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EFFECTS OF CONDITION OF PLATINUM ELECTRODE AND NATURE OF CATIONS ON OXYGEN OVERPOTENTIAL IN ALKALIS

R.I.Kaganovich and Le Min' Lap

Investigation of the mechanism of oxygen evolution from concentrated perchloric and sulphuric acids at a platinum anode and study of the influence of cations on the oxygen overpotential[1-3] have led to the hypothesis that the latter is an adsorption effect. It was of interest to compare some of these results[2,3] with data on the effect of cations on the behaviour of a platinum electrode in alkaline solutions.

The mechanism of oxygen evolution at a smooth platinum electrode in alkaline solutions has been studied by several workers[4-8], but the results are contradictory, probably owing to differences in the state of the platinum electrode resulting from differences in its treatment. We have therefore examined also the influence of the conditions of preliminary polarisation and the concentration of alkali on the oxygen overpotential, by recording polarisation, polarographic, and current–time curves.

The curves were obtained in the cell described previously[9]. All the alkaline solutions employed were prepared from amalgams which had been made up in a polystyrene cell. The solutions were stored in polystyrene vessels with ground-in covers.

Before an experiment the anode was treated with hot concentrated nitric and sulphuric acids, washed with twice distilled water, and then polarised anodically in 1 N H_2SO_4. After anodic polarisation the electrode was washed with water and placed in the anodic compartment of the cell. These operations occupied 2–3 min. The conditions of the preliminary anodic polarisation of the electrode were chosen on the basis of an investigation of the way in which the shape of the polarisation curve was affected by the duration of the preliminary polarisation and by the strength of the current.

Fig. 1 shows polarisation curves obtained in 0.5 N KOH under different conditions of anodic polarisation of the electrode (current of 6×10^{-6} and 6×10^{-4} A for 30 and 120 min). Each point on the curve was held for 5 min. The shape of the polarisation curves in alkaline solutions is seen to be similar to those obtained in acid solutions[2]. The curves consist of three parts, *I* and *III* being linear and occurring at potentials of 1.65–2.0 and 2.4–2.7 V respectively, while *II* lies between 2.0 and 2.3 V. As is shown by the data in the accompanying Table, the slopes of the individual sections of each curve depend on the conditions of preliminary polarisation of the anode, increase in the duration of polarisation producing a decrease in the slopes of sections *I* and *III*. In the case of *III* the slope depends also on the polarising current, decreasing with increase in the latter. The slope of section *II* decreases with increase in current and duration of polarisation, and on prolonged anodic polarisation of the electrode at 6×10^{-4} A this section tends to disappear. Therefore, although the most reproducible results were obtained with strongly polarised electrodes, preliminary polarisation at 6×10^{-4} A for 30 min was chosen for all experiments.

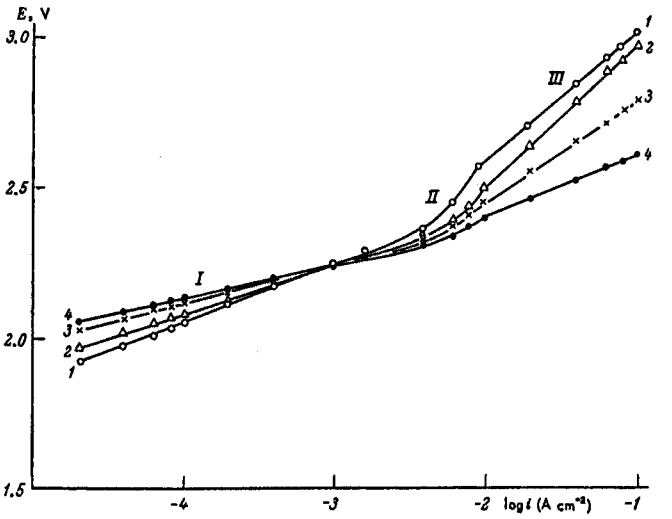

Fig. 1. Anodic polarisation curves in 0.5 N KOH with different conditions of preliminary anodic polarisation: 1) 6×10^{-6} A for 30 min; 2) 6×10^{-4} A for 30 min; 3) 6×10^{-6} A for 2 h; 4) 6×10^{-4} A for 2 h.

TABLE.

Polarising current, A	Section of curve	Duration of preliminary polarisation	
		30 min	120 min
$6 \cdot 10^{-6}$	*I*	0.16	0.11
	III	0.44	0.35
$6 \cdot 10^{-4}$	*I*	0.16	0.11
	III	0.51	0.20

Fig. 2 shows polarisation curves obtained in 0.5 N, 1.3 N, 6 N, and 12 N KOH solutions. The potentials measured against a hydrogen electrode in the same solution were converted to the normal hydrogen scale. It is evident that, over the range of current densities corresponding to the first section of the polarisation curve, the electrode potential is independent of alkali concentration, whereas between 0.001 and 0.1 A cm^{-2} (sections *II* and *III*) the potential falls as the concentration increases from 0.5 N to 12 N. At the same time the slopes of sections *II* and *III* decrease. Comparison of the curves in Fig. 2 with those for acid solutions (see Fig. 13 in Ref. 10) reveals an essential difference in the behaviour of a platinum electrode in these solutions.

Analysis of the current–time curves indicates a difference in the state of the platinum electrode in alkaline and in acid solutions. Whereas at potentials corresponding to the beginning of the second part of this polarisation curve in acid solutions the fall in the current slows down and the latter reaches a constant value within 3–5 min, in alkaline solutions this occurs only after 10–15 min. At potentials corresponding to section *II* of the curve, a constant current is reached in acid solutions after 10 min, whereas in alkaline solutions this is not established even after 30 min, the decay of the current merely slowing down. These results, together with the anodic polarographic curves,

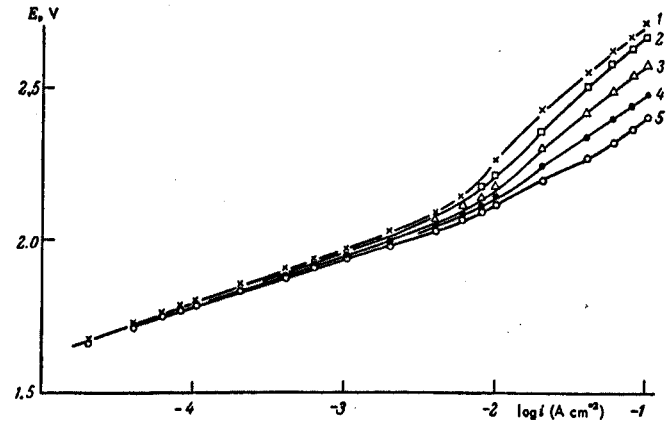

Fig.2. Anodic polarisation curves in KOH solutions of different concentrations (*N*):
1) 0.5; 2) 1; 3) 3; 4) 6; 5) 12.

show that passivation of the platinum electrode by the oxygen evolved is considerably weaker in alkaline than in acid solutions.

The nature of the cation has a similar effect on the oxygen overpotential in alkalis as in acid solutions at current densities corresponding to section *II*. From Fig.3 it is seen that the linear portions of the polarisation curves at current densities between 10^{-5} and 5×10^{-3} A cm^{-2} coincide for the alkalis CsOH, KOH, and NaOH, and that section *II* begins at lower current densities in the sequence $Cs^+ > K^+ > Na^+$. The potential increases more rapidly with CsOH than with KOH and NaOH, and the slope of section *II* becomes steeper.

Traces of carbonates (up to 10%) in the aqueous alkali do not affect the anode potential, but their addition at a concentration of 0.1 *N* has an appreciable effect, which is strongest in the region of section *II* of the polarisation curve. This is probably associated with the formation of peroxocarbonates, recalling the formation of peroxosulphates in the electrolysis of sulphates. In this case, too,

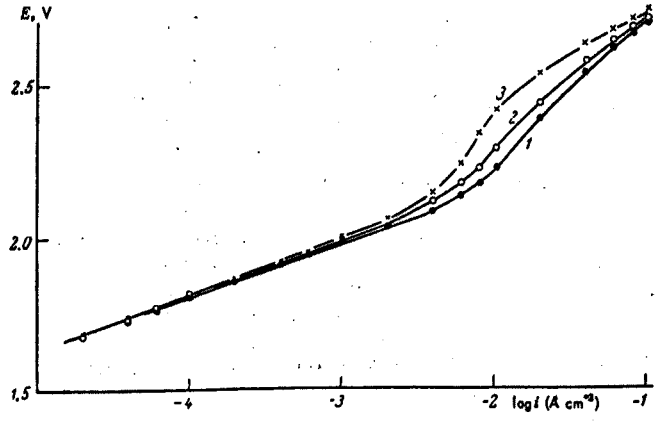

Fig.3. Anodic polarisation curves in 0.5 *N* solutions of:
1) NaOH; 2) KOH; 3) CsOH.

the cation Cs^+ is more active than K^+. Comparison of the results with work[3] on the effect of cations on oxygen overpotential in acid solutions shows the effect to be appreciably smaller in alkaline solutions. This weakening of the influence of cations in alkaline medium can probably be explained by a diminution in the adsorption effect due to a decreased quantity of adsorbed oxygen, and hence a smaller number of oxygen dipoles on the electrode surface. In our opinion this view is supported by our results on the different condition of a platinum electrode in acid and alkaline solutions, and also by published data[11] on the formation of thinner oxygen layers in alkaline than in acid solutions.

A further difference between the effects observed in acid and in alkaline solutions is that analysis of capacitance and polarisation measurements in acid solutions leads to the conclusion that the first stage in oxygen evolution on the lower part of the polarisation curve is partly reversible, the rate-determining stage of the process being the decomposition of surface oxides with evolution of molecular oxygen. The first stage in electron transfer is irreversible only on the upper part of the polarisation curve. Thus in acid solutions the transition from the first to the third section of the curve is accompanied by a change in the mechanism of the process[10]. The coincidence of the lower parts of the polarisation curves obtained in alkaline solutions of different concentrations (Fig.2) indicates that in this case the rate-determining stage of the process is irreversible transfer of an electron from a hydroxide ion to the metal, and that the rise in the anode potential on passing to the third section is due entirely to a change in the adsorption energy without change in the mechanism of the process, as was suggested by Rüetschi and Delahay[12] on the basis of Hickling and Hill's results on oxygen evolution at palladium and gold. However, this conclusion must be regarded as tentative, since it must be checked by capacitance measurements.

In conclusion we wish to thank Academican A. N. Frumkin for valuable advice in the completion and discussion of the present work.

SUMMARY

1. A study has been made of the effects of the conditions of preliminary anodic polarisation (time and current), concentration of alkali, and nature of cations on oxygen overpotential.

2. The general character of the polarisation curves obtained in alkaline solutions is the same as for acid solutions. Differences between the effects observed in these solutions arising from the nature of the cation and the concentration of the solution are explained by changes in the condition of platinum electrode and in the mechanism of oxygen evolution.

1. T. Erdey-Grúz and I. Shafarik, "Trudy IV Soveshchaniya po Elektrokhimii" (Proceedings of the Fourth Conference on Electrochemistry), Moscow, 1959, p.263.
2. R.I. Kaganovich, M.A. Gerovich, and E.Kh. Enikeev, Dokl. Akad. Nauk SSSR, 108, 107 (1956).
3. A.N. Frumkin, R.I. Kaganovich, E.V. Yakovleva, and V.V. Sobol', Dokl. Akad. Nauk SSSR, 141, 1416 (1961).
4. F. Bowden, Proc. Roy. Soc., A126, 107 (1929).
5. T. Hoar, Proc. Roy. Soc., A137, 628 (1933).
6. J. Butler and G. Armstrong, Proc. Roy. Soc., A142, 604 (1933).

7. A.Fedotov, Candidate's Thesis, Karpov Institute, 1940.
8. A.Hickling and S.Hill, Trans.Faraday Soc., 46, 550 (1950).
9. M.A.Gerovich, R.I.Kaganovich, V.M.Vergelesov, and L.N.Gorokhov, Dokl.Akad.Nauk SSSR, 114, 1049 (1957).
10. A.N.Frumkin, Electrochim.Acta, 5, 319 (1961).
11. A.D.Obrucheva, Zhur.Fiz.Khim., 26, 1448 (1952).
12. P.Rüetschi and P.Delahay, J.Chem.Phys., 23, 556 (1955).

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LAMINAR AND TURBULENT HYDRAZINE--DECOMPOSITION FLAMES

V.P.Karpov and A.S.Sokolik

The concept of turbulent burning as the propagation of a pulsating ignition leads to the relation

$$v_t \propto \nu t_0/\tau \simeq l_1/\tau, \quad (1)$$

in which t_0 is the characteristic time of diffusion along the Lagrange coordinate l_1, and τ is the "ignition delay" under conditions of turbulent mixing of fresh and burnt gases[1]. In conformity with Eqn.(1) the rate W_p of the overall reaction in the flame should be linked with the rate of turbulent burning by the relation

$$v_t \propto \tau^{-1} \simeq W_p, \quad (2)$$

in contrast to laminar flames, for which

$$v_l \propto W_p^{1/2}. \quad (3)$$

It follows from general considerations, and has been shown in several actual cases, that it is only in the case of reactions having a molecular or linear chain mechanism that the kinetic characteristics of a flame reaction obtained from relation (3) coincide with those which follow from the reaction mechanism in the absence of a flame[2]. In order to test relation (2) flames produced by the decomposition of hydrazine were chosen, this reaction having a linear chain mechanism[3]. From the activation energies of chain initiation E_0 = 60 kcal and chain growth E_1 = 7 kcal, the effective activation energy of the overall reaction was found to be $E_e = \frac{1}{2}E_0 + E_1$ = 37 kcal. Calculation by the method of steady-state concentrations gives, for the effective reaction order n_e of the decomposition, values of 1 when recombination of the radical products of decomposition occurs through binary collisions, and of 1.5 when it is produced by three--body collisions[3,4]. Measurements of rate of burning in a burner flame[5] and in a bomb[6] have shown a slight increase in v_l for pure hydrazine with increase in pressure, which has been interpreted[6] as independence of pressure, corresponding on the thermal theory of burning to the value $n_e = 2$. When the bomb method is used to determine the kinetic characteristics of these flames, it is necessary to establish the reasons for the considerable divergence in absolute values of v_l measured in a bomb and in a burner flame at atmospheric pressure[7]. This divergence cannot be fully accounted for by the difference in temperature of the hydrazine vapour (62° in the bomb and 150° in the burner), as had been supposed[6]. In fact, according to the thermal theory[8] the temperature dependence of rate of burning can be represented by the formula[2]

$$v_l \propto T_0 T_h^{1.7} (T_h - T_0)^{-1.5} \exp(-E_e/2RT_h). \quad (4)$$

Putting here E_e = 37 kcal and T_h = 1904°K with T_0 = 62°, we obtain $v_{l,150°}/v_{l,62°}$ = 1.38, compared with an actual ratio of 1.7.

Fig. 1 shows a diagram of the apparatus used. A measured quantity of liquid hydrazine was run from the burette *2* into an evacuated vaporising reservoir *1*, from which pure hydrazine vapour, as well as mixtures with water vapour, was transferred to the specified pressure in the dural bomb *5* of radius 70 mm, containing a piezoelectric transducer and windows for schlieren cinematography of flame propagation. The initial pressure of the hydrazine vapour was measured by means of a manometer *3* having a diaphragm which was balanced by a counterpressure of nitrogen, the latter being measured on a mercury manometer *8*. The whole system was maintained by electrical heating at about 110°, corresponding to a vapour pressure of hydrazine of 600 mmHg. The part of the apparatus into which the liquid hydrazine was introduced was placed in a fume cupboard (shown by broken lines in Fig. 1). The value of v_l was determined at the stage in which there was no considerable rise in pressure (less than 7% of P_{max}), from the apparent rate of flame propagation v_a by means of the relation

$$v_l = v_a/\epsilon, \quad (5)$$

where $\epsilon = (T_h/T_0)m$ was determined from published data on the equilibrium temperature of the products T_h and the change m produced by the relation in the number of molecules. Values of v_l corresponding to a T_h range of 1900–1500°K were obtained by diluting hydrazine vapour with water vapour in the reservoir and then transferring the mixture to the bomb.

These results (4) lie on the same curve (*3* in Fig. 2) as data from Ref. 6, in conformity with the value of T_h. Values of v_l for mixtures of hydrazine vapour and nitrogen (*5* in Fig. 2) are also in agreement, these mixtures being produced directly in the bomb by successively passing hydrazine vapour and then nitrogen into it, and subsequently mixing the components by means of the agitators *4* (Fig. 1). It is seen from Fig. 2 that the whole curve *3* lies considerably below curve *1* plotted from values of v_l determined in the burner flame[7]. When, however, the bomb was filled in the reverse order — first with nitrogen and then with hydrazine vapour, with subsequent mixing — values of v_l were obtained (curve *2*) which practically coincided with curve *1* up to mixtures having T_h = 1750°K. Only with further decrease in the concentration of nitrogen do the v_l values depart from curve *1* and approach curve *3*. The decrease in v_l accompanying entry of hydrazine vapour or

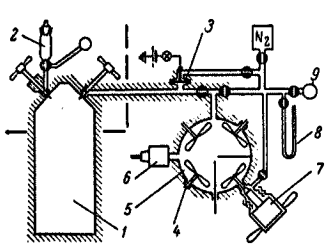

Fig.1.