OPTIMALIZATION OF THE COMPOSITION OF INITIAL SOLUTIONS FOR THE ELECTROLYTIC PRODUCTION OF CONCENTRATED SOLUTIONS OF AMMONIUM AND SODIUM PEROXYDISULPHATE WITH RESPECT TO THEIR ELECTRIC CONDUCTANCE

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Electric conductances of initial solutions and of the corresponding anolyte and catholyte solutions for the electrolytic production of concentrated solutions of ammonium and sodium peroxydisulphate have been measured for various molar ratios (P_0) of sulphuric acid to the respective sulphate in the initial solution and for various degrees of conversion of sulphates to peroxydisulphates, α. The measurements were carried out in the temperature range $10-30°C$. Composition of initial solutions corresponded to the maximum admissible concentration, leading upon electrolysis under the chosen working conditions (P_0, α, temperature) to saturated solutions of peroxydisulphate in which the remaining amounts of sulphuric acid and sulphate were present. The results showed that with respect to the maximum conductance of the solution it is of advantage to employ solutions with as high as possible P_0 and to work with a low α and at the highest possible temperature of electrolysis.

In our previous communications[1,2] we have reported the maximum admissible concentrations of initial solutions in the electrolytic production of hydrogen peroxide by the Löwenstein method *via* ammonium peroxydisulphate as the primary intermediate. Analogous data were published for the production of concentrated solutions of sodium peroxydisulphate[3,4]. The found maximum admissible concentrations of initial solutions affording under the chosen technological conditions the highest content of the product in the final solution, without any formation of solid phase in the electrolyzer, were in both cases determined for a rather wide range of possible values of both molar ratio P_0 and the degree of conversion α. The reason was that hitherto no detailed knowledge was available of the effect of these parameters on the energetic yield of electrolysis which would make possible to find their optimum value. Therefore there still exist several modifications of technical production of hydrogen peroxide *via* electrolytically produced acidic solutions of ammonium peroxydisulphate, differing in the value of molar ratio of sulphuric acid to ammonium sulphate in the initial solution as well as in the degree of conversion of sulphate to peroxydisulphate. *E.g.*, a typical initial composition of electrolyte, as given by Regner[5] or Schumb, Satterfield and Wentworth[6], corresponds to $P_0 = 1.64-1.67$ and the degree of conversion attains the value $\alpha \approx 0.63$. A similar value of α is also attained in the modified process according to Schmidt[7] which, however, works with $P_0 = 2.25$. The plants in Höllriegelskreuth and in Kufstein[8,9] worked with initial solutions allowing at $28-33°C$ the degree of conversion in the range $0.4-0.6$. The mentioned used solutions mostly do not correspond to the optimum with respect to the maximum attainable concentration of ammonium peroxydisulphate in the solution after electrolysis. For the
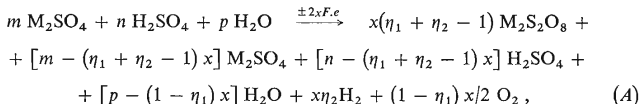
present it is not possible to draw analogous conclusions on the electrolytic production of concentrated solutions of sodium peroxydisulphate, since such a process has not yet been introduced.

One of the factors that may help to determine the optimum composition of initial solutions for the electrolytic production of concentrated solutions of ammonium or sodium peroxydisulphate, are electric conductances of the solutions. With respect to the energetic yield it is advisable that the voltage on the electrolyzer be as small as possible at the given conditions (current density, temperature). This is also affected by the conductance of the used electrolyte which determines the ohmic voltage drop between the electrodes. To make this component of the total voltage as small as possible it is necessary to choose the composition of the electrolyte having its conductance as high as possible.

Since the maximum admissible compositions of the initial solutions for the electrolytic production of concentrated solutions of ammonium or sodium peroxydisulphate can differ as to the content of individual components according to the chosen degree of conversion and to the molar ratio of sulphuric acid to the respective sulphate, one can presume that also their conductance will differ. The composition of the initial solution changes during electrolysis and using diaphragm electrolyzer this change is different in cathodic and anodic compartment. The actual composition of catholyte and anolyte is given also by the construction of the apparatus. It also depends on whether a percolating or non-percolating diaphragm is used, since in the former case all mass transport by convection, migration and diffusion proceeds through diaphragm, whereas in the latter case only migration and diffusion mass transfer goes through the diaphragm, convection being realized by by-pass. It is evident that the composition of the electrolyte can differ in different compartments of the electrolyzer and that it is affected by the construction of cells and by their regime. Thus, to estimate the influence of conductance of the processed electrolyte on the total output voltage it would be necessary to know its composition in all parts of the electrolytic plant. A certain simplification can be attained by comparing electric conductances of initial and final solutions as they are related by an unambiguous stoichiometric relation, based on the equation of total change during electrolysis. According to this equation it is possible to calculate the composition of the final solution, leaving the anodic compartment, for given values of α, P and the composition of the initial electrolyte. A disadvantage is that we do not know the actual composition of catholyte which depends on the values of transference numbers of the individual ions in both catholyte and anolyte at their respective concentrations as well as on other reaction conditions (flow rate, degree of conversion, temperature and technological parameters of electrolysis).

The present paper brings results of measurement of electric conductances of initial solutions whose composition was determined from the respective phase diagrams[1-4] under the condition that the highest concentrations of peroxidisulphate ions in the final anolyte for given values of P_0, α and temperature should be attained. For sys-

tems containing ammonium and sodium ions also the conductances of the corresponding final solutions were measured and for the system containing NH_4^+ ions also the conductances of some catholytes for certain chosen values of P_0 and α. Composition of the final solution was calculated according to equation describing the total change during electrolysis:

$$m\,M_2SO_4 + n\,H_2SO_4 + p\,H_2O \xrightarrow{\pm 2xF.e} x(\eta_1 + \eta_2 - 1)\,M_2S_2O_8 +$$
$$+ \left[m - (\eta_1 + \eta_2 - 1)\,x\right]M_2SO_4 + \left[n - (\eta_1 + \eta_2 - 1)\,x\right]H_2SO_4 +$$
$$+ \left[p - (1 - \eta_1)\,x\right]H_2O + x\eta_2 H_2 + (1 - \eta_1)\,x/2\,O_2\,, \qquad (A)$$

where M stands for cation NH_4^+ or Na^+, η_1 is the anodic current yield of peroxydisulphate ion and η_2 the cathodic current yield of hydrogen evolution. The term $(1 - \eta_1)$ includes both the current yield of anodic oxygen evolution and the amount of oxygen formed by chemical decomposition of peroxydisulphates, the term $(1 - \eta_2)$ is the current yield of cathodic reduction of peroxydisulphates which were transferred into the cathodic compartment by diffusion through diaphragm from anodic compartment (or it also may denote the current yield of the reduction of remaining peroxycompounds in the initial solution after incomplete hydrolysis of peroxydisulphates and after distilling off hydrogen peroxide, when anolyte is worked up to yield this product). The contents of individual components in the final solutions were calculated (concentrations are given in weight %) according to equations

$$x = x_0 - \frac{100 x_0 \alpha M_{M_2SO_4}/M_{M_2S_2O_8}}{100 - x_0[1 - M_{H_2SO_4}/M_{M_2SO_4} + (1 - \eta_1)\,M_{H_2O}/(\eta_1 + \eta_2 - 1)\,M_{M_2SO_4} - M_{M_2S_2O_8}/M_{M_2SO_4}]} =$$

$$= x_0 - \Delta x \quad [\text{weight \% } M_2SO_4]\,, \qquad (1)$$

$$y = y_0 - \Delta x\,M_{H_2SO_4}/M_{M_2SO_4} \quad [\text{weight \% } H_2SO_4]\,, \qquad (2)$$

$$z = \Delta x\,M_{M_2S_2O_8}/M_{M_2SO_4} \quad [\text{weight \% } M_2S_2O_8]\,, \qquad (3)$$

where M_i is molecular mass of the respective compound. It was presumed that this final composition corresponds to the composition of anolyte in the anodic compartment of a continually working electrolyzer where the evolving gaseous oxygen provides for sufficient mixing. In the case that the electrolysis is realized in a cascade of through-flow electrolyzers the calculated composition of the final solution corresponds to the composition of anolyte in the last cell of the cascade.

Compositions of the measured catholytes were taken from our hitherto unpublished results of measurements of the effects of different factors on the course of electrolysis[10] in a labora-

tory model of a through-flow continual electrolyzer. In this study, in contrast to the up to now established technical scale production, the chosen degree of conversion of sulphates to peroxydisulphates was attained in a single apparatus. Although the measured composition of such catholyte differs slightly from the composition of catholytes which would be attained in the cathodic compartments of the individual parts of the cascade, when using the same initial solutions, we can make the simplifying assumption that the conclusions obtained from the data for a single integral reactor would not differ too much from those for a cascade of difference electrolyzers. In the case of electrolytic preparation of sodium peroxydisulphate electric conductances of catholytes were not measured as their actual compositions are not known. However, we can expect that the conclusions valid for a system with ammonium salts will be, *per analogiam,* qualitatively valid also for the system with sodium salts at the same reaction conditions.

EXPERIMENTAL

Apparatus: Measurement of electric conductance was carried out by means of a Wheatstone bridge using a resistance decade Metra MLLk. The source of sinusoidal voltage of the frequency 1 kHz was an RC generator Tesla BM 218 A whose signal was led through an amplifier of our own construction. Equilibration of the bridge was performed with a zero indicator Tesla TM 622 D; capacities of the conductance cells inclusive the wiring were compensated by a capacity decade connected parallel to the resistance decade. Conductance was measured in a cell with platinum-coated electrodes whose distance was c. 12 cm. The resistance constant of the cell was determined by measuring the conductance of a calibration solution 1M-KCl and H_2SO_4 of various concentrations for which the values of specific conductance were taken from tables[11,12]. To prevent the decomposition of peroxydisulphates when working with solutions containing also these compounds, a cell was employed with a several months' old deposit of platinum black whose decomposition activity was substantially lower than with freshly prepared deposit. This could ensure that the value of conductance did not change after the temperature was stabilized, at least for 5 minutes. Test measurements proved that the resistance constant of the cell did not change with the ageing of the platinum coating. Temperature in the thermostat was maintained within $\pm 0.05°C$ and the described apparatus allowed to measure the resistance with an accuracy of ± 0.2 rel.%.

Solutions of the required composition were prepared by weighing the initial components. Crystallinic substances, (commercial products of the reagent grade purity) were recrystallized several times from redistilled water, sulphuric acid of the reagent grade purity was used without further purification. Distilled water was used for dilution of solutions and some measurements were carried out with solutions prepared with triple distilled water. However, owing to the rather high conductance of the measured solutions, no differences were found.

RESULTS

Composition of the measured solutions for the electrolytic production of concentrated solutions of ammonium and sodium peroxydisulphates are given in Tables I–IV. Compositions of initial solutions, taken from previous publications[1,3] for various values of molar ratio $P_0 = m_{H_2SO_4}/m_{M_2SO_4}$ and for the presumed degree of conversion α (under the condition of attaining the highest possible content of peroxydisulphate ions in the solutions after electrolysis) are presented in Table I and II

TABLE I

Conductivities of Initial Solutions for the Electrolytic Preparation of Concentrated Solutions of Ammonium Peroxydisulphate

t, °C	P_0	$\alpha = 0.4$			$\alpha = 0.6$			$\alpha = 0.8$		
		H_2SO_4 %	$(NH_4)_2$.SO_4 %	$\varkappa$ $\Omega^{-1}cm^{-1}$	H_2SO_4 %	$(NH_4)_2$.SO_4 %	$\varkappa$ $\Omega^{-1}cm^{-1}$	H_2SO_4 %	$(NH_4)_2$.SO_4 %	$\varkappa$ $\Omega^{-1}cm^{-1}$
10	1·0	17·99	24·25	0·417	17·41	23·47	0·420	17·27	23·28	0·420
	1·6	22·53	18·98	0·481	21·70	18·27	0·486	21·20	17·86	0·486
	2·2	25·96	15·90	0·513	24·84	15·21	0·520	24·12	14·77	0·522
20	1·0	19·73	26·86	0·469	19·29	25·99	0·475	19·05	25·68	0·478
	1·6	24·85	20·93	0·549	23·88	20·10	0·557	23·30	19·62	0·562
	2·2	28·62	17·53	0·584	27·36	16·76	0·597	26·52	16·24	0·603
30	1·0	21·41	28·86	0·516	20·76	27·97	0·524	20·58	27·71	0·527
	1·6	27·12	22·85	0·603	25·82	21·75	0·619	25·20	21·22	0·627
	2·2	31·38	19·22	0·639	29·69	18·14	0·664	28·62	17·53	0·674

TABLE II

Conductivities of Initial Solutions for the Electrolytic Preparation of Concentrated Solutions of Sodium Peroxydisulphate

t, °C	P_0	$\alpha = 0.4$			$\alpha = 0.6$			$\alpha = 0.8$		
		H_2SO_4 %	Na_2SO_4 %	$\varkappa$ $\Omega^{-1}cm^{-1}$	H_2SO_4 %	Na_2SO_4 %	$\varkappa$ $\Omega^{-1}cm^{-1}$	H_2SO_4 %	Na_2SO_4 %	$\varkappa$ $\Omega^{-1}cm^{-1}$
10	1·2	—	—	—	—	—	—	17·15	20·70	0·287
	1·6	—	—	—	—	—	—	19·17	17·36	0·342
	2·4	—	—	—	—	—	—	22·20	13·40	0·415
20	0·8	15·00	27·16	0·242	14·69	26·60	0·247	14·69	26·60	0·247
	1·2	—	—	—	—	—	—	17·90	21·60	0·332
	1·6	21·31	19·30	0·397	20·58	18·63	0·404	20·15	18·25	0·405
	2·4	25·17	15·52	0·473	24·20	14·61	0·485	23·52	14·20	0·491
30	0·8	—	—	—	—	—	—	15·16	27·45	0·284
	1·2	—	—	—	—	—	—	18·68	22·55	0·382
	1·6	—	—	—	—	—	—	21·09	19·10	0·465
	2·4	—	—	—	—	—	—	24·52	14·80	0·566

TABLE III

Conductivities of Catholytes and Anolytes in the Electrolytic Preparation of Concentrated Solutions of Ammonium Peroxydisulphate

Compositions of anolytes were calculated from those of initial solutions assuming the value of the anodic current yield, η_1 0·75. Composition of catholytes was taken from paper[10].

$t,°C$	α	P_0	Anolyte					Catholyte			
			$(NH_4)_2S_2O_8$ %	$(NH_4)_2SO_4$ %	H_2SO_4 %	P_a	κ $\Omega^{-1}cm^{-1}$	H_2SO_4 %	$(NH_4)_2SO_4$ %	P_k	κ $\Omega^{-1}cm^{-1}$
10	0·4	1·6	13·17	11·44	16·97	2·00	0·436	19·0	21·2	1·21	0·448
	0·8	1·6	24·89	3·60	10·69	4·00	0·389	10·6	24·3	0·59	0·347
20	0·4	1·0	18·63	16·18	12·01	1·00	0·391	—	—	—	—
		1·6	14·54	12·61	18·71	2·00	0·499	21·3	23·7	1·21	0·513
		2·2	12·16	10·56	23·50	3·00	0·551	—	—	—	—
	0·6	1·0	26·90	10·30	7·40	1·00	0·348	—	—	—	—
		1·6	21·00	8·00	15·00	2·50	0·479	—	—	—	—
		2·2	17·50	6·70	19·70	4·00	0·541	—	—	—	—
	0·8	1·0	35·87	5·19	3·85	1·00	0·308	—	—	—	—
		1·6	27·32	3·95	11·75	4·00	0·452	7·4	29·6	0·34	0·345
		2·2	22·60	3·27	17·00	7·00	0·531	—	—	—	—
30	0·4	1·6	15·84	13·76	20·41	2·00	0·546	22·6	26·2	1·16	0·555
	0·8	1·6	29·62	4·29	12·73	4·00	0·502	3·0	36·0	0·11	0·333

together with their conductivities. The corresponding compositions of final solutions calculated from equations $(1)-(3)$ and their conductivities are summarized in Tables III and IV. For systems with ammonium salts (Table III) also compositions and measured conductivities of corresponding catholytes are given, their compositions being taken from the hitherto unpublished results of the study of the effect of various factors on the course of persulphate electrolysis[10]. These data were obtained with solutions of pure mixtures of sulphuric acid and ammonium sulphate without any additions enhancing the current yields of peroxydisulphates. The found differences of concentration for identical molar ratios of initial solutions, P_0, and for the presumed degree of conversion, are however, not substantial and from the point of view of technical electrolysis and of this paper are negligible.

From the above mentioned results it is evident that the conductance of corresponding solutions is the higher, the higher is the temperature of electrolysis (in the range $10-30°C$). With the system containing ammonium salts this dependence is non-linear for both initial and final electrolyte (anolyte) and gradually becomes more and more flat so that the temperature dependence of conductivity at a constant P_0 of the initial solutions and at a chosen degree of conversion α has a slightly convex shape. The steepness of this dependence of initial solution increases with increasing P_0 and with increasing α. A similar slightly convex course can be observed also in the temperature dependence of conductances of anolytes which was investigated only for initial molar ratio $P_0 = 1.6$ and $\alpha = 0.4$ and 0.8. The curves for both values of α were parallel to each other (Fig. 1, curves A_4 and A_8). Also conductances of catholytes show a similar dependence for $P_0 = 1.6$ and $\alpha = 0.4$ (Fig. 1, curve K_4). From the figure it also follows

TABLE IV

Conductivities of Anolytes in the Electrolytic Preparation of Concentrated Solutions of Sodium Peroxysulphate

Compositions of anolytes were calculated from those of initial solutions[3] assuming the value of the anodic current yield $\eta_1 = 0.75$.

		Anolyte				
α	P_0	$Na_2S_2O_8$ %	Na_2SO_4 %	H_2SO_4 %	P_a	$\varkappa$ $\Omega^{-1} cm^{-1}$
0.4	1.0	16.60	14.86	10.26	1.00	0.222
	1.6	13.00	11.63	16.05	2.00	0.352
	2.4	10.45	9.34	20.97	3.25	0.443
0.8	1.0	32.25	4.81	3.33	1.00	0.158
	1.6	24.68	3.68	10.15	4.00	0.307
	2.4	18.77	2.80	15.48	8.00	0.431

that at this value of α the conductances of catholyte and anolyte are very close, however, they are lower than that of the initial solution. Conductances of catholyte are throughout greater than those of the respective anolyte.

In contrast to the previous results the temperature dependence of the conductance of catholyte for $P_0 = 1.6$ and $\alpha = 0.8$ shows an unexpected course: for both temperatures 10 and 20°C it is the same and for 30°C it is even lower than at the two preceding temperatures. (Fig. 1, curve K_8). It also is lower than that of the respective anolyte at all measured temperatures which is just the opposite than with $\alpha = 0.4$.

With the system containing sodium sulphate for which only the temperature dependence of the conductance of initial solutions was measured for $\alpha = 0.8$, a linear relation was found for various molar ratios as parameters. The slope of this dependence was found to be greater, the greater was the molar ratio of the initial solution. Increase of molar ratio of sulphuric acid to the respective sulphate results in a distinct increase of conductivity. An analogous dependence can also be expected for catholyte solutions under identical conditions (temperature and degree of conversion).

A relatively most variable effect on conductance is that of the degree of conversion of sulphates to peroxydisulphate. While the conductance of the initial solution increases with increasing α at constant temperature and molar ratio, this effect
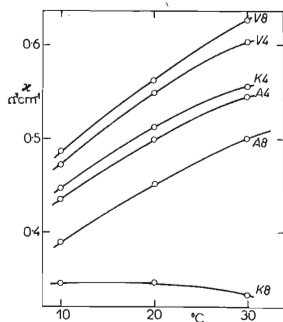

Fig. 1

Temperature Dependence of Conductivity of Initial Solutions (V), Anolytes (A) and Catholytes (K) in the Electrolytic Preparation of Ammonium Peroxydisulphate for the Degree of Conversion $\alpha = 0.4$ (4) and 0.8 (8) and for Molar Ratio of the Initial Solution $P_0 = 1.6$
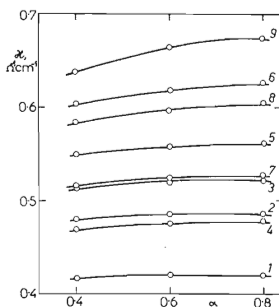
Fig. 2

Dependence of Conductivity of Initial Solutions of the Electrolytic Preparation of Ammonium Peroxydisulphate on the Presumed Degree of Conversion α

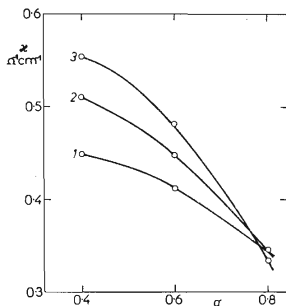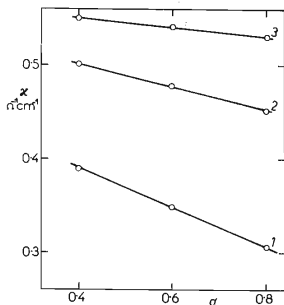1, 2, 3 10°C; 4, 5, 6 20°C; 7, 8, 9 30°C; 1, 4, 7 $P_0 = 1.0$, 2, 5, 8 $P_0 = 1.6$, 3, 6, 9 $P_0 = 2.2$.

FIG. 3

Dependence of Conductivities of Catholytes in the Electrolytic Preparation of Ammonium Peroxydisulphate on the Degree of Conversion α for Molar Ratio of the Initial Solution $P_0 = 1.6$ and for Temperatures *1* 10, *2* 20 and *3* 30°C

FIG. 4

Dependence of Conductivity of Anolytes in the Electrolytic Preparation of Ammonium Peroxydisulphate on the Degree of Conversion α for 20°C and for Different Values of Molar Ratio of the Initial Solution P_0 : 1.0 (*1*), 1.6 (*2*), 2.2 (*3*)

being greater at higher temperatures and higher P_0, the conductance of catholytes (measured only in systems containing ammonium salts, for $P_0 = 1.6$) as well as of anolytes (Figs 3 and 4) shows a reverse dependence. Analogous relations as shown in Figs 2–4 for systems with ammonium salt were also found in the case of systems containing sodium salts.

DISCUSSION

Prior to a concrete discussion of the measured data it must be accented that in our measurements the change of one examined parameter, *e.g.*, temperature (at constant values of the other factors, *e.g.*, of P_0 and α of the initial solutions) causes also a change in the actual compositions of the compared solutions (Tables I—IV). This means that the found effects of the mentioned factors on the conductivities are always a resultant of both the change of the measured parameter (*e.g.* temperature) and of the correspondingly changed maximum admissible concentration of the initial solution or of final solutions of catholyte and anolyte.

Changes in the composition of the electrolyte during electrolysis can be seen in Figs 5 and 6. Fig. 5 shows the working scheme of peroxydisulphate electrolysis with main electrode reactions on both electrodes and different flows of ions between

cathodic and anodic compartments of the electrolyzer. For the sake of simplicity only the migration flow through the diaphragm is indicated, as the diffusion has been proved as negligible[10] when using porcelain diaphragms of the same quality as in industrial electrolysis. The scheme in Fig. 5 also shows only one anodic and one cathodic compartment. The real construction of industrial electrolyzer consists usually of a central anodic compartment around which two cathodic compartments are arranged symmetrically. The flow of the initial electrolyte to these compartments is parallel. From both figures it can be seen that catolyte becomes less acid than the initial solution, since hydrogen ions are cathodically discharged to gaseous hydrogen and only a part of the discharging hydrogen ions is transferred by migration from the anodic to the cathodic compartment, since the electric current through the diaphragm is realized by migration of ammonium, sulphate and disulphate ions, too. Therefore the total content of sulphuric acid in the catholyte diminishes with increasing degree of conversion, whereas the content of ammonium sulphate increases. Consequently, the molar ratio of sulphuric acid to ammonium sulphate in the catholyte is lower than in the initial solution $(P_k < P_0)$. In the anodic compartment the content of sulphate ions is lowered by anodic discharge and by dimerization to peroxydisulphate ions and owing to partial evolution of oxygen on anode the acidity of anolyte again increases. Therefrom it results that molar ratio of anolyte $P_a > P_0$ for $P_0 > 1$ and *vice versa;* only for $P_0 = 1\cdot0$, if follows that $P_a = P_0$. However, the cases when $P_0 < 1\cdot0$ are of no importance for a technical process of continuous electrolysis with the system containing ammonium ions, since they lead to alkalinization of both catholyte and anolyte and to a loss of ammonium ions by their desorption from the solution and also by partial oxidation by the anodically formed peroxydisulphate ions which results in an undesired decrease of the peroxydisulphate yields. In the electrolytic preparation of concentrated solutions of sodium peroxydisulphate it is principally possible to work with initial solutions having molar ratio $P_0 < 1\cdot0$, so that a final solution of anolyte can be prepared, containing, in addition to a certain amount of sodium peroxydisulphate and the remaining sodium sulphate also sodium hydroxide.

The above mentioned general discussion of the changes in the composition of initial electrolyte during persulphate electrolysis makes it easier to discuss concretely the found dependences of conductances on the studied factors. A favourable effect of temperature on the conductivities of initial solutions and of the corresponding anolytes complies with the expectation. Surprising is the effect of temperature on the conductances of corresponding catholytes measured for molar ratios $P_0 = 1\cdot6$. As long as the degree of electrolysis of sulphate to persulphate is rather low $(\alpha = 0\cdot4)$ the effect of temperature is as favourable as with the initial electrolyte. The cause is that the composition of catholyte does not differ too much from that of the initial solution. The decrease of the content of sulphuric acid is counterbalanced by a corresponding increase of sulphate content at all temperatures. At high values of the

degree of conversion $(\alpha = 0.8)$ the relative differences between the composition of initial solution and that of catholyte are rather great, and above all, are influenced by the effect of temperature on the transference numbers of the migrating ions. The finding that the conductance of catholyte for $P_0 = 1.6$ and $\alpha = 0.8$ is at 20°C the same as at 10°C and for 30°C even lower, can be explained by the assumption that under the given concentration conditions the transference number of NH_4^+ ion is much more affected by temperature than it is with H^+ (or H_3O^+) ions, thus making the molar ratio of catholyte, P_k, for 30°C much lower as compared with the values for 10 and 20°C (Table III). If we compare the values of P_k for the same α at different temperatures we find that they decrease monotonously. This means that the favourable effect of temperature on the absolute mobility of ions and thus also on electric conductance for 10 and 20°C is mutually compensated by the different acceleration of the mobility of ions H^+ and NH_4^+ and consequently also by the different value of the transference number of both cations and for 30°C the effect of temperature on the relative change of transference numbers of cations prevails. A proof of this explanation, based on the measurement of the transference numbers of the individual ions in the mentioned polycomponent system and for high concentrations is, however,
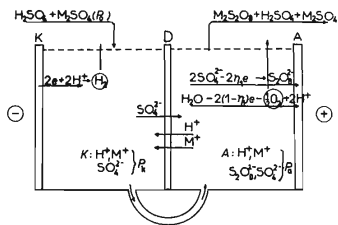

Fig. 5

Scheme of a Continuously Working Diaphragm Electrolyzer with a By-Pass for the Electrolytic Preparation of Peroxydisulphates
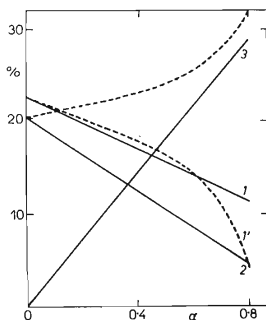
   K Catholyte, A Anolyte.

Fig. 6

Dependence of the Content (in Weight%) of H_2SO_4 (1), $(NH_4)_2SO_4$ (2) and $(NH_4)_2S_2O_8$ (3) in Anolyte (——) and Catholyte (– – – –) in the Electrolytic Preparation of $(NH_4)_2S_2O_8$ on the Degree of Conversion for the Same Initial Solution for $P_0 = 1.5$ and Temperature 20°C (according to the results in paper[10])

still lacking. Even the effect of temperature on the degree of dissociation (or association) of these compounds in the measured concentration range cannot be excluded which is supported by the fact that the conductivities of solutions with a higher content of sulphuric acid and of ammonium or sodium sulphate at the same P_0 and temperature are lower (Fig. 2) than they are with less concentrated solutions.

From theses results it also follows that the effect of temperature on conductance is more favourable with initial solutions having a higher P_0 which, at the first sight, might be in contradiction with the just mentioned assumption on the relatively higher acceleration of the mobility of NH_4^+ ion as compared with H_3O^+. The effect of temperature of course means also, under the mentioned conditions of measurement, a change in the composition. As it was found in previous papers[1,3], the concentration increases in the composition of initial solutions with temperature are the higher, the higher is the molar ratio P_0, which can explain the dependence of the temperature increases of conductance of initial solutions on P_0.

From the temperature dependence of conductance of the individual solutions, given in Fig. 1 it follows that for the given reaction conditions (P_0, α, t) initial solutions are the most conductive ones and the sequence of conductances of catholyte and anolyte is a function of the degree of conversion. For a lower degree of conversion $(\alpha = 0.4)$ and for $P_0 = 1.6$ catholyte was found to be more conductive, whereas for $\alpha = 0.8$ it was anolyte. It can be expected that the difference in catholyte and anolyte conductivities at high conversion $(\alpha = 0.8)$ will increase with decreasing P_0 of the initial solution.

The explanation of the effect of increasing molar ratio P_0 of the initial solution on the conductance of both initial solution and anolyte is also rather simple, as this means that the relative and absolute content of hydrogen ions in the measured solutions is also increased. For catholytes this effect was not studied, however a similar qualitative dependence can be expected.

What remains to be explained is the dependence of conductivities on the expected degree of conversion of sulphate ions to peroxydisulphates. This dependence showed a most interesting course with initial solutions whose conductivity increases with increasing degree of conversion. This indicates, that at a constant P_0 the conductivities diminish with increasing concentration of sulphuric acid and of ammonium and sodium sulphate, the more, the higher is the value of P_0. From the presented results it is then obvious that the studied initial solutions with a constant P_0 and with various presumed degrees of conversion lie in the region of conductance maximum or on the declining part of the concentration dependence of conductivity. This phenomenon is known with concentrated solutions of strong electrolytes: for sulphuric acid this maximum lies at $\sim 20°C$ at about 30 weight %. However, for the systems $(NH_4)_2SO_4$–H_2SO_4–H_2O and Na_2SO_4–H_2SO_4–H_2O the respective data in the desired concentration range are not available.

The decrease of conductivity of initial solutions at constant P_0 with increasing

concentration of individual components (corresponding to a decrease of the degree of conversion of sulphate ions to persulphates) would mean, when applied to the choice of solutions for electrolysis, that the original assumption on the favourable effect of the lower degree of conversion and thus of the possibility to work with more concentrated solutions was not fulfilled. However, the results of measurements of the effect of α on the conductance of anolytes (Fig. 4) and catholytes (Fig. 3) which are the most decisive for the choice of a suitable composition of initial solutions as far as conductances are concerned, indicate that the original expectation is fulfilled. Conductances of both catholytes and anolytes decrease with increasing degree of conversion of sulphates to peroxydisulphates. This means that during electrolysis the compositions of solutions have changed so that their conductances lay throughout on the ascending part of the concentration dependence of conductivity.

From the point of view of the maximum conductance of solutions in the electrolytic production of concentrated solutions of ammonium or sodium peroxydisulphate one can conclude that it is advantageous to work with initial solutions having the highest possible molar ratio of sulphuric acid to the respective sulphate and the lowest possible degree of conversion to the final product and at the highest possible temperature. These conclusions were, however, drawn from conductances of pure solutions, whereas in an electrolyzer these solutions are more or less filled with gas bubbles, evolved at the electrodes. Consequently, actual conductances of solutions are lower and the ohmic voltage drops are greater than they would be for pure solutions. The degree of saturation of the electrolyte with gas bubbles, their size and thus also their rate of escaping from the electrolyte is a complex function of viscosity, surface tension of the solution, electrode potential and current density as well as of the con-

Table V

Ohmic Voltage Drops (IR, in V) in Anodic and Cathodic Compartments of a Laboratory Model Flow Electrolyzer for the Electrolytic Preparation of Concentrated Solutions of Ammonium Peroxydisulphates for Various Molar Ratios and for Various Degrees of Conversion, α, of Initial Solutions

Temperature 20°C.

P_0	α	Ohmic voltage drop (in V) in	
		anolyte	catholyte
1·5	0·4	0·55	0·06
	0·8	0·67	0·14
2·5	0·4	0·39	0·05
	0·8	0·49	0·09

struction of the electrolyzer and of the hydrodynamic conditions of electrolyte flow. Therefore the data on the conductances of pure solutions cannot be quantitatively applied to a concrete case of electrolysis without knowing the above mentioned conditions. Nevertheless, we have made the assumption that the conclusions on the effect of the measured factors on the conductances of pure solutions are valid even for gassed solutions in the electrolyzer. This assumption was supported by the fact that maximum conductances were found always for solutions with extreme values of measured parameters, *e.g.* the highest temperature and P_0 and the lowest α.

Our presumption could also be at least in part confronted with partial results of the ohmic voltage drops, measured on a laboratory-scale model of a flow electrolyzer[10] and was found correct. This is demonstrated in Table V, which brings the mean values of ohmic voltage drops in anodic and both cathodic compartments of a model electrolyzer for electrolytic preparation of ammonium peroxydisulphate. Initial solutions had molar ratio $P_0 = 1 \cdot 5$ and $2 \cdot 5$ and $\alpha = 0 \cdot 4$ and $0 \cdot 8$, temperature was 20°C and current densities were $i_a = 2 \cdot 64$ A/cm^2 and $i_k = 0 \cdot 05$ A/cm^2. Positive effect of temperature on the decrease of ohmic voltage drops, which is not included in Table V, remained also unchanged.

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