of an experiment. Nitrite ions can in fact be produced via the reaction of hydrogen with the nitrate solvent:

$$NO_3^- + H_2 = NO_2^- + H_2O \qquad (3)$$

which is catalysed by the presence of the electrodic material.* The dashed line reported in both figures represents the theoretical plot of potential versus log [OH$^-$] calculated on the basis of the known standard potential for the electrode reaction 2 assuming the electrodes to be potentiometrically reversible.

In the absence of added hydroxide, the indicator electrodes did not take up very stable

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* In effect, recent preliminary kinetic studies performed in this laboratory in conjunction with the present investigation, have shown that even nitrite ions can accelerate reaction 3 (via an autocatalytic mechanism). On the basis of the results obtained, however, it can be calculated that this effect cannot markedly change the given [NO_2^-] in the course of an experiment [11].

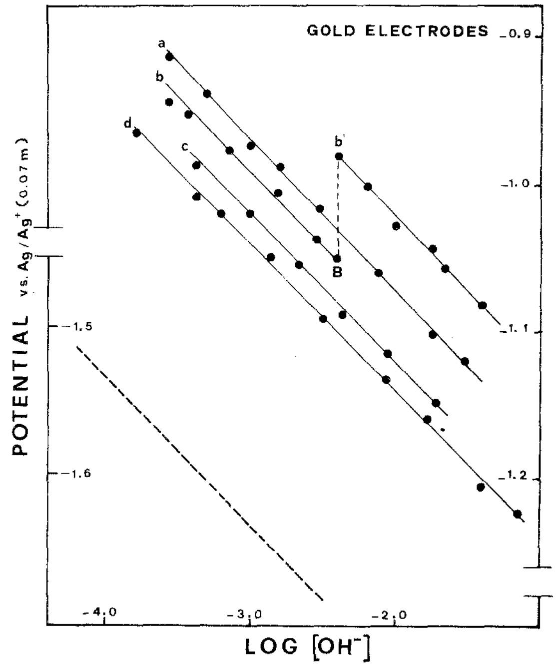

Fig. 1. Curves a and c: plots of potential versus log$[OH^-]$ for gold electrodes immersed in an equimolar (Na, K)NO_3 melt at 503 K bathed by a flux of hydrogen (1 atm) containing water vapour at a partial pressure of 18 Torr. Curves b and d: plots of potential versus log$[OH^-]$ obtained with gold electrodes immersed in a (Na, K)NO_3 equimolar mixture containing 0·5 M $NaNO_2$ and bathed by a flux of hydrogen (1 atm) containing water vapour at a partial pressure of 18 Torr. Experiments performed under magnetic stirring. Curve b′ following b has been obtained by continuing the hydroxide additions after a wait of about 24 h at B. The dashed line indicates the theoretical (reversible) curve. See text.

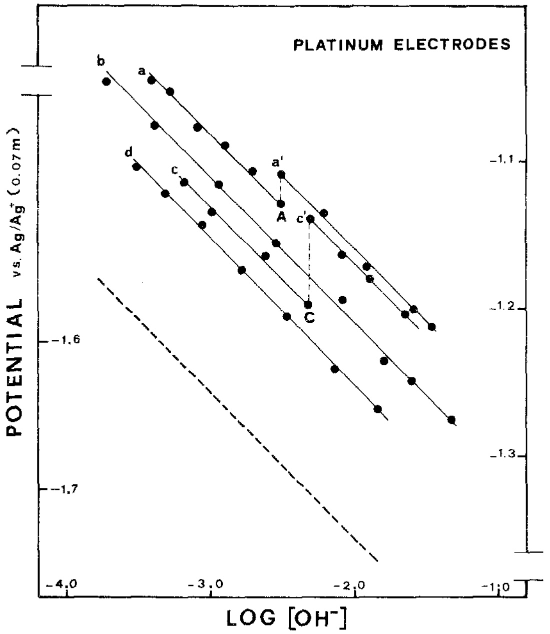

Fig. 2. Plots of potential versus log$[OH^-]$ for platinum electrodes immersed in a (Na, K)NO_3 equimolar mixture containing 0·5 M $NaNO_2$ and bathed by a flux of hydrogen (1 atm) containing water vapour at the partial pressure of 18 Torr. Experiments performed under magnetic stirring. Curves a′ and c′ following a and c have been obtained after waits of about 24 h at A and C. The dashed line indicates the theoretical (reversible) curve. See text.

potentials (probably because, in the nitrate melt, the presence of H_2 and water can produce [11] traces of OH^-). In general, the first addition of hydroxide was made about 2 h after the introduction of the electrodes into the melt. Following the first addition of hydroxide, (actual concentration in the range $10^{-4}-10^{-3}$ M) the electrodes took up more negative values which became quite stable in 10–20 min. After this waiting time the potentials did not usually change by more than ± 5 mV in 1 h. The same kind of stability has also been noted for higher hydroxide concentrations (up to 10^{-1} M). On the contrary, noticeable potential variations (usually towards more positive values) have been observed when the electrodes were left in contact with the molten solution for long periods of time. In this case, if further additions of hydroxide were then made, curves parallel to the initial curve (low hydroxide concentrations) were obtained. For instance curves b′ in Fig. 1 and a′ and c′ in fig. 2 have been obtained after waiting times, in B and in A or C respectively, of about 24 h. In general, the potential variations with gold were a little faster than with platinum.

In the course of the present investigation, the entire set of hydroxide additions during a given experiment (single straight lines in Figs. 1 and 2) were made in a time short enough (2–3 h) that, to a first approximation, the described time-dependent potential variations were negligible. This was possible since, as previously mentioned, after any hydroxide addition, the electrodes assumed quite constant potential values in a few minutes.

The stirring of the solution had a smaller influence on the potentials of the gold electrodes than on those of platinum. In the latter case, variations of 100–150 mV (towards less negative potentials) over a few minutes were observed by switching off the magnetic stirring. To a first approximation, the effect was less pronounced the longer had been the time of contact of the electrodes with the molten solution. For instance, at the end of the experiment c-c′ in Fig. 2, (time of contact about 30 h), the potential varied by only about 20 mV on switching off the stirring.

As can be seen from the figures, the slopes of the curves obtained under the described conditions by using well-polished gold and platinum electrodes are close to 100 ± 5 mV, i.e. $-2{\cdot}3\,RT/F$ at 503 K.

$$E_{(\mathrm{Au})} = K_4 - \frac{RT}{F}\ln\,[\mathrm{OH}^-] \qquad (4)$$

$$E_{(\mathrm{Pt})} = K_5 - \frac{RT}{F}\ln\,[\mathrm{OH}^-]\,. \qquad (5)$$

For both gold and platinum electrodes the slopes but not the positions were very reproducible (especially with recently polished electrodes and in nitrite containing melts). Noticeable parallel shifts of the plots of potential versus log $[\mathrm{OH}^-]$ have also been observed whilst working apparently under the same experimental conditions. With both kinds of electrodes the experimental curves are located in a region of potential less negative than that of the theoretical plot represented by the dashed line in Figs. 1 and 2.

3.2. *Influence of hydrogen partial pressure*

The influence of hydrogen partial pressure was tested by substituting pure H_2 by a mixture H_2/N_2 (1:9) at constant hydroxide and water concentration ($[\mathrm{OH}^-] = 3 \times 10^{-3}$ M; water partial pressure 18 Torr). The variation of one order of magnitude in the hydrogen concentration leads, for both gold and platinum electrodes, to reversible variations of potential of 100 ± 10 mV towards more positive values. This corresponds to a slope of the curve of potential versus log $[H_2]$ equal to $-2{\cdot}3\,RT/F$

$$E_{(\mathrm{Au})} = K_6 - \frac{RT}{F}\ln\,[\mathrm{H}_2] \qquad (6)$$

$$E_{(\mathrm{Pt})} = K_7 - \frac{RT}{F}\ln\,[\mathrm{H}_2]\,. \qquad (7)$$

3.3. *Influence of water partial pressure*

This test was performed by changing the water concentration from 2×10^{-2} to 2×10^{-3} M while the concentrations of hydroxide and hydrogen were constant ($[\mathrm{OH}^-] = 3 \times 10^{-3}$ M; hydrogen partial pressure equal to about 1 atm). The potential variations, for both kinds of electrodes, were 100 ± 10 mV which corresponds to a slope $2{\cdot}3\,RT/F$ for the curve of potential versus log $[H_2O]$.

$$E_{(\mathrm{Au})} = K_8 + \frac{RT}{F}\ln\,[\mathrm{H}_2\mathrm{O}] \qquad (8)$$

$$E_{(\mathrm{Pt})} = K_9 + \frac{RT}{F}\ln\,[\mathrm{H}_2\mathrm{O}] \qquad (9)$$

3.4. *Discussion on possible mechanisms*

The experimental findings indicate that none of the studied systems obey the Nernst equation corresponding to the overall Equation 2 and that the potential values are dependent on the electrode material. By considering the partial Relations 4, 6 and 8 for gold and 5, 7 and 9 for platinum the general expressions for the potential dependence of the two kinds of electrodes on hydroxide, hydrogen and water concentrations can be written

$$E_{(\mathrm{Au})} = K_{10} + \frac{RT}{F}\ln\frac{[\mathrm{H}_2\mathrm{O}]}{[\mathrm{H}_2]\,[\mathrm{OH}^-]} \qquad (10)$$

$$E_{(\mathrm{Pt})} = K_{11} + \frac{RT}{F}\ln\frac{[\mathrm{H}_2\mathrm{O}]}{[\mathrm{H}_2]\,[\mathrm{OH}^-]}\,. \qquad (11)$$

As apparent from the data shown in Figs. 1 and 2, the experimental values of K_{10} and K_{11} were not reproducible in the course of parallel experiments. A similar behaviour was previously [7] observed at the same temperature in the same solvent for the potentiometric behaviour (at low hydroxide concentrations) of the oxygen electrode expressed by Equation 1.

In that case† the phenomenon was attributed to the fact that the K values might include in some way the activities of the surface metal oxides (PtO, PtO_2, Au_2O_3 etc.) produced by action of the nitrate melt, which is a strong oxidizing [12, 13] agent. In effect it was found [14] that layers of oxides can be produced on the noble metal surfaces *in situ* probably according to processes such as

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† It is to be noted that in the mechanisms proposed in reference [7] the words 'fast' and 'slow' were inadvertently inverted.

$$\mathrm{Pt + NO_3^- = PtO + NO_2^-} \quad (12)$$

$$\mathrm{PtO + NO_3^- = PtO_2 + NO_2^-} \quad (13)$$

$$\mathrm{2PtO = PtO_2 + Pt.} \quad (14)$$

In the present case the experimental results summarized by Relations 10 and 11 can be expressed, in the simplest way, by electrode mechanisms such as

$$\mathrm{PtO + H_2 + OH^- \xrightleftharpoons{fast} H_2O + PtOH + e} \quad (15)$$

mechanism I

$$\mathrm{PtOH + OH^- \xrightleftharpoons{slow} PtO + H_2O + e} \quad (16)$$

and

$$\mathrm{PtO_2 + H_2 + OH^- \xrightleftharpoons{fast} H_2O + PtO_2H + e} \quad (17)$$

mechanism II

$$\mathrm{PtO_2H + OH^- \xrightarrow{slow} PtO_2 + H_2O + e.} \quad (18)$$

The species PtOH and $\mathrm{PtO_2H}$ often formulated for similar processes in low-temperature solvents, play the role of reaction intermediates (see, for example, [15]).

Analogous mechanisms can be written involving gold oxides instead of platinum oxides. Of course the activities of all these oxides can depend on the time of contact of the electrodes with the nitrate solution and, all other things being the same, on the initial 'physical' status (which is difficult to control and reproduce) of the metal surfaces.

In theory, Relations 10 and 11 can be explained also by mechanisms not involving metal oxides

$$\mathrm{Pt + H_2 + OH^- \xrightleftharpoons{fast} Pt(H) + H_2O + e} \quad (19)$$

mechanism III

$$\mathrm{Pt(H) + OH^- \xrightarrow{slow} Pt + H_2O + e.} \quad (20)$$

Non-oxidized noble metal atoms probably coexist on the electrode surfaces, with the corresponding metal oxides produced via Reactions such as 12–14. In this case, the activity of the metal can become dependent on the oxidation degree so that mechanism III can also satisfy the experimental requirements (in this case including the variability of K_{10} and K_{11}).

The potential variations (more pronounced on platinum than on gold) observed on switching off the melt stirring can be explained as follows. Recent results [11] have shown that noble metals favour (platinum more than gold) the oxidation of hydrogen by the nitrate solvent via Reaction 3. It can be reasonably supposed that this chemical gas-consumption gives rise to a certain hydrogen gradient, so that the actual hydrogen concentration is lower on the electrode than in the bulk of the melt. Since Reaction 3 is moderately-fast, the concentration at the electrode will decrease as the rate of stirring is decreased. At the same time Reaction 3 will lead to an increase in the water concentration on the electrode (this concentration will increase as the rate of stirring is decreased). These two changes of concentration can lead to a variation of the potential towards more positive values (see Equation 11) which is in agreement with the sense of the potential shifts observed on interrupting the magnetic stirring.

The fact that the stirring effect was less pronounced the longer had been the time of contact of the electrodes with the molten solution, can perhaps be related to a progressive partial shielding of the pure metal atoms, on the electrode surface, by the formed oxides. This seems to be in agreement with the mentioned findings of a better slope reproducibility (which is probably related to a fast electrode equilibration) for the potentiometric curves when the electrodes had been recently polished and/or when the melt contained a large concentration of $\mathrm{NO_2^-}$, which probably inhibits the formation of oxides (see Reactions 12 and 13).

On the basis of these considerations, mechanism III (where the 'active centres' on the electrode surface are the non-oxidized atoms) appears more probable than the others involving metal oxides in the potential-determining step.

In conclusion, the present study represents just a first approach to the problem of the behaviour of hydrogen electrodes in medium-temperature solvents and the proposed mechanisms must be considered as working hypotheses rather than final explanations. More mechanistic information needs to be obtained by other techniques which can give indications of the nature of the species formed and/or adsorbed on the electrode surfaces. Further aspects of the problem will probably be elucidated by studying the kinetics of the chemical oxidation of hydrogen in molten nitrates and the catalytic effects played by metallic surfaces. Some of these studies are in progress in this laboratory.

3.5. *Hazard note*

Attention is called to the fact that hydrogen must be introduced into the electrochemical cell only after a good deaeration of the system (for example by bubbling nitrogen for 1 or 2 h). The simultaneous presence of H_2 and O_2 can in fact initiate an explosive reaction, probably at the electrode–solution interphase or on the melt surface. In the course of the present work an explosion occurred about 30 s after the introduction of an hydrogen flux to the cell containing air even in the absence of any kind of spark. No problems were encountered after deaerating the system.

3.6. *Appendix*

The following procedure was adopted to calculate the standard potential of the 'hydrogen electrode' (Pt)H_2O/H_2, OH^- in fused alkali nitrates at 503 K.

The standard free energy relevant to the gas–phase reaction at 503 K

$$H_{2(g)} + \tfrac{1}{2}O_{2(g)} = H_2O_{(g)} \qquad \text{(a)}$$

was obtained ($\Delta G^0_g = -52290$ cal) by applying, in the absolute temperature range 298 (T_1)–503(T_2), the relationship

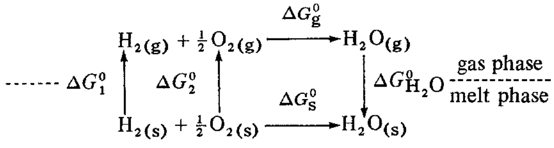
$$\frac{(\Delta G^0_g)_{T_2}}{T_2} - \frac{(\Delta G^0_g)_{T_1}}{T_1} = -\frac{\Delta H^0 m}{T_1 T_2}(T_2 - T_1) \qquad \text{(b)}$$

where [16–18] $(\Delta G^0_g)_{T_1} = -54635$ cal and $(\Delta H^0_{T_1} + \Delta H^0_{T_2})/2 = \Delta H^0 m = -58040$ cal.

From ΔG^0_g at 503 K and the ΔG^0 values relevant to the dissolution of H_2, O_2 and H_2O in the melt, it is possible to calculate ΔG^0_s, the standard free energy of formation of water according to the homogeneous phase reaction

$$H_{2(s)} + \tfrac{1}{2}O_{2(s)} = H_2O_{(s)}. \qquad \text{(c)}$$

The situation can be described by the following scheme:



and one can write

$$\Delta G^0_s = \Delta G^0_1 + \tfrac{1}{2}\Delta G^0_2 + \Delta G^0_g + \Delta G^0_{H_2O} \qquad \text{(d)}$$

$$\Delta G^0_s = -\Delta G^0_{H_2} - \tfrac{1}{2}\Delta G^0_{O_2} + \Delta G^0_g + \Delta G^0_{H_2O} \qquad \text{(e)}$$

where $\Delta G^0_{H_2}$, $\Delta G^0_{O_2}$, $\Delta G^0_{H_2O}$ are the standard free-energy variations for the dissolution of H_2, O_2 and H_2O in the melt at 503 K. The values of $\Delta G^0_{H_2}$ (+9690 cal) $\Delta G^0_{O_2}$ (+ 12340 cal) and $\Delta G^0_{H_2O}$ (+ 400 cal) can be calculated from the relevant Henry's constant [8–10]. The ΔG^0_s value calculated in this way is equal to −67750 cal (−283470 J).

Let us now consider the electrochemical system

$$-\mathrm{Pt}(H_2)/OH^-, H_2O/(O_2)\mathrm{Pt}+ \qquad \text{(f)}$$

which can be described by the two half-cell reactions

$$\text{Cathodic} \quad \tfrac{1}{2}O_2 + H_2O + 2e = 2\,OH^- \qquad \text{(g)}$$

$$\text{Anodic} \quad H_2 + 2\,OH^- = 2\,H_2O + 2e \qquad \text{(h)}$$

$$\text{Overall} \quad H_{2(s)} + \tfrac{1}{2}O_{2(s)} = H_2O_{(s)}. \qquad \text{(c)}$$

The standard electromotive force of this cell is

$$\Delta E^0 = E^0_{H_2O, O_2/OH^-} - E^0_{H_2O/H_2, OH^-}$$

$$= -\frac{\Delta G^0_s}{2F} = 1{\cdot}47\,\mathrm{V}.$$

and, from the value of $E^0_{H_2O, O_2/OH^-} = -0{\cdot}495$ V versus the Ag/Ag^+ (0·07 M) reference half cell, the standard potential (referred to the same Ag/Ag^+ system) for the electrode process *h* can be obtained: $E^0_{H_2O/H_2, OH^-} = -1{\cdot}96$ V.

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