

ELECTROCHEMICAL PREPARATION OF SODIUM CHLORATE FROM AQUEOUS SODIUM CHLORIDE.

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A detailed study has been made of the electrolytic production of chlorate by the electrolysis of sodium chloride solution. Data are given in respect of the influence on the current efficiency of chlorate formation of the following factors: the temperature, the separation and disposition of the electrodes, the electrolyte concentration, the current density and addition agents. Influence of sun light and superimposition of A. C. during the electrolysis have also been investigated. A general theory of chlorate formation, *electrochemically*, is discussed.

Desite the fact that alkali chlorates are of very great commercial importance and especially as a war material, no systematic and detailed data are available in the literature in regard to the various factors involved in their preparation, electrochemically, which is increasingly superceding other well known methods. The present work was undertaken to study the efficiency of an experimental 'chlorate cell' over a certain range of conditions.

EXPERIMENTAL.

The cell consisted of a cylindrical glass vessel 6" in height and about 2" in diameter. It was closed with a well fitting cork which carried a platinum anode, a graphite cathode, a thermometer and an exit tube for the evolved gases. The temperature of the cell was controlled by immersion in a thermostat kept at the appropriate temperature. A fixed volume, *viz.*, 100 c.c. of NaCl solution of known concentration represented the bath; to this was added 0.4 g. of $K_2Cr_2O_7$ in all experiments except those reported in Table V showing the influence of the various "*addition agents*" on the efficiency of the chlorate formation. The circuit included an ammeter, an adjustable resistance and voltmeter between the electrodes. After electrolysis, a known volume of the solution was analysed for (i) chlorate and (ii) total available chlorine *i.e.*, free chlorine and that present as hypochlorite which was determined by titration against a standard sodium arsenite solution. The current efficiency was calculated in respect of (i). These results and also those for (ii) are returned in the following tables, which illustrate the influence of such factors as the temperature (Table I), '*separation*' or the

inter-electrode distance, the vertical and horizontal disposition of the electrodes (Table II), initial concentration (Table III) and current density (Table IV), and 'addition agents' (Table V).

TABLE I.

Current = 1.5 amp. Distance between the electrodes = 2 cm.
Current density = 1 amp./sq. cm. Current passed for 1 hour.

No.	Temp.	P. D. applied.	Strength of available Cl_2 in c.c. of arsenite soln.	Current efficiency of chlorate formation.
1	30°	5 volts.	2.3	32.69%
2	40	5	2.0	51.93
3	50	4.8	1.7	57.95
4	60	4.8	1.4	71.68
5	70	4.7	1.1	86.02
6	80	4.7	0.9	91.75
7	90	4.6	0.7	96.24

TABLE II.

Variation of current efficiency with the separation of electrodes.

Current = 1 amp. Temp. = 50° Current density = 0.667 amp./sq. cm.
Current passed for 2 hours.

Separation of electrodes.	Voltage.	Strength of available Cl_2 in c.c. of arsenite s. in.	Current efficiency of chlorate formation	Separation of electrodes.	Voltage.	Strength of available Cl_2 in c.c. of arsenite soln.	Current efficiency of chlorate formation.
Both the electrodes horizontal.				Both the electrodes vertical.			
1 cm.	5.4	2.2	57.45%	1 cm.	4.5	0.9	77.19%
2	5.6	2.8	59.12	2	4.5	1.3	82.11
3	5.7	3.1	60.85	3	4.6	1.4	83.75
4	5.7	4.0	64.93	4	4.7	1.5	84.57
5	5.7	4.0	71.45	5	4.7	1.6	87.03
6	5.9	3.6	65.75	6	4.8	1.6	82.93
7	5.9	3.8	61.59	7	4.8	1.6	80.47
8	6.0	4.1	59.12	8	4.8	1.6	79.66

Evidently the current efficiency is greater with electrodes vertical than when they are horizontal.

TABLE III.

Variation of current efficiency with the initial concentration of sodium chloride.

Current strength = 1 amp. Current density = 0.667 amp./sq. cm.
Current passed for 2 hours.

Conc. of sodium chloride	Strength of available chlorine in c.c. of arsenite soln.	Current efficiency of chlorate formation.
5%	1.3	75.54%
10	1.4	75.54
15	1.4	77.34
20	1.5	79.66
25	1.6	80.46
Saturated	1.6	92.94

TABLE IV.

Variation of current efficiency with the current density.

Temp. = 60°. Distance between the electrodes = 2 cm. Quantity of electricity passed = 2 ampere-hours.

Anodic current density in amp per sq. cm.	Cathodic current density in amp. per sq. cm.	Strength of available Cl ₂ in c.c. of arsenite soln.	Current efficiency of chlorate formation.
2	1	1.35	64.88%
1	1	1.3	61.63
0.667	1	1.25	60.01
0.5	1	1.25	59.18
0.25	1	1.2	58.28
1	2	1.3	60.01
1	1	1.3	61.63
1	0.4	1.2	63.25
1	0.25	1.2	64.06
1	0.136	1.2	65.69

TABLE V.

The effect of addition agents on the current efficiency.

Current strength = 1 amp. Temp. = 50°. Current density = 0.667
amp./sq.cm. Current passed for 2 hours.

Addition agent.	Strength of available chlorine in c.c. of arsenite soln.	Current efficiency of chlorate formation.	Addition agent.	Strength of available chlorine in c.c. of arsenite soln.	Current efficiency of chlorate formation.
	0.8	48.45%	CaCl ₂	1.7	57.69%
K ₂ Cr ₂ O ₇	2.3	80.46	Dd(NO ₃) ₃	0.9	53.55
KMnO ₄	2.4	77.18	RbCl	0.7	48.45
YtCl ₃	0.6	76.38	CsCl	0.8	48.45
Na ₂ WO ₄	1.2	75.54	V ₂ O ₅	1.7	45.16
NH ₄ VO ₃	1.2	72.38	ThCl ₄	0.9	40.24
CeCl ₃	1.2	67.86	TlCl	0.8	27.92
UO ₂ (NO ₃) ₂	1.3	65.69	(NH ₄) ₂ MoO ₄	0.5	20.52
Zr(SO ₄) ₂	0.6	61.89	MnCl ₂	0.8	9.85
LaCl ₃	1.5	61.59	FeCl ₃	0.9	6.38
MgCl ₂	1.9	60.72	Ti(SO ₄) ₂	2.6	5.61
V ₂ O ₅	3.0	59.72			

DISCUSSION.

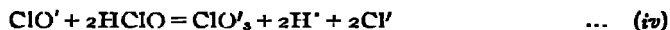
When a solution of an alkali chloride is electrolysed, hydrogen is liberated at the cathode and chlorine at the anode because of the high overvoltage necessary for the continuous discharge of OH' ions. If the electrodes are near each other and the anodic and cathodic solutions allowed to mix freely, the chlorine forms hypochlorite by secondary reactions with the OH' ions :



The concentration of the hypochlorite is, however, kept below a certain equilibrium value because it is used up in a number of side-reactions, the chief among which are (a) reduction at the cathode, (b) discharge of the ClO' ion at the anode and (c) chemical formation of the chlorate. The hypochlorite ion has a much lower discharge potential than the chloride ion (Foerster and Muller, *Z. Elektrochem.*, 1902, 8, 634) and is therefore, preferentially discharged. In an alkaline solution all the hypochlorite is ionised; the whole of it, therefore, can be discharged. In acid solutions, however, proportion of the ClO' ions is very low as the hypochlorous acid is a very weak one and its ionisation is further suppressed by the free acid present. In an acid solution with a high concentration of the chloride, the discharge of ClO' ions is expected to be very much smaller than that of the Cl' ions. The discharged ClO' ions, however, are converted into chlorate with the liberation of oxygen (Foerster and Muller, *Z. Elektrochem.*, 1902, 8, 665).



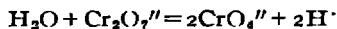
The chemical transformation of hypochlorite into chlorate can take place only in slightly acidified solutions because it is a reaction between the hypochlorite ion and the free hypochlorous acid (Foerster and Jorre, *J. prakt. Chem.*, 1899, 59, 53).



If the hypochlorite is converted into the chlorate by the electrochemical reaction (iii), then it requires 6 faradays of electricity more for 2 molecules of the chlorate. If the conversion is effected by the thermochemical reaction (iv), no electricity is used up and the formation of each molecule of the chlorate requires only 6 faradays necessary for producing 3 molecules of the hypochlorite. But the electrochemical conversion requires 9 faradays per molecule and so there is a relative reduction in efficiency of 33·3%. Usually in any process of electrolytic oxidation, oxygen evolution at the anode causes a loss in efficiency. According to the earlier workers, if the main reaction occurring at the anode is the electrochemical formation of ClO'_3 ion by the oxidation of ClO' ions according to equation (iii), there will be a loss in efficiency of 33·3% corresponding to a loss of $\frac{1}{3}$ of the total active oxygen.

To get 100% efficiency, therefore, it is necessary to prevent reaction (iii) from occurring and increase the speed of reaction (iv). A slight acidification and a high concentration of chloride should serve the purpose

because, the hypochlorous acid being a weak acid will not be ionised in amounts sufficient to permit the discharge of ClO' ions to any appreciable extent and by the law of mass action, speed of the reaction (iv) will be proportional to the square of the concentrations of free hypochlorous acid. There are of course other considerations which determine the acidity. A high acidity means a low solubility of chlorine and prevention of reaction (i) and (ii). So a good amount of the chlorine will escape. Moreover, free hypochlorous acid being volatile, much of it will be lost, especially at higher temperatures. The protective film formed by the dichromate will dissolve if the acidity increases. So the acidity is not allowed to rise and is kept within the required range by the addition of $\text{K}_2\text{Cr}_2\text{O}_7$ which acts as a buffer [Pamfilov, *Bull. Inst. Polyt. Ivanovo. Voznesensk*, 1921, 4, 113].



Owing to the weakness of the hypochlorous acid very slight acidity is sufficient to suppress the formation of ClO' ions. The dichromate is also the best 'addition agent' found so far, for the prevention of cathodic reduction in chlorate cells. The effect of variation of temperature on the current efficiency is shown in Table I. Since acidic solutions have been used throughout, formation of the chlorate comes about chiefly by the thermochemical reaction (iv) and so the yield increases with temperature. But at higher temperatures the increase is not so great; so there must be some other factors which decrease the yield and the effects of which are much more pronounced at higher temperatures. The increased discharge of ClO' and OH' ions due to decrease in the oxygen overvoltage at high temperatures and the volatility of the free hypochlorous acid may act in this direction. Due to the fall in overvoltage and the greater conductivity at higher temperatures the voltage is less.

No adequate information is available in the literature to show the effect of the variation of the interelectrode distance in chlorate cells. It has been taken for granted that the electrodes must be as near each other as possible. But the results given in Table II go to show that there exists an optimum distance of maximum yield. Unless the solution is very vigorously stirred, there will be formed a zone where the anodic and cathodic solutions meet and react to form the hypochlorite. From this zone the ClO' ions would move towards the anode and get discharged if in the meanwhile they do not react chemically. So the farther away the neutral zone from the anode, the less will be the discharge of ClO' ions and so the loss in efficiency will be comparatively small. But when the separation

becomes great, the chlorine not finding a sufficiency of OH' ions escapes and produces a loss. So there is a region of optimum efficiency where the combined loss due to these two causes is at a minimum.

The effect of an increase in the initial concentration of sodium chloride is to increase the yield because a high concentration of Cl' ions reduces the discharge of ClO' ions. A very high yield results if the solution is kept saturated throughout the course of the electrolysis. These are shown in Table III.

Table IV records data for the variation of current densities. Increase of the anodic current density increases the yield. This is probably due to the increased oxygen overvoltage and the consequent decrease in the amount of OH' and ClO' ions discharged.

For the prevention of cathodic reduction, it is necessary to add some foreign substance. Potassium dichromate was very early recognised to be effective in this respect and it has been hitherto the most useful *addition agent*. Though it acts catalytically, fairly large quantities are required. It is supposed to form a film of chromium chromate which prevents the contact between the nascent hydrogen and the hypochlorite and chlorate. For example Muller (*Z. Elektrochem.*, 1899, 5, 469; 1901, 7, 398; 1902, 8, 109) showed that no prevention of reduction takes place at a mercury cathode where no coherent film could be formed. Table V shows that substances which are capable of forming an insoluble film round the cathode such as the alkaline and rare-earth elements, generally show a high yield. Manganese, iron and titanium are marked by the fact that their salts reduce the yield considerably. This is probably due to the fact that their salts get easily oxidised at the anode and subsequently reduced at the cathode and thus consume much of the current used.

When the cell is exposed to sunlight neither chlorate nor hypochlorite is found amongst the end products. Perhaps this is due to the fact that the hypochlorous acid is decomposed on exposure to sunlight giving off oxygen and chlorine.



That means, it is necessary to avoid sunlight in chlorate cells. When alternating current is substituted for direct current, no chlorate is formed. The platinum dissolves and gets plated out in the black form. It may be that platinum which is ordinarily 'passive' gets charged during the transient

cathodic component with hydrogen and loses its passivity and so it dissolves during the next anodic component of the current (Margules, *Ann. Phys.*, 1898, **65**, 629; **66**, 540). This dissolved platinum gets plated out as platinum black during the cathodic half if in the mean while it has not entered into a complex. Moreover, A. C. reduces the overvoltage to a very low value (Reitlinger, *Z. Elektrochem.*, 1914, **20**, 261; Grube and Dulk, *ibid.*, 1918, **24**, 237) and so there is nothing to prevent the discharge of OH' ions in preference to Cl' ions. Since the solution is acidic OH' ions are practically absent; so some Cl' ions may also be discharged. The liberated chlorine will not escape until enough of it has accumulated to form bubbles and escape. But before this takes place the current gets reversed and the chlorine is ionised either cathodically or by reaction with the hydrogen liberated in an active state. So whether Cl' ions are discharged or not no chlorate will be formed.

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