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The Electrochemistry of Hydroxide Melts

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The results of the study of electrode potentials and processes in molten alkalis have been analysed. The influence of acid-base equilibrium on the mechanism and kinetics of the reactions which take place at indifferent electrodes in hydroxide melts between 200 and 500 °C has been demonstrated. The results of the study of the decomposition voltage and the electrochemical transformations at the cathode and anode when direct current is passed through these electrolytes have been examined. The bibliography contains 85 references.

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I. INTRODUCTION

Hydroxide melts exhibit specific physicochemical properties, which distinguish these media as a special class of high-temperature electrolytes. The electrolysis of molten alkalis is distinguished by a number of characteristic features. It was in the study of the electrolysis of hydroxide melts that the phenomenon of metal transport from the cathode to the anode was first observed[1]. Review articles and widely known monographs[2-4] devoted to ionic melts, however, contain practically no information on the chemistry and electrochemistry of molten alkali metal hydroxides. The study of the electrochemistry of alkali melts has been particularly intensive over the last 10–15 years in connection with the promising possibilities provided by their application in various branches of the new technology. The present review is devoted chiefly to an analysis and generalisation of work carried out in recent years, and the electrochemical properties of "pure" alkalis are examined.

II. EQUILIBRIA IN HYDROXIDE MELTS

In the molten state, alkalis are dissociated[5] to give the cations Li^+, Na^+, K^+, Rb^+, and Cs^+, and hydroxide ions OH^-. Recent work[5-16] has established that in molten alkalis there exist a number of oxygen-containing ions (O^{2-}, O_2^{2-}, O_2^-) and molecules (O_2, H_2O). The solubility of molecular oxygen is low[7]. At the same time, it reacts with the melt according to the scheme

$$2NaOH + 0.5O_2 \rightleftarrows Na_2O_2 + H_2O .$$

Rahmel and Krueger[17] were able to determine the solubility of oxygen in NaOH by a gravimetric method. At an oxygen pressure of 1 atm, the equilibrium concentration of O_2 in the melt increases with temperature, and amounts to 0.8 cm^3 and 4.2 cm^3 per cm^3 NaOH at 350 °C and 500 °C respectively. The same authors[17] obtained experimental isotherms giving the change in the concentration of water in a sodium hydroxide melt at different pressures of H_2O in the atmosphere above the electrolyte. There is a linear relationship between the increase in the water vapour pressure above the melt and the increase in the mass of the melt Δm, that is Henry's law is obeyed.

$$\Delta m = k p_{H_2O}.$$

The constant k changes with temperature according to the Van't Hoff equation

$$\lg(k/k_0) = A/T,$$

where k_0 and A are constants, equal to 2.88×10^{-7} mg g^{-1} $mmHg^{-1}$ and 3.21×10^{-3} K respectively. This equilibrium is established in 2–3 h.

The principal chemical reactions taking place with the participation of oxygen-containing species are described[6] by the following equations

$$O^{2-} + 0.5O_2 \rightleftarrows O_2^{2-} , \quad (1)$$

$$O_2^{2-} + H_2O \rightleftarrows 2OH^- + 0.5O_2 , \quad (2)$$

$$2O_2^- + H_2O \rightleftarrows 2OH^- + 1.5O_2 , \quad (3)$$

$$O_2 + O_2^{2-} \rightleftarrows 2O_2^- , \quad (4)$$

$$3O_2 + 2O^{2-} \rightleftarrows 4O_2^- . \quad (5)$$

Of the three simple oxygen anions (O^{2-}, O_2^{2-}, O_2^-), the O^{2-} ion is the most highly reduced species[7]. It cannot coexist with water. The peroxide ion O_2^{2-} is an ampholyte; it is reduced to O^{2-} or oxidised to O_2. The superoxide ion O_2^- also exhibits amphoteric properties; it is an oxidising agent with respect to O_2^{2-}, and a reducing agent with respect to O_2. Sodium oxide and peroxide, and also gaseous oxygen, are relatively sparingly soluble in the NaOH–KOH eutectic at 227°.[7] According to the data of Lux and coworkers[18], however, the action of dry oxygen (1 atm, 410 °C) for 5–16 h (as far as complete equilibration) leads to the formation, in the melt, of 3 mass % Na_2O_2 in NaOH, 54 mass % K_2O_2 (or 22 mass % KO_2) in KOH, 137 mass % Rb_2O_2 (or 57 mass % RbO_2) in RbOH, and 165 mass % Cs_2O_2 (or 64 mass % CsO_2) in CsOH. In LiOH, the formation of Li_2O_2 and LiO_2 was not detected. The equilibria for the formation of peroxides and superoxides, for example Eqns.(2) and (3), indicates that the concentrations of O_2^{2-} and O_2^- should show a definite dependence on the partial pressures of oxygen and water vapour above the melt. This was confirmed experimentally by Lux and coworkers[18], and it was shown that NaOH contains the peroxide Na_2O_2 in solution, whereas in KOH, RbOH, and CsOH the superoxides KO_2, RbO_2, and CsO_2 predominate.

Appropriate experiments[18] established that in molten NaOH the reaction with oxygen takes place according to Eqn.(2), since the following relationships derived from it are obeyed:

$$c_{O_2^{2-}} = k' p_{O_2}^{1/2} \text{ for } p_{H_2O}/c_{OH^-}^2 = \text{const}$$

$$c_{O_2^{2-}} = k'' c_{OH^-}^2 / p_{H_2O} \text{ for } p_{O_2} = \text{const.}$$

Oxygen reacts with KOH, RbOH, and CsOH according to Eqn.(3), as indicated by the fact that the following relationships are obeyed:

$$c_{O_2^-} = k_1 p_{O_2}^{3/4} \text{ for } p_{H_2O}/c_{OH^-}^2 = \text{const}$$

and

$$c_{O_2^-} = k c_{OH^-} / p_{H_2O}^{1/4} \text{ for } p_{O_2} = \text{const.}$$

With increase in temperature, the concentration of higher oxygen compounds of the alkali metals increases[18] ($p_{O_2} = 0.94$ atm, $p_{H_2O} = 0$ mmHg, $\tau = 4$–5 h):

t, °C	360	410	460	510
Concentration of Na_2O_2 in NaOH, mass %	1.70	2.19	2.60	3.65
Concentration of KO_2 in KOH, mass %	—	21.97	26.49	31.88

The efficiency of the formation of peroxides and superoxides in the reaction of hydroxides with atomic oxygen, generated in a glow discharge:

Alkali	Concentration, mass %		
	peroxide	superoxide	hydroxide
NaOH	31.4	11.4	57.2
KOH	нет	80.5	19.2

is considerably greater than that in the O_2–molten NaOH or KOH systems.

The chemical properties of molten alkalis, used as solvents, are related chiefly to the properties of the OH^- ions, which dissociate according to the equation[5-9]:

$$2OH^- \rightleftarrows H_2O + O^{2-} . \quad (6)$$

The constant for this equilibrium is equal to the product of the activities of H_2O and O^{2-}, and corresponds to the product of the concentrations of the components in the given dilute solution:

$$K_i = [H_2O][O^{2-}]. \quad (7)$$

The concentration of OH^- ions is taken as constant, since the degree of dissociation according to Eqn.(6) is small. The ionic product (7) has a definite value for a given mixture of alkalis and a given temperature. For the NaOH–KOH eutectic at 227 °C, it is given by[7] $pK = -\lg K = 11.5 \pm 0.7$.

Eqn.(7) can be used to determine[5] the acid–base properties of molten alkalis. Just as in aqueous solution the H_3O^+ ion is a complex proton, solvated by a molecule of the solvent H_2O, so in molten hydroxides it is also possible to regard H_2O as a complex, that is a compound of the proton H^+ with the ions of the solvent OH^-. Thus in hydroxide melts, H_2O is the most "acidic" species, and O^{2-} the most "basic".

By analogy with the pH scale in water, it is possible[5] to introduce for molten alkalis an analogous scale, which Goret called the pH_2O scale ($pH_2O = -\lg [H_2O]$). The value of the ionic product $pK_i = -\lg K_i$ determines the range of pH_2O values which can be achieved in a given medium. If $[H_2O] = 1$, then $pH_2O = 0$, and the concentration of O^{2-} ions is very low, since

$$pH_2O = pK_i + \lg[O^{2-}],$$
$$pO^{2-} = 11.5 - pH_2O.$$

Neutrality of the medium corresponds to the pure anhydrous eutectic mixture KOH–NaOH at 227 °C, where $pH_2O = pO^{2-} = 1/2\ pK_i = 5.75$. Molten alkalis rich in water correspond to "acidic" media, and those rich in O^{2-} ions correspond to "basic" media. It is possible to change the acidity of a medium by introducing non-dried alkalis or alkali metal oxides (Na_2O, KO_2, etc.). In the examination of acid–base equilibria in hydroxide melts, it is assumed[5] that in these media, all compounds (ions) which facilitate the appearance of water behave as "acids". The examination of the behaviour of metal cations is of particular interest in this connection. For these, the following phenomena may be observed, depending on the magnitude of pH_2O.

1) In a very acidic medium (rich in water), strong acceptors of O^{2-} ions form complex oxides, for example the cations Ni^{2+}, Pt^{2+}, and Al^{3+} give the sparingly soluble oxides NiO, PtO, and Al_2O_3. Oxygen-containing species such as CO_2 and PO_3^- behave as acids and form CO_3^{2-} and PO_4^{3-} ions:

$$CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O ,$$

$$PO_3^- + 2OH^- \rightarrow PO_4^{3-} + H_2O .$$

On going to more basic media (with the removal of water), higher complex compounds may be formed. Thus alumina is more soluble in a dehydrated medium and is transferred to the melt in the presence of the O^{2-} ion by the reaction

$$Al_2O_3 + O^{2-} \rightarrow 2AlO_2^- .$$

In molten alkalis, in addition to equilibria (1)–(5), dissociation according to the equation[14,19,20]

$$2MOH \rightleftarrows M_2O + H_2O \quad (8)$$

is observed. Since M_2O is a strong O^{2-} donor, reactions (8) and (6) are displaced to the left.

Table 1. Calculated dissociation constants K^* of molten alkalis at different temperatures[14] (the hypothetical values corresponding to temperatures below the solidification temperature are given in brackets).

t, °C	LiOH	NaOH	KOH	RbOH	CsOH
227	(7.0)	(13.1)	(17.7)	(18.6)	(18.9)
350	(4.3)	9.7	13.1	13.7	14
400	(3.5)	8.5	11.8	12.3	12.5
477	2.5	7.4	10.3	10.5	10.8
577	1.8	6.2	8.8	8.7	9.0
723	1.1	5.0	7.1	6.8	7.0

By applying the law of mass action to equilibria of type (8), it is possible to obtain different values of the dissociation constants, depending on the method of expressing the activities of the components[14]. If the standard states of MOH, M_2O, and H_2O are taken as the liquid hydroxide, the pure solid oxide, and water dissolved at a vapour pressure of 1 atm respectively, then

$$a_{M_2O} p_{H_2O} / a_{MOH}^2 = K^* .$$

If $a_{MOH} = 1$, then

$$p a_{M_2O} - \lg p_{H_2O} = -\lg K^* = p K^* .$$

The values of pK^* for different alkalis have been calculated[14]

from thermochemical data using the equation

$$2.3RT\,\mathrm{p}K^{\bullet} = \mu^{\bullet}_{M_2O} + \mu^{\bullet}_{H_2O} - 2\mu^{\bullet}_{MOH}$$

and are given in Table 1.

The degree of dissociation of alkalis at a given temperature increases with decrease in the radius of the cation: LiOH dissociates when the alkali is melted; KOH, RbOH, and CsOH are less extensively dissociated, and NaOH occupies an intermediate position.

For analytical calculations, the preferred definition of the constant pK is

$$\mathrm{p}K = \mathrm{pO^{2-}} + \mathrm{pH_2O},$$

when the standard state is taken as the solution having O^{2-} and H_2O concentrations equal to unity. The experimental determination of pK presents considerable difficulty, however. Its value has been determined only for the KOH–NaOH eutectic mixture[7]. The values of pK for NaOH at different temperatures have been calculated[14] using published data[17,21–23] on equilibrium in the NaOH–Na_2O and NaOH–H_2O systems:

t, °C	360	420	500	600	700
pK	8.75	7.50	6.25	5.00	4.0

These calculated data have been confirmed[15] by potentiometric measurements.

III. ELECTRODE POTENTIALS IN ALKALI MELTS

As described above, various oxygen-containing ions may be present in hydroxide melts when the atmosphere above them contains O_2 and H_2O. These ions are involved in the electrode equilibria, which are characterised by definite potentials and influence the characteristics of technical electrolysis or the operation of a galvanic cell.

Antropov and Tkalenko[24,25] compiled nine equations (Table 2) corresponding to possible redox systems involving oxygen-containing anions. Using thermochemical data, they calculated the standard potentials of the reactions represented in Table 2 in NaOH, KOH, and LiOH melts relative to the reference electrode M/M^+, where M is the corresponding alkali metal. These calculations were used to construct the plots of the potential against the acidity of the medium, analysis of which showed that in these hydroxide melts ($c_{H_2O} > 0.01\%$), the potential-determining system is system 1 (Table 2). In particular, in an NaOH melt, the potential of the oxygen electrode is determined by system 1 at values of $pH_2O < 4.75$, and by system 5 at values of $pH_2O > 4.75$; in a KOH melt, the potential-determining system is system 1 at values of $pH_2O < 2.2$, and system 4 at values of $pH_2O > 2.2$. The E–pH_2O diagram for LiOH does not show regions corresponding to the preferential formation of the peroxide or superoxide. The calculated values[25] of the concentrations of active oxygen in mole litre^{-1} in NaOH and KOH melts at $p_{H_2O} = 1$, $p_{O_2} = 0.2$, and $T = 700$ K are given below:

Melt	Peroxide	Superoxide
NaOH	$1.5\cdot10^{-4}$	$7.6\cdot10^{-2}$
KOH	$1.78\cdot10^{-5}$	$4.52\cdot10^{-4}$

At an oxygen partial pressure of ~1 atm and pH_2O = 2 in an LiOH melt at 750 K, concentrations of peroxide and superoxide equal to 6.3×10^{-7} M and 2.5×10^{-5} respectively are established. Thus under identical conditions, the concentration of active oxygen in a KOH melt is 160 times that in an NaOH melt. When an LiOH melt is in contact with oxygen, O_2^{2-} and O_2^- ions may also be present in this medium, but in extremely small quantities. These data are confirmed by the results of direct measurements of the concentrations of peroxide and superoxide in hydroxide melts[18,26].

Using electrochemical data, Ogryz'ko-Zhukovskaya[27] represented the reactions involved in the formation of higher oxgyen compounds in molten alkalis by the equations:

$$2OH^- + 1.5\,O_2 \rightleftarrows 2O_3^- + H_2O\,,$$

$$2OH^- + 0.5\,O_2 \rightleftarrows O_2^{2-} + H_2O\,.$$

The equilibrium constants for these equations

$$K_1 = [O_3^-]^2\,[H_2O]/[p_{O_2}]^{3/2},$$

$$K_2 = [O_2^{2-}]\,[H_2O]/[p_{O_2}]^{1/2}$$

in KOH at 200 °C are 6×10^{-4} and 2.5×10^{-6} respectively. In this melt at $c_{H_2O} = 10\%$, $p_{O_2} = 1$ atm, and $T = 200$ °C, the concentration of O_3^- is 7.75×10^{-3}M, and that of O_2^{2-}, 2.5×10^{-7} M. The concentration of KO_2, determined experimentally for these conditons, is 7.2×10^{-3} M.[27]

Table 2. Standard potentials of the redox systems.

No.	System	ΔG, kcal mole^{-1}	$E°$, V	ΔG, kcal mole^{-1}	$E°$, V	ΔG, kcal mole^{-1}	$E°$, V
		KOH, 700 K		NaOH, 700 K		LiOH, 750 K	
1	$O_2 + 2H_2O + 4e \rightleftarrows 4OH^-$	187	2.03	202	2.2	262	2.85
2	$O_3^- + 2H_2O + 3e \rightleftarrows 4OH^-$	144	2.09	164	2.37	225	3.26
3	$O_2^{2-} + 2H_2O + 2e \rightleftarrows 4OH^-$	104.5	2.27	116	2.52	160	3.47
4	$O_2 + e \rightleftarrows O_2^-$	42.7	1.85	39	1.69	36.8	1.60
5	$O_2 + 2e \rightleftarrows O_2^{2-}$	82.5	1.79	85.9	1.86	102.5	2.23
6	$O_2 + 4e \rightleftarrows 2O^{2-}$	122.8	1.33	152.2	1.65	218	2.37
7	$O_3^- + e \rightleftarrows O_2^{2-}$	—	1.73	—	2.03	65.8	2.86
8	$O_3^- + 3e \rightleftarrows 2O^{2-}$	—	1.16	—	1.63	183	2.63
9	$O_2^{2-} + 2e \rightleftarrows 2O^{2-}$	—	0.87	—	1.44	115.5	2.51

A number of papers have been published on the potentiometric study of redox systems involving oxygen-containing ions in hydroxide melts. Thus a study of the $Pt(O_2)$ electrode by measuring the e.m.f. of the following concentration cell at 500 °C and at 350–600 °C[15]

$$\mathrm{Pt(O_2/H_2O)\,|\,NaOH,\ O^{2-}\ \ or\ \ O_2^{2-}\,\|\,NaOH,\ O^{2-}\ \ or\ \ O_2^{2-}\,|\,Pt(O_2/H_2O)}$$

showed that the dependence of its potential on the partial pressures of oxygen and water vapour is described by the following equation:

$$E = E^{\bullet} + \frac{RT}{4F}\ln p_{O_2} + \frac{RT}{2F}\ln p_{H_2O}. \qquad (9)$$

The concentration of the species taking part in reactions (1)–(5) are inter-related, so that the potential E in Eqn.(9) is a function of four different combinations of variables, ($a_{O^{2-}}$, p_{O_2}), ($a_{O_2^{2-}}$, p_{O_2}), ($a_{O_2^{2-}}$, p_{H_2O}), and ($a_{O_2^{2-}}$, a_{O_2}). Using Eqn.(9), Kureger and coworkers[6] took as reference potential the potential established at platinum in NaOH at $p_{O_2} = 0.98$ atm and $p_{H_2O} = 0.02$ atm. The results of the measurements show that the values of the prelogarithmic (Nernst) coefficients $\Delta E/\Delta \lg p_{O_2} = 38.3$ mV and $\Delta E/\Delta \lg p_{H_2O} = 76.5$ mV correspond to the theoretical values, that is $2.3RT/4F$ and $2.3RT/2F$ respectively.

Afanas'ev and Gamazov[28,29] were the first to measure the e.m.f. of gas concentration cells of the type

$$(p'_{O_2})\,M\,|\,NaOH\,|\,alundum\,|\,NaOH\,|\,(p''_{O_2})\,M$$
$$M = Pt, Ni, Au$$

and concluded that platinum, nickel, and gold behave as reversible oxygen electrodes, and that $\Delta E = 0.0383 \lg (p'_{O_2}/p''_{O_2})$ at 500 °C.

Using the dependence of the potential of the platinum–oxygen electrode on the concentration of oxygen ions in the sodium hydroxide melt, Krueger and coworkers[6] established that the addition of Na_2O and NaOH produces practically no change in the e.m.f. of the cell. From this it was concluded that the reaction

$$O_2 + 4\,e \rightleftarrows 2\,O^{2-}. \qquad (10)$$

is not potential-determining. Moreover, contrary to widespread opinion, Krueger and coworkers[6] concluded that the electrode reaction which corresponds to Eqn.(9) and as a result of the combination of Eqns.(6) and (10) gives the relationship

$$O_2 + 2H_2O + 4\,e = 4OH^- \qquad (11)$$

similarly cannot be potential-determining. Here it is assumed that reaction (6) takes place fairly rapidly, and that Na_2O is dissociated to Na^+ and O^{2-} ions.

At the same time it has been established[6,28] that the dependence of the potential of the platinum electrode on the concentration of sodium peroxide in NaOH is given by the equation

$$E = E^0 + \frac{RT}{2F} \ln c,$$

where c is the concentration of O_2^{2-} ions. It follows from these data that the electrode reaction

$$O_2 + 2e = O_2^{2-}, \qquad (12)$$

which is the reduction of oxygen to the peroxide ion, takes place rapidly and is potential-determining. The corresponding Nernst equation

$$E = E^0 - \frac{RT}{2F} \ln \frac{a_{O_2^{2-}}}{p_{O_2}}$$

shows good agreement with the experimental data.

On the other hand, according to the data of Krueger and coworkers[6], the electrode reaction

$$O_2^{2-} + 2e = 2O^{2-} \qquad (13)$$

cannot be potential-determining. From the experimental data given by Kruger and coworkers[6], it follows that the potential of an indifferent (platinum) electrode depends chiefly on the formation of peroxide and its decomposition according to Eqn.(2). This result agrees with the conclusion[18] that the establishment of equilibria (2) and (3) takes place more rapidly in a moist atmosphere than in an atmosphere of dry oxygen. In an atmosphere of O_2, the removal of the water produced is decisive. Thus with increase in the rate of flow of oxygen there is an increase in the intensity of peroxide formation, as confirmed[6] by the experimental data.

It follows from Eqns.(2), (3), and (11) that the redox potentials of the corresponding systems are influenced by the concentration of OH^- ions in the hydroxide melt. This has been demonstrated experimentally[19,28–30]. The studies reduced to the measurement of the e.m.f. of concentration cells of the type

$$M\,|\,NaOH\,|\,alundum\,|\,NaOH—NaNO_3\,(N)\,|\,M$$
$$(M = Pt, Ni, Au)$$

at 500 °C[28,29] and 340 °C.[30] The potential difference between the electrodes is a linear function of the logarithm of the mole fraction of sodium hydroxide in the melt. The slopes of the straight lines obtained by plotting E against $\lg [OH]$[28,29] are practically identical (0.156–0.160), and for a number of electrons n equal to 4 they correspond to the theoretical value in the equation

$$E = -\frac{2,3RT}{nF} \lg [OH^-]^4,$$

describing the change in the potential associates with the electrode process (11). With change in the concentration of LiOH from 2 mole % to 18 mole % in a eutectic melt of lithium, sodium, and potassium carbonates at 600 °C, the potential of a gold electrode is also described by the semi-empirical equation[19]

$$E = a - b \lg [OH^-].$$

In this expression, the value of the prelogarithmic coefficient is $b = 2.3RT/F = 0.194$. Thus the experimental data described above indicate that at 350–600 °C, platinum, nickel, and gold electrodes, like iron and silver electrodes[31,32], behave as reversible oxygen electrodes.

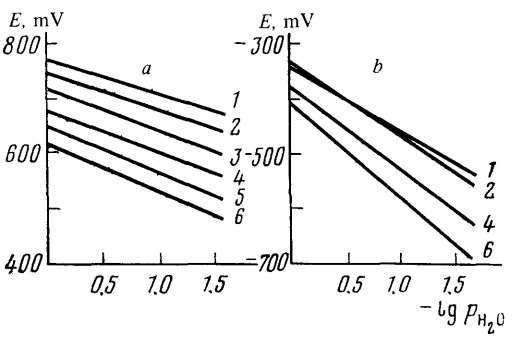


Figure 1. Isotherms giving the dependence of the potentials of oxygen (*a*) and hydrogen (*b*) electrodes in NaOH on the acidity of the electrolyte: *1*) 350, *2*) 400, *3*) 450, *4*) 500, *5*) 550, *6*) 600 °C.

The electrode processes described by Eqns.(2), (3), and (11) are not the only ones in which the hydroxide anion OH^- may take part. For example, Doisneau and Tremillon[15], who established an atmosphere of H_2 and H_2O above NaOH and used Pt and Ni electrodes at 350–600 °C, showed experimentally (Fig.1) that the electrode reaction taking place

$$4OH^- + 2H_2 \rightleftarrows 4H_2O + 4\,e$$

is described by the equation

$$E_{H_2} = E^*_{H_2} + \frac{2.3RT}{F} \lg p_{H_2O} - \frac{2.3RT}{2F} \lg p_{H_2}.$$

The calculated values of $E^*_{H_2}$ and $E^*_{O_2}$ show good agreement with the values obtained by extrapolating the straight lines (Fig.1) for $p_{H_2} = 1$ atm and $p_{O_2} = 1$ atm. The difference in

the standard potential $E^*_{O_2} - E^*_{H_2}$ corresponds to the e.m.f. of a cell of the form

$$Pt(H_2)\,|H_2O,\ NaOH|\,|NaOH,\ H_2O|\,(O_2)Pt,$$

in which the reaction

$$1/2O_2 + H_2 = H_2O \qquad (14)$$

takes place. The results of the calculation of this potential difference from the values of the Gibbs free energy show good agreement with experimental data[15].

IV. ELECTRODE PROCESSES

In recent years, original studies have been made of the electrode processes taking place at indifferent electrodes in alkali melts, involving alkali metal ions, water, and the anions OH^-, O^{2-}, and O_2^-. The concentrations of these ions and water can be varied by creating different atmospheres above the melt (p_{H_2O}, p_{O_2}) and by adding the oxides H_2O, Na_2O, and Na_2O_2 to the electrolyte. The products liberated at the electrodes may be the alkali metal, hydrogen, and hydride at the cathode, and water, oxygen, peroxide, and superoxide at the anode.

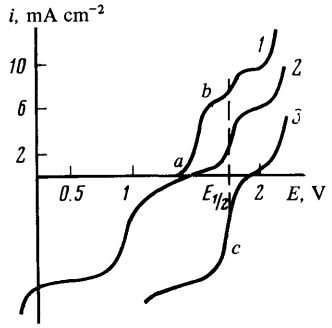


Figure 2. Polarisation curves characterising the electrochemical reaction $O_2^{2-} = 2O^{2-} - 2e$; *1*) Na_2O concentration in the melt 10^{-2} M, *2*) with oxygen bubbled through, *3*) the same after a long time interval; $2O^{2-} - 2e \rightarrow O_2^{2-}$ (*a*), $O_2^{2-} - e \rightarrow O_2^-$ (*b*), $O_2^{2-} + e + O_2^-$.

The behaviour of oxygen-containing anions in KOH–NaOH and NaOH melts has been studied in detail[5,7,15]. First of all, the behaviour of the O_2^{2-} and O_2^- ions at platinum and nickel electrodes was studied in a eutectic melt of sodium and potassium hydroxides at 220–270 °C and in sodium hydroxide at 350 °C. In particular, the electrode reaction (12) was studied at a rotating platinum electrode and at a nickel oxide electrode. A weighed specimen of sodium oxide was added to the melt, and the polarisation curves were recorded potentiodynamically. Two successive waves were observed (Fig.2), the height of the first being twice that of the second. The O^{2-} ion can be oxidised to peroxide and then to superoxide by the reactions

$$2O^{2-} - 2e \rightarrow O_2^{2-}, \qquad (15)$$

$$O_2^{2-} - e \rightarrow O_2^-. \qquad (16)$$

The O_2^{2-} ion is stable only in a basic medium; it exhibits amphoteric properties, and can be reduced to the oxide ion O^{2-} or oxidised to superoxide O_2^-. Oxidation according to the equation

$$O_2^- - e \rightarrow O_2$$

is not observed, since the hydroxide ions OH^- of the solvent are oxidised earlier: $E^0_{O_2-/O_2} = 2.33$ V.[10]

The half-wave potential of the first wave is not constant, and changes with change in the Na_2O concentration, but the potential $E_{1/2}$ of the second wave (Fig.2) remains unchanged. The limiting current of the first wave is proportional to the concentration of Na_2O in the melt[15]. The potentiodynamic studies[15] showed that the solubility of sodium oxide in NaOH at 350 °C is 2.3 mole kg^{-1} which is close to the value obtained (2.4 mole kg^{-1}) by measurements using a different method[21].

The existence of intermediate degrees of oxidation between O^{2-} and O_2 is confirmed by the disappearance of the wave for the oxidation of O^{2-} when dry oxygen is bubbled through the melt. When its passage is continued through a dilute solution of sodium oxide in an NaOH–KOH melt, a decrease in the height of the first wave and an increase in the height of the second is observed at first (Fig.2) as far as the appearance of curve *2*. When the bubbling is continued, the second oxidation wave also disappears[7] (curve *3* in Fig.2). Curve *3* shows only the wave corresponding to the reduction of O_2^- ions.

Under the conditions of this experiment, the oxide ion O^{2-} is oxidised by oxygen, first to peroxide according to Eqn.(1). Curve *2* (Fig.2) corresponds to the case where all the O^{2-} ions in the solution are converted into O_2^{2-} ions. This curve is characterised by a wave corresponding to the oxidation (16) and a wave corresponding to the reduction (13), the height of the latter being twice that of the former. The limiting current density for the cathodic reduction of Na_2O_2 in NaOH at 500 °C is also proportional to the concentration of peroxide in the melt[6]. The peroxide ions are then oxidised by oxygen according to Eqn.(4).

Curve *3* (Fig.2) corresponds to the case where the solution contains O_2^- ions, but O_2^{2-} ions are not present, since they have been oxidised by oxygen to superoxide. To some extent, these reactions "in solution" are analogous to the action of oxygen on solid K_2O, which forms K_2O_2 and then KO_2.

The experimental results indicate that the electrode reaction (16) is rapid, and its kinetics are determined by stationary diffusion[7]

$$E = E^0_{O_2^{2-}/O_2^-} + \frac{RT}{F} \ln \frac{[O_2^-]}{[O_2^{2-}]},$$

$$E = E_{1/2} + \frac{RT}{F} \ln \frac{i - i_1}{i_2 - i},$$

where i_1 and i_2 are the limiting currents of the reduction and oxidation respectively. They are proportional to the concentrations of O_2^- and O_2^{2-} in the solution:

$$i_1 = -k_1[O_2^-],$$

$$i_2 = k_2[O_2^{2-}].$$

$E_{1/2} = 1.75$ V relative to the sodium reference electrode.

It should be noted that at a platinum electrode, the wave corresponding to the oxidation (15) is observed from $E > 1.4$ V, but the wave corresponding to the reduction (13) appears only below 0.95 V ($\Delta E_{1/2} \cong 0.55$ V). This redox system is slow (like the H_2O_2/OH^- system in aqueous solution). These differences in the kinetics of the two systems (15) and (16)

being considered can be explained[7] from the structure of the species taking part in the reactions. Between peroxide and superoxide, only simple electron transfer involving two diatomic species takes place, whereas between peroxide and oxide the exchange of electrons is accompained by the rupture or formation of a covalent bond (oxide is monatomic, and peroxide diatomic). The authors cited[7] point out that the kinetics in the superoxide/oxide system, if they could be observed, would also be rapid, since they involve only two diatomic species.

It is possible to explain from this viewpoint the experimental fact[6] that at 500 °C in an NaOH melt, reaction (12) is rapid, whereas the electrode reaction (10) is slow.

A characteristic feature[7] is that the electrochemical reaction (15) ($E^0 = 1.4 \pm 0.05$ V) is rapid and reversible at a nickel oxide electrode, which catalyses the O^{2-}/O_2^{2-} system. This phenomenon is not new: in aqueous medium the decomposition of H_2O_2 is catalysed by nickel or cobalt oxides. It was also established[7] that when water is gradually added to an anhydrous dilute solution of O_2^{2-} ions, the height of the wave corresponding to the oxidation of these ions decreases, until it disappears completely. At the same time, O_2^- ions appear, and their reduction is reflected on the polarisation curves. This phenomenon is attributed[7] to the reaction taking place in the melt

$$3O_2^{2-} + 2H_2O \rightarrow 2O_2^- + 4OH^-$$

which corresponds to the dismutation equilibrium:

$$3O_2^{2-} \rightleftarrows 2O_2^- + 2O^{2-}. \qquad (17)$$

Like peroxide, superoxide may undergo dismutation, as follows:

$$4O_2^- \rightleftarrows 3O_2 + 2O^{2-}.$$

In the absence of water (strong O^{2-} acceptor), this reaction, like reaction (17), goes from right to left. It may be assumed that in the presence of H_2O, reaction (3) proceeds to the right, but the removal of the superoxide ion is difficult to achieve in practice. Prolonged bubbling of nitrogen leads to the gradual disappearance of superoxide (and also peroxide) as a result of dismutation, brought about by the removal of gaseous oxygen from the system. From an examination of the reactions of anionic oxidation in alkali melts, it was concluded[7] that the electrochemical oxidation of OH^- ions is probably accompanied by the formation of superoxide O_2^- by the reaction

$$4OH^- - 3e \rightarrow O_2^- + 2H_2O.$$

When a high current density is reached, however, the very high concentration of O_2^- ions and water may bring about partial dismutation of superoxide at the electrode according to Eqn.(3), and this is responsible for the familiar phenomenon of oxygen liberation in the electrolysis of molten NaOH. On the other hand, water does not react with superoxide, but facilitates its reduction.

These characteristic features of the course of reactions involving oxygen-containing species and the ranges of their existence can be represented graphically in the form of a E–pH_2O diagram (Fig.3): the method for constructing this diagram has been described in detail[7]. This diagram is similar to that for aqueous solutions on coordinates E–pH, which characterises the familiar redox equilibrium of water. The redox systems of oxygen differ (Fig.3), depending on whether water is present or absent, that is their ranges of existence are functions of pH_2O.

The above examination dealt chiefly with processes of oxidation at the anode. To obtain a complete picture of the electrochemical behaviour of molten alkalis, it is necessary to have information on the reactions of cathodic reduction. As already noted, the cathode products may be hydrogen, sodium, and sodium hydride. First of all, the values of the standard potentials of these electrode processes are of interest. Taking, as is usually done, as standard state the state of the electrochemical system in which all its components are in the state of pure substances, Doisneau and Tremillon[15] used thermochemical data to calculate E^* for the corresponding electrode reactions. These results, obtained with the condition $E^*_{M/M^+} = 0$, are given in Table 3.

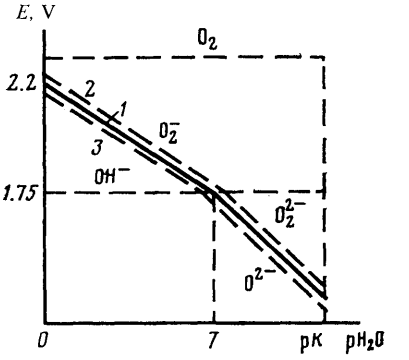


Figure 3. E–pH_2O diagram for oxygen redox systems at 227 °C; concentration of O_2^{2-} and O_2^- ions equal to: 10^{-2} M (*1*), 10^{-1} M (*2*), and 10^{-3} M (*3*).

Table 3. Standard potentials E^*, V of the electrochemical systems of molten alkali metal hydroxides.

t, °C	LiOH	NaOH	KOH	RbOH	CsOH
			H_2		
350	—	1.227	—	0.952	0.877
400	—	1.175	1.077	0.897	0.820
477	1.702	1.112	1.014	0.816	0.737
577	1.625	1.035	0.937	0.713	0.632
723	1.518	0.940	0.830	0.566	0.482
			MH		
350	—	0.655	—	—	—
400	—	0.612	0.545	—	—
477	1.031	0.547	0.478	—	—
577	0.952	0.465	0.394	—	—
723	0.837	0.218	0.272	—	—
			O_2		
350	—	2.330	—	2.055	1.979
400	—	2.264	2.166	1.987	1.940
477	2.771	2.181	2.083	1.885	1.806
577	2.667	2.077	1.979	1.755	1.674
723	2.517	1.940	1.829	1.566	1.482
			MO_2		
350	—	2.506	—	2.176	1.795
400	—	2.442	2.258	2.117	1.721
477	—	2.367	2.176	2.028	1.605
577	—	2.271	2.073	1.925	1.470
723	—	2.141	1.924	1.771	1.263
			M_2O_2		
350	—	2.701	—	2.710	2.601
400	—	2.628	2.566	2.639	2.499
477	3.033	2.552	2.457	2.528	2.369
577	2.934	2.461	2.386	2.405	2.221
723	2.799	2.364	2.234	2.170	1.995

The calculations were carried out with the assumption that the reactions taking place in the cell are

$$H_2O+M\rightarrow 1/2H_2+MOH,$$
$$H_2O+2M\rightarrow MH+MOH,$$

for which the standard e.m.f.'s are

$$E^*_{H_2}=\frac{\Delta G^*}{F}=\frac{1}{F}\left(\mu^*_{H_2O}-\frac{1}{2}\mu^*_{H_2}-\mu^*_{MOH}+\mu^*_M\right),$$
$$E^*_{MH}=\frac{\Delta G^*}{2F}=\frac{1}{2F}(\mu^*_{H_2O}-\mu^*_{MH}-\mu^*_{MOH}+2\mu^*_M).$$

Similar methods were used to calculate the standard potentials of the oxidation reactions accompanied by the formation of oxygen, peroxide, and superoxide:

$$4MOH\rightleftarrows O_2+2H_2O+4M\ ,$$
$$4MOH\rightleftarrows MO_2+2H_2O+3M,$$
$$4MOH\rightleftarrows M_2O_2+2H_2O+2M\ .$$

The data obtained are given in Table 3.

It can be seen that the electrode potentials of the reactions (relative to the M/M^+ reference electrode) depend on the acidity of the melt, as follows

$$E_{H_2}=E^*_{H_2}+\frac{2.3RT}{F}\lg p_{H_2O}-\frac{2.3RT}{2F}\lg p_{H_2},$$
$$E_{MH}=E^*_{MH}+\frac{2.3RT}{2F}\lg p_{H_2O}-\frac{2.3RT}{2F}a_{MH},$$
$$E_{O_2}=E^*_{O_2}+\frac{2.3RT}{4F}\lg p_{O_2}+\frac{2.3RT}{2F}\lg p_{H_2O},$$
$$E_{MO_2}=E^*_{MO_2}+\frac{2.3RT}{3F}\lg a_{MO_2}+\frac{2\cdot 2.3RT}{3F}\lg p_{H_2O},$$
$$E_{M_2O_2}=E^*_{M_2O_2}+\frac{2.3RT}{2F}\lg a_{M_2O_2}+\frac{2.3RT}{F}\lg p_{H_2O}.$$

The electrode reactions are described by the equations:

$$H_2O+e\rightarrow 1/2H_2+OH^-\ ,$$
$$H_2O+M^++2e\rightarrow MH+OH^-\ ,$$
$$4MOH\rightarrow O_2+2H_2O+4M^++4e\ ,$$
$$4MOH\rightarrow MO_2+2H_2O+3M^++3e\ ,$$
$$4MOH\rightarrow M_2O_2+2H_2O+2M^++2e\ . \qquad (18)$$

The potentials of the cathode processes make it possible to characterise the conditions, for example the acidity of the medium, under which H_2, MH, and M are formed. An equilibrium is usually established between these products and MOH, but one of them predominates. Reduction leads to the formation of H_2 in an acidic medium, MH in a neutral medium, and M in a basic medium. Three cases can be distinguished, depending on the nature of the alkalis[15]. In LiOH, the acid–base dissociation, characterised by the quantity pK*, is not extensive, so that the reduction product is hydrogen, irrespective of the acidity. The second case corresponds to hydroxide having a high value of pK* (KOH, RbOH, CsOH). Since there are no data for Rb and Cs hydrides, it has been possible to carry out the calculations only for KOH. In this case, hydrogen is liberated in an acidic medium, and ptoassium in a basic medium. There is practically no range of acidity in which the solid hydride can exist. The third case corresponds to NaOH: close to the melting point, NaOH is reduced to hydrogen in an acidic medium and to the hydride in a basic medium, and at a higher temperature, the behaviour of NaOH is identical to that observed for KOH at the melting point. The conclusions reached agree with experimental data on reaction in the M–MOH system[33–43].

As in the case of the reduction reactions, different oxidation reactions are realised by creating a definite acidity of the medium: the coefficients of $\lg p_{H_2O}$ are also different. Oxidation takes place to oxygen in strongly acidic media, and to peroxide in the most basic media; in the intermediate acidity range, hydroxide is oxidised to superoxide. As far as the nature of the hydroxides themselves are concerned, examination of the oxidation reactions makes it possible to distinguish three cases. The first category corresponds to hydroxides having a low degree of dissociation (high value of pK*)—KOH, RbOH, and CsOH. In a neutral medium, the formation of superoxide takes place in an acidity range whose extent increases with the size of the cation of the solvent (Cs > Rb > K). Here, the CsOH represents an exceptional case, since it is oxidised to CsO_2 throughout the entire range of acidity at 350 °C, whereas KOH and RbOH are oxidised to O_2 in a strongly acidic medium and to peroxide in a strongly basic medium; LiOH is oxidised only to oxygen, irrespective of the acidity. As before, NaOH represents an intermediate case: there is no acidity range in which oxidation to superoxide could take place; oxidation leads to the liberation of oxygen in an acidic medium, and to peroxide formation in a basic medium. Thus oxygen acts on all molten hydroxides in a basic medium, with the exception of LiOH.

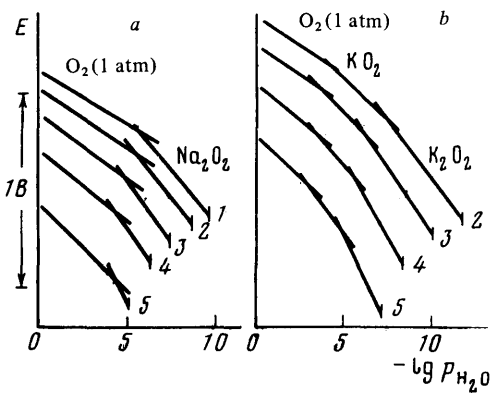


Figure 4. Isotherms giving the dependence of the equilibrium potentials in NaOH (*a*) and KOH (*b*) melts on the acidity of the medium in the presence of a strong oxidising agent at identical activities; *1*) 350, *2*) 400, *3*) 477, *4*) 577, *5*) 727 °C.

Fig. 4 shows the influence of the acidity of the medium on the electrode potential at different temperatures and equal activities (unity) of the oxidising agent. The results given for molten NaOH and KOH reveal the thermal instability of peroxides and superoxides, the range of formation of which decreases with increase in temperature. These data show good agreement with the results of thermochemical calculations[24] for the reactions involved in the oxidation of NaOH and KOH at 350 °C.

To some extent, the regular features described above can be represented by plotting the potential against the acidity of the medium, as shown in Fig.5. The difference in potentials between the upper and lower lines represents the "electro-activity region", that is the range of potentials lying between reduction and oxidation of the medium. In this case, for activities of the oxidising agent and reducing agent equal to unity, the extent and form of the "electro-activity range" (Fig.5) depends on temperature and, to a large extent, the nature of the cation. These ranges have been determined theoretically and confirmed experimentally[15]. At the same time it should be noted that the difference in the potentials $E^*_{O_2} - E^*_{H_2}$ is independent of the cation of the solvent, and is equal to the e.m.f. of the cell $Pt(H_2)\,|H_2O\,||\,H_2O\,|(O_2)Pt$. The current-producing process in the latter is reaction (14), which does not depend to a significant extent on the nature of the hydroxide. The potentials of the cathode and anode in this case are given by the following equations:

$$E_{H_2} = E^*_{H_2} - \frac{2,3RT}{2F}\lg p_{H_2} + \frac{2,3RT}{F}\lg p_{H_2O} - \frac{2,3RT}{F}\lg a_{NaOH},$$

$$E_{O_2} = E^*_{O_2} + \frac{2,3RT}{4F}\lg p_{H_2O} - \frac{2,3RT}{F}\lg a_{NaOH}.$$

Here, $E^*_{H_2}$ and $E^*_{O_2}$ are calculated from the data for the hypothetical cell in which the activities (partial pressures) of O_2, H_2, H_2O, and NaOH are equal to unity.

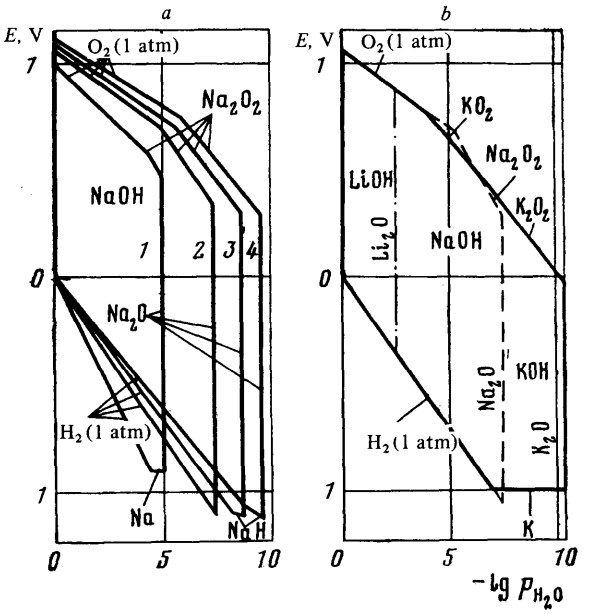


Figure 5. Dependence of the electro-activity ranges on the acidity of the medium; *a*) molten NaOH at different temperatures: *1*) 723, *2*) 477, *3*) 400, *4*) 350 °C; *b*) molten LiOH, NaOH, KOH at 477 °C.

As far as the stability of the products of the anodic oxidation are concerned, the following regular features may be noted[15]. In the solid state, the stability of peroxides increases with decrease in the radius of the alkali metal cation in the order $Cs_2O_2 < Rb_2O_2 < K_2O_2 < Na_2O_2 < Li_2O_2$, whereas the stability of the superoxides changes in the opposite order. In a molten alkali, a large radius for the cation facilitates the formation of superoxide and does not lead to the formation of peroxide.

The experimental study of the electrochemical behaviour of the ions O_2^{2-} and O_2^- in alkali melts was described above. It is of no less interest to examine the regular features of the liberation and consumption of the "visible" products of the electrode reactions, for example gaseous hydrogen and oxygen, and the alkali metals. This information is also important for the technical electrolysis of molten hydroxides.

The part played by the study of the electrolytic reduction of hydrogen ions from aqueous solutions is well known. A large number of studies have been devoted to this question. This problem is also of interest for the electrochemistry of ionic melts, since according to experimental data, hydrogen ions may be present in salt mixtures and molten slags at high temperatures. Water is also present in alkali melts, and in these electrolytes it is a product of an anode reaction[44-51]. Moreover, as noted above, the solution of H_2O in NaOH obeys Henry's law. In this connection, the processes involved in the discharge and ionisation of hydrogen in molten alkalis will be examined first.

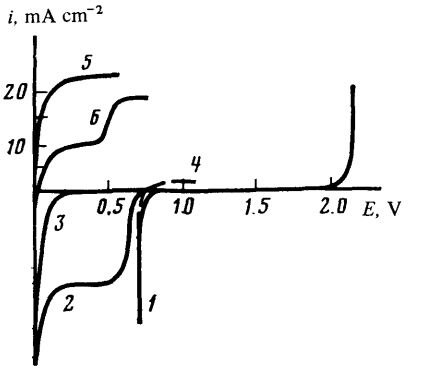


Figure 6. Polarisation curves obtained at a polished platinum electrode in an NaOH–KOH melt at 200 °C: *1* and *2*) reduction of H_2O from concentrated and dilute solutions respectively; *3*) decomposition of an anhydrous NaOH–KOH melt; *4*) oxidation of hydrogen, H_2O atmosphere; *5*) oxidation of sodium dissolved in an anhydrous melt; *6*) oxidation of sodium dissolved in an acidic melt.

The cathodic reduction of hydrogen ions in an NaOH–KOH eutectic melt at 220 °C was studied by Goret[5]. At a platinum electrode, when a potentiostatic method is used, the electroactivity range (decomposition voltage) of H_2O is 1.45 V. Reaction (18) takes place at the cathode.

In an NaOH–KOH melt not subjected to dehydration, and containing a high concentration of H_2O, the limiting current for the recduction of hydrogen is not observed (Fig.6). After drying (450 °C in a stream of dry nitrogen), a limiting current is observed on the *I–V* curve. The height of the corresponding wave (Fig.6) is proportional to the concentration of water in the melt. This wave is not observed in an anhydrous medium (curve *3* in Fig.6).

The oxidation of hydrogen in NaOH–KOH [5,52] and KOH (70–90 mass %)–H_2O (10–30 mass %) [52] melts has also been studied. A hydrated melt was used[5], and an atmosphere of hydrogen established ($p_{H_2} = 1$ atm). Since the solubility of hydrogen is low, the oxidation wave (curve *4* in Fig.6) shows a small limiting current. Its magnitude increases when a platinised platinum electrode is used[5].

Vasilistov and coworkers[52] used a palladium anode of the membrance type. With increase in temperature and the hydrogen pressure (from 0.2 atm to 1.5 atm), the activity of the process of H_2 ionisation increases sharply even in the initial polarisation range, and reaches 160 mA cm^{-2} at $E = 0.3$ V and $p_{H_2} = 1.5$ atm. In a hydrated KOH melt, this process takes place more effectively with increase in the H_2O concentration from 70% to 90%. At the same time, the exchange current increases from 1×10^{-4} A cm^{-2} to 5×10^{-4} A cm^{-2}. In the opinion of the authors cited[52], the anode reaction being considered takes place more intensively only through the formation and subsequent decomposition of a chemosorbed hydrate complex, which functions as an intermediate compound. According to their data[52], the anode current for the oxidation of hydrogen is controlled by its diffusion in metallic palladium. The activation energy of the last process is 3.5 kcal $mole^{-1}$.

According to Goret's results[5], reaction (18) is fast and reversible. The wave for the reduction of hydrogen is described by the equation

$$E = \text{const} + 0.050 \lg[(i - i_d)^2/i],$$

where i_d is the limiting current for the reduction of H_2O. The prelogarithmic coefficient calculated from the experimental data is close to 0.047.

It has also been shown[53,54] that reaction (18) at Pd [53] and Au [54] cathodes in an NaOH–KOH melt is a fast electrode reaction at 200–400 °C, and is described by the equation for diffusion kinetics. The height of the limiting current of the wave is proportional to the H_2O concentration, which decreases with time.

Since the concentration of water in the melt is proportional to the partial pressure of its vapour in the atmosphere, it is to be expected that increase in p_{H_2O} will lead to an increase in i_{d,H_2O}. This has been confirmed experimentally[6] by a potentiokinetic method at a platinum cathode at 500 °C using NaOH as background. The maxima formed, or more accurately the decrease in the current after the maxima, are attributed[6] to a decrease in the concentration of water in the catholyte. The current begins to increase at a potential of 1.3 ± 0.1 V, and, in the opinion of the authors cited, is due to reaction (18). The latter has been studied[55] by a chronopotentiometric method in an equimolar KOH–NaOH mixture at 460–530 K. An interesting feature is that the concentration of H_2O in the melt[55] was varied by adding SiO_2 to the cell. The silicon dioxide reacted quantitatively according to the scheme[56,57]:

$$SiO_2 + 4OH^- \rightarrow SiO_4^{4-} + 2H_2O \cdot$$

The chronopotentiometric curves for the reduction of hydrogen ions are described by the equation

$$E = E^0 + \frac{RT}{2F} \ln [H_2O] \left(\frac{D_{H_2}}{D_{H_2O}}\right)^{1/2} + \frac{RT}{2F} \ln \left\{2\left[1 - \left(\frac{t}{\tau}\right)^{1/2}\right]^2 / \left(\frac{t}{\tau}\right)^{1/2}\right\}.$$

Here, D_{H_2} and D_{H_2O} are the diffusion coefficients of hydrogen and water, t the time at a given point, and τ the transition time; the other symbols are generally adopted in electrochemistry.

According to the experimental data[55], the temperature dependence of the diffusion coefficient of water in the hydroxide melt is approximated by the relationship:

$$\lg D_{H_2O} = (1.143 \pm 0.18) - (2717 \pm 8.8)/T.$$

The activation energy of this process is 12.4 ± 0.4 kcal $mole^{-1}$. As noted above, polarography (volt–amperometry) can be used to determine the concentration of water in a hydroxide melt. It has been pointed out[55] that chronopotentiometry can also be used successfully for this purpose, although in the electrolyte the concentration of H_2O changes from 1 mmole kg^{-1} to 30 mmole kg^{-1}.

Most authors[3,45,58–60] consider that the subsequent increase in the cathodic current after the attainment of i_{d,H_2O} is due to the liberation of the alkali metal. This process, and also the reverse reaction, that is the ionisation of Na, have been studied[5,6]. At 220 °C in an NaOH–KOH melt, the Na^+ ion is reduced at a potential which is 0.65 V more negative than in the case of H_2O.[5] By dissolving metallic sodium in the anydrous NaOH–KOH eutectic, it was possible[5] to carry out the reaction

$$Na - e \rightarrow Na^+ .$$

The polarisation curve *5* (Fig.6) was obtained, and it was shown that this reaction, like the reverse reaction, is rapid. The result obtained makes it possible to recomment the Na/Na^+ electrode as a reference electrode in hydroxide melts. In this connection, somewhat unexpected results were obtained in a potentiokinetic study (rate of scanning 10 mV min^{-1}) [61] of the ionisation of sodium in an NaOH–KOH melt in the range 215–315 °C, where it was shown that the transfer coefficient $\beta = 0.35 \pm 0.05$, and the activation energy of this process is 6.8 ± 0.4 kcal $mole^{-1}$; the overvoltage reaches 300 mV at a current density of ~1 A cm^{-2}.

If H_2O is added to a solution of sodium in the anhydrous eutectic NaOH–KOH, the height of the wave for the oxidation of the alkali metal decreases (curve *6* in Fig.6). At the same time, a second oxidation wave is observed, the position of which is 0.5 V more electropositive than the sodium oxidation wave. Since this wave was also observed when sodium was added to the anhydrous melt in an atmosphere of hydrogen, Goret[5] tentatively attributed it to an electrode reaction involving the oxidation of the hydride:

$$2NaH - 2e \rightarrow 2Na^+ + H_2 .$$

This reaction should be slow, since the corresponding waves for the reduction of H_2O and H_2 to H^- are not observed.

Finally, published data on the characteristics of an anode reaction of the type

$$4OH^- - 4e \rightarrow 2H_2O + O_2 \qquad (19)$$

can be considered. As early as the start of the present century, LeBlanc[62], Sacher[63], and other workers, studying this reaction from the I–V polarisation curves, reported that the liberation of oxygen is irreversible. Quantitative information on the discharge of OH^- ions was first obtained in a study[64] of the anodic polarisation of platinum and nickel electrodes in NaOH at 318–340 °C by automatic recording of the polarisation curves from very low current densities to 1 A cm^{-2}. It was established that reaction (19) takes place with overvoltage, which reached 0.2 V at the maximum current density used. Except for the data obtained at low current densities, the experimental results are described by the equation

$$\eta = b \lg(I/A),$$

where $A = 4$–9 mA cm^{-2}, $b = 0.121$ V.

In the liberation of oxygen into the atmosphere from alkali metal chloride melts at a zirconium anode[65] at 850–900 °C the data correspond to the semilogarithmic relationship

$$\Delta E = a + b \lg i, \qquad (20)$$

the coefficients of which are given below:

Melt		t, °C	a	b
NaCl — LiOH	(10 mole %)	850	1.348	0.785
NaCl — NaOH	(10 mole %)	850	1.117	0.655
NaCl — NaOH	(10 mole %)	900	0.925	0.310
KCl — KOH	(10 mole %)	850	1.456	0.560

Eqn.(20) indicates that the electrochemical process is irreversible. The data given were obtained on a "conditioned" (oxidised and passivated) anode. The $I-V$ curve was unstable at the start of the experiment, and became stable after several hours[65]. When "fresh" electrodes were used, the anodic polarisation curve[5,6,50,66] showed limiting currents due to the oxidation of the metals (Ni, Pt, Au) and the formation of sparingly soluble oxides on their surface. Lower oxides are formed first, followed by higher oxides. The oxides conduct electricity, and this is responsible for the subsequent increase in the current with increase in the potential. In this case, free oxygen is liberated. According to the results[5], the ability to undergo anodic oxidation, accompanied by solution of the metal in the electrolyte, decreases in the order Ag > Ni > Pt > Au.

The reaction of interest include not only the oxidation of the oxygen ions but also the reverse process, that is the electrolytic recduction of O_2 in alkali melts. The densities of the limiting current for the reduction of oxygen (mA cm^{-2}) at a smooth nickel electrode in alkali melts at 427 °C[67] are given below:

Melt	NaOH	KOH — NaOH (eutectic)	KOH	5 N KOH solution (25 °C)
$p_{O_2} = 0.2$ atm	0.66	13.3	69	—
$p_{O_2} = 1$ atm	1.08	18.6	110	0.02

These results show that the limiting currents for the reduction of oxygen in alkali melts[67] are appreciably greater than those in aqueous solutions. At the same time, i_d in KOH is two orders of magnitude greater than in NaOH, and in molten KOH–NaOH mixtures the limiting current increases with increase in the concentration of KOH in the electrolyte[22]. The value of i_d increases with increase in the concentration of water and in the temperature, and for a melt containing 78.6 mole % of KOH and 21.5 mole % NaOH the experimental data are described by the relationship

$$i_d = A \exp(-U/RT),$$

where U is the activation energy of the reduction, equal to 4.8 kcal $mole^{-1}$. This value is close to the activation energy for viscous flow of the melt.

From these data, it was concluded[68] that the rate of the reduction of oxygen in hydroxide melts is determined chiefly by the rate of diffusion of the reagents, and the measured limiting current is a diffusion current.

These regular features were attributed[67,69] to the formation in the electrolyte of higher oxygen compounds (Na_2O_2, KO_2), which act as carriers of oxygen from the oxygen–melt interface to the electrode surface. The general equations for the cathode processes associated with the electrolytic reduction of oxygen can be written[67,70] as follows:

$$O_2^{2-} + 2H_2O + 2e \rightarrow 4OH^-, \; E(\text{KOH}, 200\,^\circ\text{C}) = 1.45B, \qquad (21)$$

$$O_2^- + 2H_2O + 3e \rightarrow 4OH^-, \; E(\text{KOH}, 200\,^\circ\text{C}) = 1.27B. \qquad (22)$$

The limiting current for the cathodic reduction is determined chiefly by the rate of diffusion of the ions O_2^{2-} and O_2^-. Additional proof of this is provided by the observed[27,67] linear relationship between the density of the limiting current for the reduction of oxygen and the concentration of higher oxygen compounds in the hydroxide melt. The polarisation curves recorded at 200 °C at a platinum disc electrode in a KOH–H_2O (10%) melt containing KO_2 depolariser were used to calculate the valency of reaction (22), which was found to be equal to 3, and $D_{KO_2} = 8.25 \times 10^{-6}$ cm^2 s^{-1}.[24]

It follows from Eqns.(21) and (22) that for the reduction of oxygen to take place intensively, it is necessary to ensure a high rate of supply of H_2O to the electrode surface. It was established experimentally that for each specific set of conditions there is a minimum concentration of water below which the rate of the overall process is limited by its diffusion. The corresponding concentrations are marked by maxima on the $i_d = f(c_{H_2O})$ curves. The maxima divide the range of values into two sections; in one, the rate of reduction of oxygen is limited by the diffusion of peroxides and superoxides, and in the other by the diffusion of water.

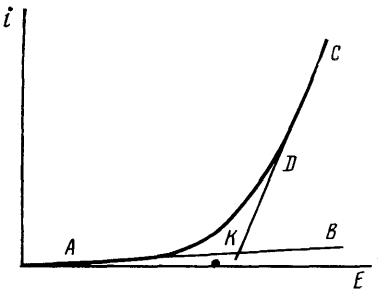


Figure 7. Determination of the decomposition voltage of an electrolyte.

In conclusion, the results of the measurement of the decomposition voltage of molten alkalis will be considered. It should first of all be noted that the concept of "decomposition voltage" has no strict scientific definition; for this reason, evidently, it is not encountered in handbooks and monographs of theoretical electrochemistry[71–73]. In textbooks on the electrochemistry of molten salts[2,3,74], the decomposition voltage is identified directly or indirectly with the e.m.f. of a reversible chemical cell, the magnitude of which can be calculated from thermodynamic data (this last assumption is rejected by Levin[75]), The concept of "decomposition voltage" has also been defined using such indefinite expressions as "visible products appear", "the e.m.f. reaches a certain definite value"[76], "minimum voltage", "for prolonged electrolysis to take place"[3].

The decomposition voltage E_d is usually determined from a graph (Fig.7) obtained by plotting current against voltage, at the point of intersection of the straight line CD with the abscissa. It should be noted that the concept of anodic decomposition voltage is encountered[77], but LeBlanc[62] does not consider it possible to record the residual current on the polarisation curve. In addition, completely different values of E_d for NaOH are obtained[62,78], depending on whether a micro-cathode or a micro-anode is used. Without going into a detailed analysis of this complex question here, it will probably be most correct to return to the source, that

is to the definition of decomposition voltage given by LeBlanc, who introduced this concept.

It is first of all necessary to take account of the fact that, in accordance with LeBlanc's theory, until the applied voltage becomes equal to or greater than the value E_d, no electrode processes are possible, and no current should pass through the cell[2]. It is obvious that this quantity E_d as a rule cannot be calculated from thermodynamic data; it depends on the nature and concentration of the electrolyte, the electrode materials, depolarisation and polarisation effects, and temperature. The experimentally determined value of E_d characterises a given specific electrolyte under fixed electrolysis conditions. In this connection, the section of the residual current A (Fig.7) distorts the determination of the decomposition voltage, which is apparently best obtained at the point K of intersection of the tangents AB and CD to the sections of the curves for the residual current and the electrolyte decomposition current.

It is generally accepted[3,45,78,85] that on the application of a direct current voltage (2.1–2.3 V) to indifferent electrodes immersed in a hydroxide melt, alkali metal is liberated at the cathode ($M^+ + e \rightarrow M$), and oxygen and water are liberated at the anode. In the case of a hydrated electrolyte, hydrogen is liberated at the cathode at a voltage of 1.1–1.3 V. The experimentally measured decomposition voltages of NaOH are given in Table 4. The decomposition voltage of molten potassium hydroxide at 390 °C is 2.1 V according to Ref.69, and 2.15 V according to Ref.79. In the latter case[79], an attempt was made to determine the decomposition voltage of molten LiOH. The value obtained at 460 °C was 1.3 V, which is clearly too low. Liberation of metal at the cathode was not observed.

Table 4. Measured values of the decomposition voltage of sodium hydroxide.

Method	Cathode	Anode	t, °C	E_d, V		Refs.
				I	II	
According to LeBlanc	Ni	Ni	350	1.3	2.2	62
According to LeBlanc	Fe	Fe	390	1.16	2.2	63
E.m.f. of the chemical cell	Fe	Ag	370	1.17	2.28	31
According to LeBlanc	Ag	Ag	393	—	2.32	80
According to LeBlanc	—	—	350	1.3	2.05	84
According to LeBlanc	Ni	Ni	450	1.28	1.96	58
According to LeBlanc	Fe	Fe	460	1.2	2.08	77
Potentiodynamic (KOH - NaOH melt)	Pt	Pt	200	1.45	2.10	5
Back e.m.f. in the electrolysis vessel	Cu	Ni	325	1.35	2.25	45
Back e.m.f. in the electrolysis vessel	Cu	Ni	300	—	2.3	45
According to LeBlanc	Ni	Ni	340	—	2.2	79
Polarisation curves	—	—	450	—	2.1	85

The temperature coefficient of the decomposition voltage of NaOH is 2.95×10^{-3} V K^{-1} according to Ref.79, and 1.3×10^{-3} V K^{-1} according to Ref.31. The temperature coefficient of the decomposition voltage of KOH is 2.15×10^{-3} V K^{-1}.[79]

A number of authors report that other electrode processes take place at the cathode and the anode. Thus an inflection was recorded on the $I-V$ curve at 1.87–2.00 V,[80] and its appearance was attributed to the reduction of the oxides Na_2O and Na_2O_2. In the opinion of the authors cited[80], these oxides are formed in well dried NaOH. As early as 1902, LeBlanc[62] noted the presence of an additional inflection on the polarisation curve for dried sodium hydroxide. Two inflections were also observed[81] on the $I-V$ for NaOH, at 1.73–2.04 V and 2.12–2.2 V, in the range 460–338 °C, but the first inflection was attributed[81] to the formation of sodium hydride at the cathode:

$$NaOH + e \rightarrow NaH + O^{2-} \qquad (23)$$

and to the following reaction at the anode:

$$O^{2-} - 2e \rightarrow 1/2O_2.$$

The second inflection was attributed to the overall reaction:

$$2NaOH + 2e \rightarrow 2Na + H_2O + 1/2O_2 . \qquad (24)$$

It was shown experimentally[81] that at current densities which are lower than those at which the liberation of sodium takes place but which ensure that the first reaction takes place, NaH is obtained with a current efficiency of up to 91%. This viewpoint[81] may be confirmed by the experimental fact that the first inflection on the $I-V$ disappears at 515 °C, since NaH does not exist under these conditions. Other workers[80] also did not observe the first inflection on the polarisation curve at 543 °C, and this was attributed[81] to the same factors.

Table 5. Comparison of the experimental values of the decomposition voltage and the values calculated for reactions (23) and (24) at different temperatures and the current density (i_c) at which liberation of sodium begins at these temperatures.

t, °C	E_1, V (first inflection)		E_2, V (second inflection)		i_c, A cm^{-2}
	experiment	calculation	experiment	calculation	
338	2.04	1.68	2.28	2.34	0.41
368	1.93	1.66	2.35	2.28	0.40
401	1.86	1.64	2.21	2.24	0.51
440	1.78	1.62	2.15	2.18	0.60
460	1.73	1.61	2.12	2.14	0.65
515	—	—	2.04	2.06	0.04

The experimental values of E for the formation of NaH (Table 5) are slightly higher than the values calculated by the same authors[81] from thermochemical data; this is due to the low activity of NaH in the melt in the experiment. The low values of E_d for NaOH are due to depolarisation phenomena resulting from the absence of separation between the electrode compartments and the fact that two parallel cathode processes are taking place at similar potentials.

An even more unusual conclusion was reached by Krueger[6], from whose results it would be expected that in pure NaOH at 500 °C the reaction taking place at the cathode would be

$$2OH^- + 2e \rightarrow 2O^{2-} + H_2,$$

and not the process

$$Na^+ + e \rightarrow Na;$$

that is sodium oxide and hydrogen, and not sodium, would be obtained as cathode products. According to Krueger's calculations[6], the decomposition voltage of NaOH in this case at 500 °C by the reaction

$$2NaOH = {}^1/_2O_2 + {}^1/_2H_2O + {}^1/_2H_2 + Na_2O$$

would be 2.1 V, which is close to that observed experimentally. No proof of the anodic formation of peroxide was obtained by Krueger[6].

At the same time, as early as 1895, Janeczek[82] suggested that the discharge of OH^- anions takes place with the formation of peroxide, and that the liberation of oxygen is brought about by a secondary reaction involving the decomposition of H_2O_2. This opinion was also held by Carrier[83]. Much later, Tremillon and coworkers[7,10] concluded that the OH^- ion is oxidised to superoxide O_2^-. When appreciable concentrations of this anion are reached (this is facilitated by high current densities), the dismutation process (3) takes place, accompanied by the liberation of oxygen into the atmosphere (as is usually the case in the electrolysis).

Thus in spite of the relatively large number of studies of the decomposition voltage of molten alkalis, this question requires further detailed study. It is necessary to obtain reliable experimental proof that the liberation of oxygen is a secondary reaction which is preceded by the electrochemical production of peroxide or superoxide. It is necessary to obtain unambiguous indications of additional inflections on the cathodic polarisation curves, and reliable experimental data on the decomposition voltage of pure molten potassium and lithium hydroxides.

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