THE INFLUENCE OF REACTION CONDITIONS ON THE COURSE OF ELECTROLYTIC PREPARATION OF AMMONIUM PEROXODISULPHATE: THE INFLUENCE OF THE RELATIVE DEGREE OF SATURATION OF STARTING SOLUTION AND OF THE TEMPERATURE

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The current yield of the electrolytic preparation of concentrated solutions of ammonium peroxodisulphate was found to decrease with decreasing degree of saturation of the starting solution. It is therefore preferable to work with a starting solution of maximum allowable concentration with respect to the given temperature of electrolysis. As the temperature is increased, the current yield decreases progressively even if starting solution of maximum allowable concentration has been used; at the same time, the voltage on the electrolytic cell somewhat decreases. The observed effect of temperature on the current yield is a resultant of its effects on a number of simultaneously occurring electrochemical and chemical processes in the anode compartment.

The hydrogen peroxide manufacture by the Loewenstein process involves anodic oxidation of sulphate ions in acidic medium to form relatively concentrated ammonium peroxodisulphate solutions which are subsequently subjected to hydrolysis. Hydrogen peroxide formed in the second stage is distilled off under vacuum[1-3]. After an addition of water and, if necessary, an adjustment of the composition to the initial molar ratio $P_0 = c_{H_2SO_4}/c_{(NH_4)_2SO_4} \doteq 1\cdot6$, the remaining solution of ammonium sulphate and sulphuric acid is returned to the cell. After World War II, the Schmidt modification[4] of the process was introduced, which used a more acidic electrolyte of a molar ratio $P_0 = 2\cdot25$. Other electrochemical processes for hydrogen peroxide manufacture operate via peroxodisulphuric acid (Weissenstein–Degussa process) and potassium peroxodisulphate (Pietsch–Adolph process)[1-3]. In spite of some improvements introduced in the electrochemical manufacture of hydrogen peroxide[4-7], this process still requires large amount of power (8—13 kWh/kg 100% H_2O_2). This is why it has lately been replaced by non--electrochemical methods[1-3,8] which are more economical, especially at large production capacities.

Despite these developments, the preparation of hydrogen peroxide *via* peroxodisulphates has not been completely abandoned. Moreover, peroxodisulphates, especially the ammonium, sodium and potassium salts, have been increasingly applied as initiators of polymeration reactions, and as oxidizing, bleaching, and etching agents. Therefore, we have undertaken investigation on the influence of individual reaction conditions on the course of the process, with the aim of assembling information necessary

for the process optimization. So far published technology-oriented reports (for a survey, see ref.[1-3,9]) do not provide such information, and fundamental-research studies are mostly directed at elucidation of the mechanism of peroxodisulphate ion formation[10-23].

In this communication, and several other to follow, we shall report on our several years' research on the influence of various reaction conditions on the course of electrolytic preparation of concentrated solutions of ammonium peroxodisulphate as an intermediate of hydrogen peroxide production by the Loewenstein process. The reaction conditions have been chosen so as to approach, as close as possible, those of industrial operation.

EXPERIMENTAL

Cell Design

The experiments were carried out in a laboratory-scale flowthrough integral electrolytic cell of monopolar type. The elements of the cell construction were chosen so that operating conditions of industrial electrolytic process could be approached as closely as possible. The acryl prism-shaped electrolytic cell was divided by two plate porcelain diaphragms of 3 mm thickness (Deutsche Porzellanfabrik, Berlin) into one central anode and two side cathode compartments. The diaphragms were of the same quality as used in industrial electrolyzers. The anode consisted of a rectangular, perfectly insulated copper frame flanked on either side by welded tantalum plates dipping into the electrolyte, to which platinum anodes of a chosen shape (horizontally extended wires or foils) were spotwelded. The current was supplied at the upper part of the frame. Each cathode was a lead plate (hard lead containing 7% Sb) of $10 \times 10 \times 0.2$ cm in dimensions, provided with lead cylindrical current leads of 8 mm in diameter. On each side of the anode and on the outer sides of the cathodes were placed glass cooling tubes of a total cooling area of 300 cm^2, through which thermostatted water was run.

The anode and both cathodes together with the coolers were fixed to separate bell-shaped tops, which allowed convenient detachment of the electrodes when their repair or adaptation to altered experimental conditions was needed. The tops were partially immersed in water seals ensuring gas-tightness of the electrode compartments and quantitative sampling of the gases evolving at the electrodes. A disadvantage of this arrangement was a spread (within ± 2 mm) in the spacing of the electrodes with repeated cell assembling. The anode compartment was 3.2 cm wide, and the distance between the cathodes and the diaphragms was 6 to 8 mm, so that the distance between the central anode and each side cathode was 23 ± 2 mm.

The electrode potentials and the components of the total cell voltage were measured at the corresponding interfaces with the aid of Hg/Hg_2SO_4 reference electrode with terminal Luggin capillaries. The Luggin capillaries were fastened to the tops covering the electrode compartments. Also mounted to the tops were mercury glass thermometers for measuring the temperature of the solutions. A schematic cross-section of the electrolytic cell is shown in Fig. 1.

The cell was fed with direct current from a YE-1T regulated power supply (Mesit, Uherské Hradiště). With the exception when the effect of variations in the current concentration in the anode compartment was examined, the current load was kept at a constant value of 9A corresponding to a constant current concentration in the anode compartment $I_{a,v} = 27$ A dm^{-3}, and constant cathodic current density $j_c = 0.045$ A cm^{-2} (geometric area). The anodic current

density was varied by varying the number of platinum wires of foils spot-welded to the tantalum supports. The current flowing between the anode and the two cathodes connected in parallel (the difference between the currents on both cathodes never exceeded 2%) was measured by a METRA ammeter (with a precision of 0·2%). The total voltage and its components, and the electrode potentials were measured by a MT 100 digital voltmeter (Metra, Blansko). As reference electrode, a Hg/Hg_2SO_4 electrode was used in a 23·9% H_2SO_4 + 20·1% $(NH_4)_2SO_4$ solution which represented the mean composition of the solutions used in the measurements. The diffusion potential of the liquid junction was neglected, since its magnitude was comparable with the experimental error (± 15 mV). The potential of the reference electrode measured against the equilibrium potential of hydrogen electrode in the same solution was 611 mV at 20°C, with the temperature coefficient $dE_r/dT = -0·29$ mV K^{-1}. The electrode potentials quoted in this paper have been calculated with respect to the equilibrium potential of the hydrogen electrode in the same solution (RHE).

The flow of electrolyte through the cell was effected by using a laboratory peristaltic pump (Developmental Workshops, Czechoslovak Academy of Sciences) with silicon tubes of different diameters, allowing adjustment of the flow rate in a stepwise manner. The starting electrolyte was introduced at a chosen constant flow rate into the bottom of both catholyte compartments whence it was carried off through outlet tubes at the liquid level. After both the streams had joined, the solution entered the bottom of the anode compartment and flowed out through a tube at the anolyte level at the opposite wall as the final solution. When the influence of additives on the current yield was examined, the solution of the additive under study was introduced into the electrolyte at the inlet of the anode compartment. The rate of gas evolution at the electrodes was measured without application of pressure, by a bubble flowmeter enclosed in a thermostatted jacket, which left the electrolyte flow rate unchanged during the measurement and gas sampling. The gas stopcocks and ground joints in the anodic line were sealed with KEL-F 90 ozone-resistant grease (Analabs, New Haven, Conn., USA).
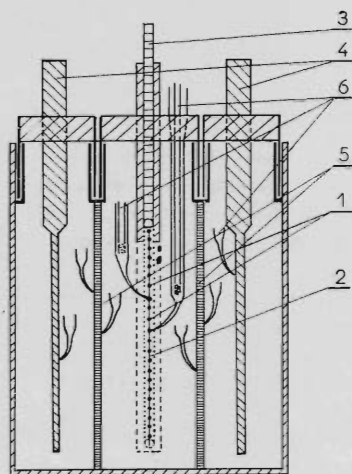

FIG. 1

Schematic cross-section of laboratory-scale flow-through electrolyzer of monopolar type. 1 Pt wire anode; 2 Ta support of anode; 3 Cu anode frame with current supply; 4 Pb cathodes with current leads; 5 porcelain diaphragms; 6 electrolyte junctions with Luggin capillaries

Measurement

The electrolytic cell charged with electrolyte of a chosen composition was thermostated at the required temperature. After certain time of subsequent electrolysis, the peristaltic pump, adjusted to a chosen rate of flow, was switched on. It took several hours to tens of hours, depending on the flow rate used, for a steady-state composition to be attained in both anolyte and catholyte. In the same time, the other parameters of electrolysis (current yield, temperature, voltage, electrode potentials, and surface characteristics of the platinum anode[24,25]) had mostly reached sufficiently steady values as well. During this steady state, which was maintained for several further hours, 2—3 analyses were made of anolyte, catholyte, and anodic and cathodic gases, and all the other quantities (total cell voltage and its components, temperatures in the anode and cathode compartments) were determined. The variation of the measured data, due mainly to fluctuations in the pump outlet, was within $\pm 2\%$. For a given composition of the starting solution and the other reaction conditions, the steady-state values of the followed quantities were measured at several electrolyte flow rates, and thereby dependences of the quantities on the actually attained degree of conversion of ammonium sulphate to peroxodisulphate were established. So obtained data afforded extrapolation to maximum conversion degree, α_{max}, for a given composition of the starting solution, at which the anolyte is just saturated with the final product, *i.e.* with ammonium peroxodisulphate. When α_{max} was exceeded, the salt crystallized out in the anode compartment, causing a breakdown of the continuous electrolytic process which could mostly be remedied only after interrupting the operation.

Samples of anolyte and catholyte withdrawn during the electrolysis were analyzed for the contents of sulphuric acid and ammonium sulphate and the total content of peroxocompounds (expressed as $(NH_4)_2S_2O_8$). In the anolyte, peroxomonosulphuric (Caro's) acid was determined in addition. The sulphuric acid content was determined by acidimetric titration with $0.1M$-NaOH using methyl red as indicator. The content of ammonium sulphate was obtained as the difference between the total content of ammonium salts determined by the method of Hanuš[26] and the total content of peroxo compounds, expressed as ammonium peroxodisulphate, determined permanganometrically by the method of Le Blanc and Eckardt[27]. The peroxomonosulphuric acid was determined iodometrically by the method of Palme[28] or permanganometrically as described by Czányi and Solymosi[29]. Tests for hydrogen peroxide in the effluent anolyte were negative in all cases. The ozone content of the anodic gas was determined by iodometric method[30]. The cathodic gas was pure hydrogen.

Chemicals

The starting solutions were made up from distilled water, sulphuric acid of analytical grade, and ammonium sulphate of the same quality additionally recrystallized with simultaneous removal of Fe^{3+} by ammoniacal precipitation. Because of considerable amounts of the starting solution necessary for carrying out the electrolysis on a continuous basis, the effluent anolyte was collected and boiled at atmospheric pressure to decompose all peroxo compounds, and after adjusting to the required starting composition it was returned to the process.

RESULTS AND DISCUSSION

The measurement of the rate of cathodic gas evolution indicated that the current yields of hydrogen evolution at the cathode were always practically 100%, at arbitrarily high content of peroxodisulphate ions in the anode compartment. This

implies that the diffusion resistance of the diaphragms used was so great that no observable diffusion of peroxocompounds could occur from the anode to the cathode compartment during the electrolysis. The concentration changes in both catholyte and anolyte were therefore due only to the electrode reactions and to the migration of ions through the diaphragms by the effect of the electric field. The criterion for the attainment of steady state was such a value of the anolyte molar ratio, $P_a = c_{H_2SO_4}$: : $c_{(NH_4)_2SO_4}$, that satisfied the relation

$$P_a = (P_0 - \alpha)/(1 - \alpha), \tag{1}$$

where α is the degree of conversion of ammonium sulphate to peroxodisulphate at the time of measurement. The electrolysis could be considered to have reached the steady state when the actual anolyte molar ratio P_a differed to a maximum of 5% from the theoretical value given by Eq. (1), for in this case the current yield and the other quantities under study agreed, within experimental error, with the steady-state values.

The ozone content of the anodic gas was found to be of the order of 10^{-1} vol.%, which was in agreement, within experimental error, with previously established dependence on other reaction conditions[31]. This finding justified neglection of the fraction of current consumed in anodic formation of ozone in the overall current balances. Thus, the instantaneous current yields of peroxodisulphate could be calculated from the measured rate of anodic evolution of oxygen according to the relation

$$\chi_{S_2O_8} = 100 - \chi_{O_2} \, (\%). \tag{2}$$

The current yield of oxygen, χ_{O_2}, was calculated from the relation

$$\chi_{O_2} = 7\,846 \cdot 25 \, . \, V_{O_2} \, . \, P/(I \, . \, T) \, (\%), \tag{3}$$

where V_{O_2} represents the volume of oxygen evolved in 1 min at the temperature T and the relative pressure P by the current I. The instantaneous current yields of peroxodisulphate determined by gas analysis compared closely to those determined by chemical analysis of the effluent anolyte.

At a total current load of 9 A, the temperature in the anode and the cathode compartment was only by $1 \cdot 3 \pm 0 \cdot 1$ K and $1 \cdot 0 \pm 0 \cdot 1$ K, respectively, higher than that of cooling water thermostatted at the temperature to which the composition of the applied solution of maximum allowable concentration of the starting components was related. This reflects very good heat transfer between the cooling tubes and the passing electrolyte.

The starting solutions used were always of maximum allowable concentration[32] with respect to the chosen molar ratio, P_0, of the starting components (ranging from

1·0 to 2·5), the temperature of cooling water (ranging from 10° to 30°C), and the expected final degree of conversion, α_{max}, of ammonium sulphate to peroxodisulphate (in the range 0·4−0·8). The compositions of the solutions used are given in Table I. In this connection, it should be realized that a change in the above specified parameters, which are useful for characterization of reaction conditions of industrial--scale electrolysis, necessitates a corresponding change in the composition of the starting solution. The established dependences therefore always reflect the influence of the simultaneously varied composition of the starting solution. This procedure was chosen in an effort to investigate the influence of the other studied quantities under conditions where the starting solution was invariably of maximum allowable concentration. Moreover, the results obtained in this way may be applied in full-scale operation without major corrections.

The extent to which the individual factors under study influence the current yield of peroxodisulphate ions may be assessed by examining their influence on various quantities that determine the current yield

$$\chi = 1/\left[1 + z_2 k_2 a_{H_2O}(1 - \theta) \exp\left(FW_1/RT\right))/(z_1 k_1 c_{SO_4^{2-}} \theta)\right], \tag{4}$$

where

$$W_1 = \left[\alpha_2 n_2(E - E_{r,2}) - \alpha_1 n_1(E - E_{r,1})\right]. \tag{5}$$

Eq. (4) was derived[33] on the simplifying assumptions that (i) peroxodisulphate ions

TABLE I
Compositions of the applied starting solutions of maximum allowable concentration[32] (in wt.%)

| Molar ratio P_0 | Starting component | 10°C | | 20°C | | 30°C | |
| | | α_{max} | | α_{max} | | α_{max} | |
		0·4	0·8	0·4	0·8	0·4	0·8
1·0	H_2SO_4	17·99	17·27	19·73	19·05	21·41	20·58
	$(NH_4)_2SO_4$	24·25	23·28	26·86	25·68	28·86	27·71
1·5	H_2SO_4	21·88	20·63	24·22	22·65	26·30	24·56
	$(NH_4)_2SO_4$	19·65	18·53	21·77	20·34	23·62	22·07
2·0	H_2SO_4	24·90	23·18	27·46	25·54	30·10	27·60
	$(NH_4)_2SO_4$	16·78	15·62	18·50	17·21	20·29	18·59
2·5	H_2SO_4	27·57	25·55	30·37	28·08	33·25	30·15
	$(NH_4)_2SO_4$	14·90	13·75	16·36	15·15	17·95	16·25

are formed predominantly by the discharge of sulphate ions while the rate of their generation by the discharge of HSO_4^- ions is negligible at comparable concentrations of SO_4^{2-} and HSO_4^- ions, and (ii) the principal anodic reactions are the peroxodisulphate formation and the evolution of gaseous oxygen by the discharge of water molecules. In Eqs (4) and (5), the subscripts 1 and 2 refer to the reaction producing peroxodisulphate and to the formation of gaseous oxygen by the discharge of water, respectively; θ represents the fraction of the surface on which peroxodisulphates are formed, and $(1 - \theta)$ stands for the fraction of the surface on which gaseous oxygen is evolved.

Although earlier studies[1-3,11-13,20-23,34] have pointed out that the current yield of peroxodisulphate increases with increasing concentration of sulphate ions in the solution, they do not allow quantitative conclusions to be drawn about the influence of the relative degree of saturation, β, of the starting solution on the current yield of the Loewenstein process. The quantity β is defined as the ratio of the actual content of one of the starting components in the inlet solution to its content in a solution of maximum allowable concentration[32] with respect to the values of P_0, α_{max}, and the temperature of electrolysis, i.e.,

$$\beta = (c_i/c_{i.max})_{P_0, \alpha_{max}, t} . \tag{6}$$

The influence of β on the current yield was investigated on starting solutions of molar ratio $P_0 = 1.5$, prepared by gradual dilution of a basic solution of composition corresponding to $\beta = 1.0$, $\alpha_{max} = 0.8$ and 20°C. The results are shown in Fig. 2 in the form of a plot of the integral current yield of peroxodisulphate against the actually attained conversion degree α. The anodic current density, j_a, was kept at 0·83 A cm^{-2} which is the optimum value for the operation without additives[35]. The integral current yield of peroxodisulphate is seen from Fig. 2 to decrease with decreasing degree of conversion of ammonium sulphate to peroxodisulphate, the decrease being the steeper the higher the conversion degree. The same pattern of behaviour holds throughout the measured range of degree of saturation of the starting solution, $\beta = 1.0$ to 0·798. For four values of the actually attained conversion degree, pairs of current yield and saturation degree values were read off from the lines and plotted in Fig. 3.

Fig. 3 shows that the current yield of peroxodisulphate decreases with decreasing relative degree of saturation of the inlet solution. Within the covered range of the actually attained conversion degree, $\alpha = 0.3$ to 0·8, the decrease $(-\Delta\chi)$ is almost independent of the value of α, and may be expressed by the relation

$$-\Delta\chi = 122\beta(1 - \beta) \tag{7}$$

which fits the measured values within $\pm 1.7\%$.

Variation of the relative degree of saturation of the starting solution within the range from 1·0 to 0·8 produced no effect, within the reproducibility of measurements, on the total voltage of the cell (Fig. 2, curve *4*). Similar situation may be expected for other values of P_0, j_a, and t.

The observation that the current yield of peroxodisulphate is the lower the less concentrated solutions are used in the electrolysis clearly confirms our previous assumption[32] that maximum current yields are attained with solutions of maximum allowable concentration of the starting components. On electrolysis under the considered reaction condditions, such solutions will provide just saturated solutions of ammonium peroxodisulphate. It is therefore advisable, as pointed out in the previous paper[32], that the compositions of solutions used in the industrial practice be as near as possible to maximum allowable concentrations with respect to chosen reaction conditions $(P_0, \alpha_{max}, \text{ and } t)$. At the same time, however, one should bear in mind that under these conditions the solubility of ammonium peroxodisulphate, which is the least soluble component in the system, may easily be reduced as a consequence of a decrease in the temperature of cooling water. Crystallization of the salt in the cell or in the offtake pipe could put the production unit out of operation. It is therefore advisable to work with somewhat more dilute starting solutions (with β ranging from 0·98 to 0·96) and to ensure a steady temperature regime in the cooling system.
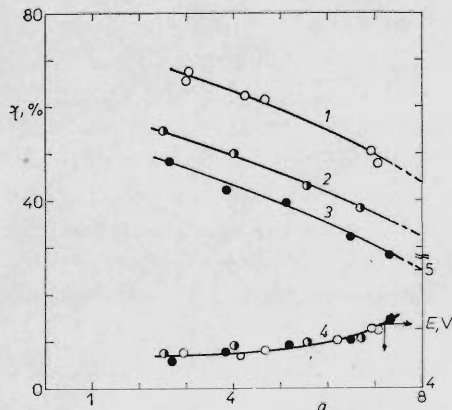

Fig. 2

Dependence of the current yield of peroxodisulphate *1—3* and the voltage of the cell *4* on the actually attained degree of conversion of ammonium sulphate to peroxodisulphate, $\alpha . 10^1$ in electrolysis of solution with $P_0 = 1·5$, $\alpha_{max} = 0·8$, and various degrees of saturation, β: 1·0 ○; 0·905 (◑); 0·798 (●)
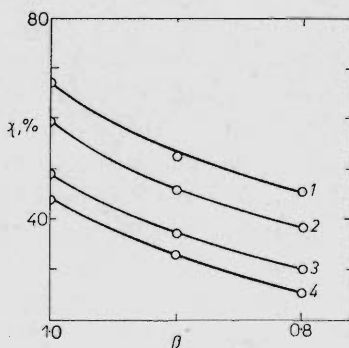
Fig. 3

Dependence of the current yield of peroxodisulphate on the degree of saturation, β, of starting solution with $P_0 = 1·5$, $\alpha_{max} = 0·8$ at 20°C for various actually attained degrees of conversion of ammonium sulphate to peroxodisulphate, α: *1* 0·3; *2* 0·5; *3* 0·7; *4* 0·8

Fig. 4 shows the variation in the current yield of the process under study during electrolysis of solutions of maximum allowable concentrations with respect to given temperatures (i.e., $\beta = 1\cdot0$ in all cases) as a function of temperature. The data points were obtained in the above described way from the plots of the current yield against the conversion degree, α, for given parameters of electrolysis $(P_0, \alpha_{max}, t, j_a)$. Curves 1 and 2 represent measurements with starting solutions of molar ratio $P_0 = 1\cdot0$ and composition corresponding to $\alpha_{max} = 0\cdot8$ and $0\cdot4$, respectively. Curve 3 relates to measurements with $P_0 = 2\cdot0$ and $\alpha_{max} = 0\cdot8$. In all these cases the electrolysis was carried out at a current density of $2\cdot72$ A cm^{-2}, without any anodic additives for increasing the current yields. The measurement with $P_0 = 1\cdot5$ and $\alpha_{max} = 0\cdot8$ (curve 4) was performed at $j_a = 0\cdot22$ A cm^{-2}, with continuous supply to the anolyte of an ammonium thiocyanate solution in amount optimal with respect to the given temperature[35]. In contrast to the previous cases, curve 5 represents the temperature dependence of the current yield during electrolysis of a starting solution of constant composition at all temperatures of measurement. The applied composition was that corresponding to the maximum allowable concentration with respect to $P_0 = 1\cdot5$, $\alpha_{max} = 0\cdot8$, and $t = 10°C$. At higher temperatures of electrolysis, this solution was
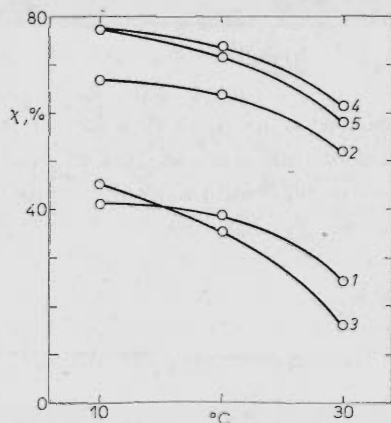

FIG. 4

Temperature dependence of the current yield of peroxodisulphate under various conditions of electrolysis. 1 $P_0 = 1\cdot0$; $\alpha_{max} = 0\cdot8$; 2 $P_0 = 1\cdot0$; $\alpha_{max} = 0\cdot4$; 3 $P_0 = 2\cdot0$; $\alpha_{max} = 0\cdot8$; 4, 5 $P_0 = 1\cdot5$; $\alpha_{max} = 0\cdot8$; 1—3 no additives; 4, 5 NH$_4$SCN addition; 1—4 $\beta = 1\cdot0$ at all temperatures; 5 $\beta = 1\cdot0$ at 10°C only; at the other temperatures, the same composition as at 10°C
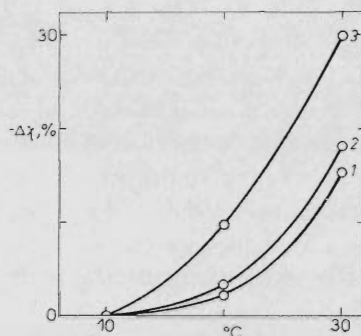
FIG. 5

Influence of temperature on the current yield of peroxodisulphate for various values of P_0 of the starting solution with the degree of saturation $\beta = 1$. P_0: 1 $1\cdot0$; 2 $1\cdot5$; 3 $2\cdot0$

therefore more dilute than corresponded to the maximum allowable concentration for the given temperature; its degrees of saturation at 20°C and 30°C were 0·91 and 0·84, respectively. This series of measurements was also carried out with an optimum amount of ammonium thiocyanate added into the anolyte.

As is evident from Fig. 4, a temperature increase in the anodic compartment from 11·5 to 31·5°C causes the current yield of peroxodisulphate to decrease progressively. Moreover, comparison of the curves indicates that the decrease in the current yield with temperature becomes more pronounced with increasing value of the molar ratio P_0, *i.e.*, with increasing content of sulphuric acid in the electrolyzed solution (Fig. 5). On the other hand, the temperature appears to have about the same effect, under otherwise identical conditions, on electrolysis of solutions with various assumed maximum conversion degree, α_{max}, even though somewhat different compositions of the starting and especially the final solutions are involved. The results further indicate that in the process under study the decrease in the current yield with increasing temperature is independent of whether or not the thiocyanate is added to the anolyte, though an addition of this compound causes the current yield to increase noticeably under otherwise the same conditions of electrolysis.

In assessing the influence of temperature on the current yield of the process under study, it should be borne in mind that the temperature affects several simultaneously occurring electrode and chemical reactions and phenomena: *a*) the anodic formation of peroxodisulphate by the discharge of sulphate or hydrogen sulphate ions; *b*) the anodic evolution of oxygen by the discharge of water molecules; *c*) the hydrolysis of peroxodisulphate ions in acidic medium to peroxomonosulphuric acid; *d*) the anodic decomposition of peroxomonosulphuric acid to form gaseous oxygen; *e*) the composition, or ionic strength, of starting solutions of maximum allowable concentration, and hence the kinetics of the processes *a*) to *d*).

Up to now, the influence of temperature has been examined in sufficient detail only in the case *c*) (see ref.[38]) and partly in the case *e*) (ref.[32]). Therefore, comparison of the observations presented herein with the available incomplete information on the temperature dependences of the processes *a*) to *d*), examined mostly under different reaction conditions, can only be made on a general level.

Considering that the rate of anodic formation of peroxodisulphates does not show any strong dependence on temperature[36,37], we can easily understand why the current yields of ammonium peroxodisulphate decrease progressively with increasing temperature. This is because an increase in temperature has a much more pronounced effect on both the rate of anodic evolution of oxygen[39,40] and the rate of hydrolysis of peroxodisulphate to peroxomonosulphuric acid[38] than on the peroxodisulphate formation. This is also evidenced by increasing content of peroxomonosulphuric acid found in the effluent anolyte which has been electrolyzed at different temperatures to the same conversion degree, $\alpha_{max} = 0\cdot8$ (Fig. 6). Fig. 6 also shows that the increase in the peroxomonosulphuric acid content of the effluent anolyte is the greater,

the higher is the molar ratio, P_0, of the starting solution, *i.e.*, the higher is the sulphuric acid content of the anolyte. This finding is in agreement with the previously known fact that hydrogen ions have an accelerating effect on the rate of the hydrolysis reaction, which has been explained by recently proposed mechanism[38]. However, the observed increase in the rate of peroxomonosulphuric acid formation with increasing value of P_0 is partly due also to an increase in the ionic strength of the solution which likewise increases with increasing P_0 (at constant temperature, see Table I) causing an enhancement of the rate constant of peroxodisulphate hydrolysis[38].

The negative influence of temperature on the current yield of peroxodisulphate ions is undoubtedly due partly to the fact that the true concentration of SO_4^{2-} ions, whose discharge predominates in peroxodisulphate formation[23], decreases with increasing temperature in concentrated solutions under study, as indicated by Raman spectroscopy[41,42].

Although the influence of temperature on the rate of anodic decomposition of peroxomonosulphuric acid yielding oxygen has not yet been properly investigated, it would seem to be more pronounced than the influence of temperature on the anodic formation of peroxodisulphates.

Fig. 7 illustrates the influence of temperature on the total voltage on the laboratory-scale electrolyzer. In the first series of measurements at anodic current density $j_a = 2.72 \text{ A cm}^{-2}$, starting solutions of molar ratios $P_0 = 1.0$ and 2.5 were used
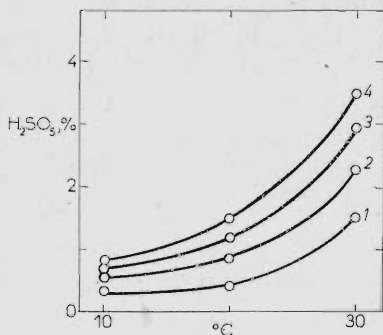

FIG. 6

Influence of temperature on the content of peroxomonosulphuric acid (wt.%) in the effluent anolyte for various values of P_0, conversion degree $\alpha = 0.8$ and current density $j_a = 2.72 \text{ A cm}^{-2}$. P_0: *1* 1·0; *2* 1·5; *3* 2·0; *4* 2·5
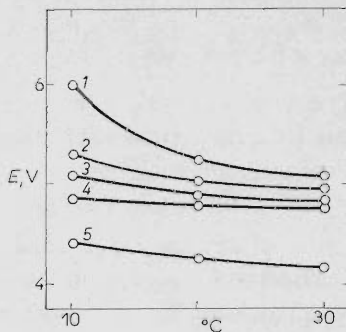
FIG. 7

Influence of temperature on the voltage of electrolyzer under different conditions. P_0: *1* 1·0; *2* 1·5; *3* 2·0; *4* 2·5; α: *1—4* 0·5; *5* 0·8; j_a: *1—4* 2·72 A cm^{-2}; *5* 0·22 A cm^{-2}

without anodic additives. The second series was run at $j_a = 0.220 \text{ A cm}^{-2}$ on solutions of $P_0 = 1.5$ with ammonium thiocyanate additions in optimum amounts with respect to the individual temperatures[35]. The molar ratio and current yield ranges covered were those of technical interest. The composition of the starting solutions always corresponded to $\alpha_{max} = 0.8$. The voltage values refer, however, to the actually attained conversion degree $\alpha = 0.5$.

The influence of temperature is seen from Fig. 7 to be most pronounced in the electrolysis of solutions with the molar ratio $P_0 = 1.0$, weakening gradually with increasing P_0. Therefore, in the electrolytic production of hydrogen peroxide by the Loewenstein process the influence of temperature on the total voltage is not too marked, since somewhat more acidic starting solution, with $P_0 \geq 1.5$, must be used. The electrolysis of less acidic starting solutions may be employed, for example, in the electrolytic manufacture of crystalline peroxodisulphates[43] where the effect of an increase in temperature of electrolysis in lowering the total voltage on the electrolyzer can be exploited to advantage.

It is further evident from Fig. 7 that at a given molar ratio P_0, the cell voltage decreases more rapidly with increasing temperature in the interval $(10°C, 20°C)$ than in $(20°C, 30°C)$.

The increasingly less pronounced influence of temperature on the total voltage with increasing molar ratio P_0 at a given conversion degree α may be explained by the fact that the increase in conductivity of more acidic starting solutions due to increased temperature is smaller than that of less acidic solutions. However, previous measurements[44] have shown that electrical conductivities of solutions in the individual compartments of the peroxodisulphate electrolyzer depend considerably also on the attained sulphate-to-peroxodisulphate conversion degree. Since the resulting values are affected to some extent by variations in the composition of starting solutions of maximum allowable concentrations with varying temperature of electrolysis, the detailed quantitative description of the influence of temperature on the individual technical and economical parameters of the process under study is rather complicated, and is beyond the scope of the present contribution.

In view of the presented results, it appears preferable to conduct the process at a temperature not much exceeding 20°C. Higher temperatures would result in undesired lowering of the current yield and an increase in the peroxomonosulphuric acid content, while producing no substantial drop of the total voltage on the cell, expecially when electrolyzing solutions of a molar ratio $P_0 > 1.5$.

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