

TABLE 4.

Pressure, mm Hg	Experiments	$(k_1 + k_2)C_{H_4}$, litre $W^{-1} h^{-1}$
28	first 17 (up to inflection)	0.0470
	remaining 6 (after inflection)	0.0745
18	first 8 (up to inflection)	0.0387
	remaining 6 (after inflection)	0.0651

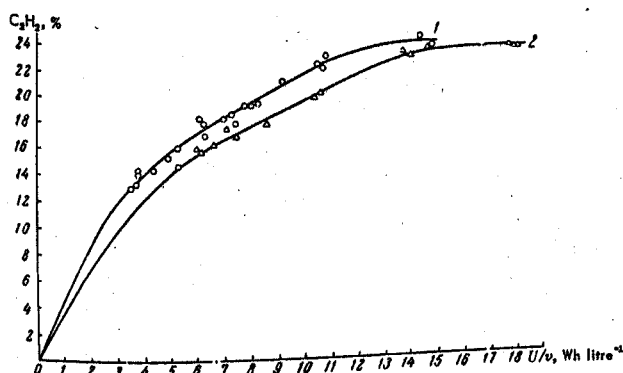


Fig. 5. Dependence of the percentage of acetylene in the reaction products on the specific energy in the cracking of a methane-ethylene mixture: 1) at 28 mm Hg; 2) at 18 mm Hg.

The mean values of $k_1 + k_2$ calculated from points before and after the inflection in the curve (Table 4) show that the change in the effectiveness of the discharge results in an almost twofold increase in the sum of the constants. It is evident from Figs. 3 and 4 (curves 3 and 4) that the experimental data fall into two groups, which satisfactorily lie on the first-order curves calculated from the mean values of $(k_1 + k_2)C_{H_4}$.

On the basis of the available data, it is possible to draw certain inferences about the influence of pressure. Fig. 5 shows the dependence of the percentage of acetylene in reaction products on the specific energy during cracking of the mixture at pressures of 28 mm Hg (curve 1) and 18 mm Hg (curve 2) in the discharge tube. With decrease in pressure, there is a slight fall in the percentage of acetylene, which can be explained by the greater effectiveness of the glow discharge at high pressures. The same conclusion follows from Figs. 3 and 4, which show that the highest value of Δ is attained at a lower specific energy (14.8 Wh $\times$ litre $^{-1}$) at 28 mm Hg than at 18 mm Hg (18.0 Wh litre $^{-1}$). The consumption of energy α (Wh per litre of C_2H_2) is also correspondingly smaller for reactions at 28 mm Hg (Table 3).

SUMMARY

1. A study has been made of the kinetics of the conversion of ethylene in mixtures with hydrogen and methane in a glow discharge at a reduced pressure.
2. The presence of hydrogen does not influence substantially the rate of conversion of ethylene. When methane and ethylene are mixed, they are cracked at rates of the same order (difference not greater than by a factor of 2.6).
3. The data obtained confirm the earlier conclusion¹ that the conversion of methane does not proceed exclusively or predominantly *via* ethylene as on intermediate.
4. The curves relating the degree of total conversion of methane to the specific energy have inflections which are connected with an increase in the rate constants and hence in the effectiveness of the discharge.

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MECHANISM OF THE RECTIFYING ACTION OF SOLID ELECTROLYTIC CAPACITORS

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The nature of the unipolar conductance of oxide layers on tantalum has recently excited great interest because of the use of this metal in electrolytic capacitors both with liquid and with solid electrolytes¹⁻⁶.

The rectifying action is normally associated with the formation of an oxide film during anodic polarisation at the tantalum-electrolyte boundary, either an insulating film of stoichiometric Ta_2O_5 or a layer of p -type Ta_2O_5 . Since in solid electrolytic capacitors such layers can form on account of the oxygen from semiconductor oxides (MnO_2 , PbO_2 , Ni_2O_3) serving as the other plate of the capacitor, it was of interest to investigate how the electrophysical characteristics of a solid electrolytic capacitor are related to the oxygen content of the MnO_2 , PbO_2 , or Ni_2O_3 .

EXPERIMENTAL

Preparation of the Electrodes

A cylindrical porous electrode with an apparent area of about 0.57 cm², made by sintering tantalum powder *in vacuo* at 2000°, was covered with an oxide film about 1200 Å thick

by anodising in 0.1 N H_2SO_4 at room temperature, at a current density of 10 mA cm^{-2} and a voltage of 120 V. After this the electrode was maintained at the same voltage for 8 h so as to reduce the leakage current as far as possible (in this case down to $0.08 \mu\text{A}$). Then a layer of manganese dioxide, lead dioxide, or nickel oxide was applied to the surface of the oxide film. The manganese dioxide was applied to the Ta_2O_5 by impregnating the electrode with a 50% $\text{Mn}(\text{NO}_3)_2$ solution and then heating it in an oven for 2 min, where at 400° the $\text{Mn}(\text{NO}_3)_2$ decomposed to give MnO_2 . The lead dioxide was applied as follows: the electrode was impregnated with a saturated solution of $\text{Pb}(\text{NO}_3)_2$ and then heated in an oven for 2 min, the lead nitrate adsorbed on the surface decomposing at 500° to give Pb_3O_4 . The resulting deposit of Pb_3O_4 was oxidised to PbO_2 in an acidified solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$. To form the layer of Ni_2O_3 , the electrode was impregnated with a solution of $\text{Ni}(\text{NO}_3)_2$ at 60° and then heated at 300° for 2 min. The thermal decomposition of the respective nitrates was carried out on each electrode 14 times for MnO_2 , 18 times for PbO_2 , and 20 times for Ni_2O_3 . After every fourth pyrolysis of adsorbed $\text{Mn}(\text{NO}_3)_2$ or $\text{Pb}(\text{NO}_3)_2$, the oxide layer was treated with a solution of boric acid and borax for 1 hour. After this, the electrodes were washed, dried, and coated with a layer of 5% aqueous graphite suspension.

The electrophysical characteristics of the electrode were measured with the electrode immersed in mercury, which served as the other connection to the capacitor. The oxygen content of the semiconductor oxides was varied by preliminary cathodic polarisation of the oxide using an external platinum connecting lead taken to the graphite layer. The cathodic polarisation was carried out in 4 N KOH at room temperature, in an atmosphere of nitrogen and at a current density of 0.1 mA cm^{-2} , up to a given value of steady-state potential as measured 10 min after switching off the current. This potential corresponds to a certain content of oxygen in the oxide. After the cathodic polarisation, the electrode was washed and dried, and its electrophysical characteristics were measured once more. Cathodic polarisation followed by measurement of characteristics was repeated on the same specimen until the oxides were almost converted to the corresponding oxides in a lower valence state.

Measurement of Electrophysical Characteristics of a Solid Electrolytic Capacitor

We measured the capacitive and resistive components of impedance of the capacitor with an a.c. bridge at various values of d.c. anode potential applied to the Ta electrode under test (see Fig.1), under the following conditions: temperature 20° , frequency 1000 c/s, and a.c. voltage amplitude 0.50 V. A compensation technique was used for measuring the impedance, the resulting capacitance and resistance values for the series-connected case being converted to those for the parallel-connected case. We also measured the leakage current of the capacitor with a positive d.c. voltage applied to the Ta electrode.

The results for capacitors of the Ta| Ta_2O_5 | MnO_2 system are shown in Figs.2 and 3, which give the percentage conversion of MnO_2 (or the quantity of electricity passed during cathodic polarisation) along the x axis and the various electrophysical characteristics along the y axis. As the oxygen content of the MnO_2 decreases (Fig.2), the capacitance gradually decreases, and starts to fall sharply

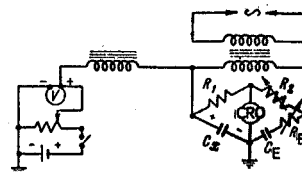


Fig.1. Measuring circuit: C_x — capacitance to be measured; C_E — capacitance in bridge circuit with resistance R_E ; CRO — oscilloscope.

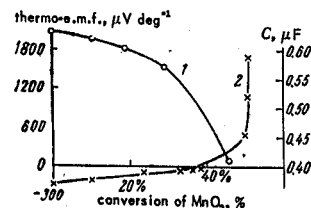


Fig.2. Capacitance and thermo-e.m.f. for Ta| Ta_2O_5 | MnO_2 capacitors as a function of the degree of conversion of MnO_2 into $\text{MnO}(\text{OH})$: 1) C , μF ; 2) thermo-e.m.f.

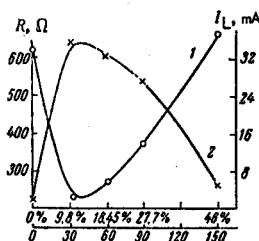


Fig.3. Resistance and leakage current I_L for Ta| Ta_2O_5 | MnO_2 capacitors as a function of the quantity of electricity passed during polarisation: 1) R , Ω ; 2) I_L , mA.

at about 46% conversion of MnO_2 to Mn_2O_3 [or, more precisely, to $\text{MnO}(\text{OH})$]. At the same time the resistance of the capacitor (Fig.3) passes through a minimum and the leakage current through a maximum. The test results for Ta| Ta_2O_5 | PbO_2 capacitors are given in Figs.4 and 5, with the PbO_2 potential 10 min after switching off shown along the x axis and the characteristics along the y axis. As this potential becomes more positive, i.e. as the PbO_2 is reduced (Fig.4), the capacitance increases, at first slowly and then more steeply, while the resistance decreases, at first rapidly and then more slowly, and the leakage current (Fig.5) follows the resistance variation. Figs.6 and 7 show the results for Ta| Ta_2O_5 | Ni_2O_3 capacitors, with the Ni_2O_3 potential 10 min after switching off plotted along the x axis and the characteristics along the y axis. As the potential

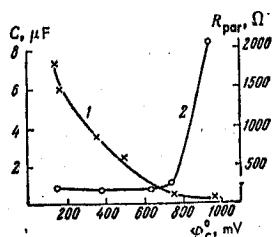


Fig. 4. Capacitance and resistance of Ta|Ta₂O₅|PbO₂ capacitors as a function of the PbO₂ potential measured 10 min after switching off the polarising current: 1) C_{par} , μF , $V = 0$; 2) R_{par} , Ω , $V = 0$.

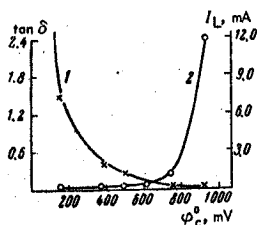


Fig. 5. Leakage current and loss-angle tangent for Ta|Ta₂O₅|PbO₂ capacitors as a function of the PbO₂ potential measured 10 min after switching off the polarising current: 1) I_L , mA; 2) $\tan \delta$.

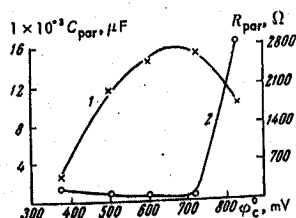


Fig. 6. Capacitance and resistance of Ta|Ta₂O₅|Ni₂O₃ capacitors as a function of the Ni₂O₃ potential measured 10 min after switching off the polarising current.

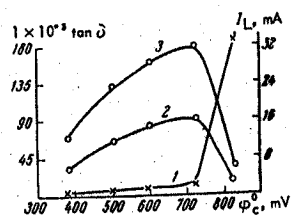


Fig. 7. Leakage current and loss-angle tangent for Ta|Ta₂O₅|Ni₂O₃ capacitors as a function of the Ni₂O₃ potential measured 10 min after switching off the polarising current: 1) $\tan \delta$; 2) I_L , mA, $V = 1$ V; 3) I_L , mA, $V = 2$ V.

of the nickel oxide electrode becomes less positive (Fig. 6), i.e. as the Ni₂O₃ is reduced, the capacitance at first rises and then falls more rapidly. At the same time the resistance of the capacitor first falls rapidly and then rises slowly, with the leakage current (Fig. 7) following it.

DISCUSSION

These experimental findings indicate the correctness of the theoretical assumption that the second plate in a solid electrolytic capacitor is not just an electrical connection but also has a substantial effect on the electrophysical properties of the Ta₂O₅ oxide film, apparently close to its phase boundary with the MnO₂, PbO₂, or Ni₂O₃. Sasaki's theory³ thus meets with no experimental confirmation.

Let us first consider the reasons for the appearance of extremal points in the plots of electrophysical properties against oxygen content in the MnO₂ and Ni₂O₃. We could explain the nature of the relationship between the electrophysical characteristics of the Ta|Ta₂O₅|MnO₂ capacitor and the oxygen content of the manganese dioxide by supposing that, as MnO₂ undergoes cathodic polarisation and conversion to MnO(OH), the type of its conductivity changes, i.e. MnO₂, an *n*-type semiconductor, is converted into the *p*-type MnO(OH). Thus as the oxygen content of MnO₂ falls, the number of majority carriers (electrons) increases, so that the conductance rises and the resistance falls. However, the decrease in oxygen content due to conversion into *p*-type MnO(OH) must also lead to annihilation of holes by electrons, i.e. to a fall in conductance and rise in resistance. This supposition fits in with the observed values of thermo-e.m.f. of copper-MnO₂ thermocouples for various oxygen contents in the MnO₂.

For thermo-e.m.f. measurement, we prepared electrodes by compressing on to a platinum grid MnO₂ powder obtained by pyrolysis of Mn(NO₃)₂ at 400°. These electrodes were covered with a polymer film to prevent the MnO₂ from disintegrating into dust, and were exposed to cathodic polarisation in 4 N KOH for a given time corresponding to a certain percentage conversion of MnO₂ into MnO(OH); finally, after steeping in the electrolyte solution for three days, they were washed and dried, and thermo-e.m.f. measurements were made on each one separately. The results are given in Fig. 2: this shows that at a mean conversion ratio of 40% there is a change in the sign of the thermo-e.m.f., and consequently in the type of conductivity. A change in conductivity type with decrease in oxygen content is also known to occur with Ni₂O₃. Nickel monoxide is a recognised *p*-type semiconductor⁷. It is also probable that the pyrolysis of Ni(NO₃)₂ produces a nickel oxide deficient in oxygen and with a stoichiometric surplus of nickel atoms, i.e. *n*-type Ni₂O₃.¹² An investigation of the conductivity type of Ni₂O₃ as a function of oxygen content, made from measurements of thermo-e.m.f., has shown that pyrolytic decomposition of Ni(NO₃)₂ at 300° gives an *n*-type nickel oxide which goes over to *p*-type NiO (see Fig. 8). The initial potential of the Ni₂O₃ electrode, referred to the Cd electrode, is lower (by about 0.5 V) than the known e.m.f. of the alkaline accumulator⁸, and this directly demonstrates that the pyrolysis gives an oxide of nickel which is very deficient in oxygen.

For the Ta|Ta₂O₅|PbO₂ capacitor, a fall in the oxygen content of lead dioxide does not apparently change the type of its conductivity. Lead dioxide is known as an *n*-type semiconductor⁹. Work on the electrolytic reduction

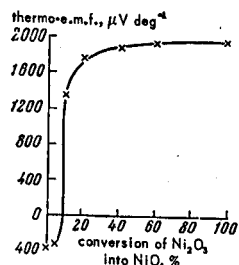


Fig. 8. Thermo-e.m.f. of $\text{Ta}|\text{Ta}_2\text{O}_5|\text{Ni}_2\text{O}_3$ capacitors as a function of the degree of conversion of Ni_2O_3 into NiO .

of PbO_2 in alkaline solution at room temperature¹⁰ has shown that this process over the given range of potentials is practically terminated by the formation of PbO , which is also an n -type semiconductor¹¹.

The variation in the electrophysical properties of solid electrolytic capacitors of the various systems with change in the oxygen content of the MnO_2 , PbO_2 , and Ni_2O_3 can be explained by postulating that the rectifying action is related to phenomena taking place at the boundary separating the Ta_2O_5 from these oxides. Let us examine this in greater detail, taking the $\text{Ta}|\text{Ta}_2\text{O}_5|\text{MnO}_2$ system as example. Ta_2O_5 is known to be an n -type semiconductor. If it is in contact with MnO_2 , the difference in chemical oxygen potentials between the two oxides will give rise to a transfer of oxygen from the MnO_2 to the Ta_2O_5 , with a simultaneous transfer of electrons in the opposite direction; this process will continue until the chemical oxygen potentials in the two oxides are equalised. When anodic polarisation is applied to the tantalum electrode, the electrons reaching the MnO_2 from the external circuit will reduce Mn^{4+} to Mn^{3+} ions and will cause oxygen ions to migrate from the MnO_2 into the surface layer of the Ta_2O_5 . This will lead to the formation at the $\text{Ta}_2\text{O}_5|\text{MnO}_2$ phase boundary of an insulating layer of stoichiometric Ta_2O_5 , or of a thin inversion layer of p -type Ta_2O_5 , which will act as an obstacle to any further passage of current in this direction. Thus at the moment of switching on, MnO_2 is electrolysed in the solid electrolytic capacitor in a way similar to the electrolytic decomposition of water occurring in the wet electrolytic capacitor.

Since the formation of both stoichiometric Ta_2O_5 and p -type Ta_2O_5 at the $\text{Ta}_2\text{O}_5|\text{MnO}_2$ phase boundary is accompanied by migration of oxygen from MnO_2 to Ta_2O_5 , we may consider that a change in the oxygen content of the MnO_2 should affect not only the conductivity of the manganese dioxide itself but also the properties of the Ta_2O_5 film near its phase boundary with the MnO_2 . As the oxygen content of the manganese dioxide decreases and the type of its conductivity changes, its resistance should pass through a minimum. The formation of an insulating or p -type layer of Ta_2O_5 at the phase boundary will be impeded by a decrease in the oxygen content of the MnO_2 , since this decreases the chemical oxygen potential of the MnO_2 , and this should cause the resistance of the layers in question to fall. Thus the overall resistance of the $\text{Ta}|\text{Ta}_2\text{O}_5|\text{MnO}_2$ system at the $\text{Ta}_2\text{O}_5|\text{MnO}_2$ phase boundary, which may be considered as the algebraic sum of the above two resistances, should also pass through a minimum, though the rising branch of the curve should be less steep.

Let us now consider the variation in capacitance of the $\text{Ta}|\text{Ta}_2\text{O}_5|\text{MnO}_2$ system as the oxygen content of the MnO_2 is decreased. Clearly the cathodic polarisation of the MnO_2 should cause a regular expansion of the dielectric layer in the solid electrolytic capacitor by the inclusion of more and more reduced MnO_2 in this layer. This increases the distance between the plates of the capacitor and so reduces the capacitance of the $\text{Ta}|\text{Ta}_2\text{O}_5|\text{MnO}_2$ system. This effect agrees with our experimental observations (see Figs. 2 and 3). An analogous variation occurs in the $\text{Ta}|\text{Ta}_2\text{O}_5|\text{Ni}_2\text{O}_3$ system. In the $\text{Ta}|\text{Ta}_2\text{O}_5|\text{PbO}_2$ system the conductivity type of the PbO_2 does not change, and no extremal points are to be seen in the curves of Figs. 4 and 5. The insulating layer of stoichiometric Ta_2O_5 (or layer of p -type Ta_2O_5) forms at the $\text{Ta}_2\text{O}_5|\text{PbO}_2$ boundary much less easily than in capacitors of the $\text{Ta}|\text{Ta}_2\text{O}_5|\text{MnO}_2$ type, and this is evidently because the chemical potential of oxygen in lead dioxide prepared as above is lower.

SUMMARY

1. A study has been made of the dependence of electro-physical characteristics (capacitance, resistance, leakage current) of $\text{Ta}|\text{Ta}_2\text{O}_5|\text{MnO}_2$, $\text{Ta}|\text{Ta}_2\text{O}_5|\text{PbO}_2$ and $\text{Ta}|\text{Ta}_2\text{O}_5|\text{Ni}_2\text{O}_3$ solid electrolytic capacitors on the degree of conversion of the manganese dioxide, lead dioxide, and nickel oxide into lower oxides.
2. In $\text{Ta}|\text{Ta}_2\text{O}_5|\text{MnO}_2$ capacitors, as the manganese dioxide is converted into $\text{MnO}(\text{OH})$, the capacitance at first decreases slowly and then sharply; the resistance of the capacitor passes through a minimum and the leakage current through a maximum.
3. The capacitance of a $\text{Ta}|\text{Ta}_2\text{O}_5|\text{PbO}_2$ capacitor increases as the lead dioxide is converted into lower oxides, at first slowly and then more steeply; at the same time the resistance falls steeply and the leakage current increases considerably.
4. The capacitance of a $\text{Ta}|\text{Ta}_2\text{O}_5|\text{Ni}_2\text{O}_3$ capacitor at first increases as the Ni_2O_3 is reduced, but then falls rapidly; the resistance falls sharply at first and then slowly increases, while the leakage current passes through a maximum.
5. The thermo-e.m.f. of copper- MnO_2 and copper- Ni_2O_3 thermocouples was studied as a function of the oxygen content of these oxides. As this decreases, the type of their conductivity changes: in particular, n -type manganese dioxide passes into p -type $\text{MnO}(\text{OH})$, and n -type Ni_2O_3 passes into p -type NiO .
6. It has been suggested that the rectifying action in $\text{Ta}|\text{Ta}_2\text{O}_5|\text{MnO}_2$, $\text{Ta}|\text{Ta}_2\text{O}_5|\text{PbO}_2$, and $\text{Ta}|\text{Ta}_2\text{O}_5|\text{Ni}_2\text{O}_3$ capacitors is related to the formation, during anodic polarisation of the Ta , of an insulating layer of stoichiometric Ta_2O_5 or a layer of p -type Ta_2O_5 at the boundary between the Ta_2O_5 and the manganese dioxide, lead dioxide, or nickel oxide. The resistance of these layers depends on the content and bond strength of the oxygen in the oxides that are in contact with the Ta_2O_5 , and also on the type of their conductivity.

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DYNAMICS OF EXCHANGE ON EDE-10P ANION EXCHANGER AS A FUNCTION OF THE FLOW RATE WHEN THE SORPTION ISOTHERM IS CONCAVE

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We have made a detailed investigation of the dynamics of anion exchange on N-O and EDE-10P anion-exchangers, the main results of which were reported in a previous paper¹. The present paper deals with the dynamics of the exchange of bromide for nitrate ions as a function of the flow rate of the solution, under conditions such that the sorption isotherm is concave ($K > 1$), when there is a gradual broadening of the sorption front with time. This case has been examined from both theoretical²⁻⁴ and practical⁴ points of view. A concave sorption isotherm corresponds to displacement from the column of a strongly sorbed by a weakly sorbed ion, an example of which is the regeneration of an ion-exchange column⁴. In spite of the great practical importance of this process, comparatively little work has been done on the dynamics of ion exchange when the isotherm is concave. Our aim in the present work was to check experimentally some general theoretical relations which have been suggested to describe ion exchange under such conditions.

EXPERIMENTAL

An EDE-10P fraction having a grain diameter of ~ 0.038 cm was used, and the exchange constant for the system R-Br + NO_3^- was found, by the technique described previously¹, to be 1.23. The capacity was $S_m = 4.34$ mg-equiv. g⁻¹. Elution curves were obtained by the method described earlier¹. Columns of cross-section $Q_0 = 0.513$ cm² were filled with sorbent (saturated with bromide ions) and washed through with 0.075 M KNO_3 solution. The heights x of the layer of sorbent were 10, 13, 19.5, and 25.5 cm, corresponding to weights of ion-exchange resin of 1.5, 2, 3.0, and 4.0 g respectively. The flow rates V of the solution were 1, 2, and 3.3 ml min⁻¹. The ionic ratio was

$h = 0.055$. Fig. 1 shows the elution curves obtained in these experiments. The Table contains some data required for the subsequent calculations: $V_{0.50}$, $V_{0.15}$, and $V_{0.85}$, the volumes of effluent solutions corresponding to three concentration points on the elution curves; δV , the widths of the elution curves, equal to the differences $V_{0.15} - V_{0.85}$; and $x/V_{0.50}$, a measure of the rate of advance of the sorption front. The Table includes also some calculated results required for the subsequent discussion.

DISCUSSION

Both Fig. 1 and the Table show that the sorption front becomes broader as the bed height and the rate of flow of the solution increases, in conformity with a value of $K > 1$. The plots of x against V in Fig. 2 show that points in the front having $y = 0.85$ and 0.15 move at constant but different rates. Similar results were obtained² in a study of the exchange of potassium and sodium ions on KU-2 cation-exchange resin. In these experiments the exchange constant was 1.4 ($K > 1$). Fig. 3 shows that the width of the elution curves varies almost linearly with the bed height of the sorbent. Similar results have been obtained³ for the desorption of Ca^{2+} ions by hydrogen ions on KU-2. The width of the front was found³ to vary little with the flow rate. Under our conditions such variation is clearly evident, probably owing to the greater influence of kinetic factors in anion than in cation exchange. This fact is probably associated with the slower diffusion of anions compared with cations¹.

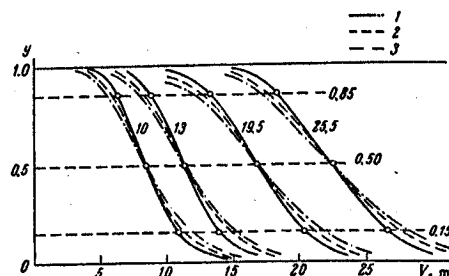


Fig. 1. Elution curves $y = f(V)$ for different bed heights of the sorbent $x = 10, 13, 19.1, 25.5$ cm and different volume flow rates V (ml min⁻¹): 1) 1; 2) 2; 3) 3.3.

TABLE. Calculation of dynamic parameters for the R-Br + NO_3^- system with a concave isotherm.

x , cm	V	$V_{0.85}$	$x/V_{0.85}$	$V_{0.50}$	$V_{0.15}$	δV	$\delta V/V_{0.50}$	ζ_{exp} , ml	ζ_{calc} , cm	Q_0 , cm ²	ΔV
10	1	84	0.119	63	110	47	26.8				
	2	83	0.120	59	114	55	36.4				
	3.3	83	0.120	55	119	64	49.4			0.43	
13	1	113	0.115	88	142	54	25.7	7	0.8		
	2	114	0.114	84	148	64	36.3	9	1.0		
	3.3	112	0.116	80	154	74	48.6	10	1.2	1.4	0.45
19.5	1	168	0.116	133	204	71	30.0	24	2.8		
	2	167	0.117	127	212	85	43.3	30	3.5		
	3.3	167	0.117	121	218	97	56.2	33	3.8	3.9	0.45
25.5	1	226	0.113	185	226	81	29.0	34	3.9		
	2	225	0.113	178	275	97	37.4	42	4.8		
	3.3	224	0.114	172	282	110	53.6	47	5.3	6.4	0.46