

from Bushmakin *et al.*¹² In the experimental treatment of the results the mean value of α was used, which for the concentration range investigated is 1.076.¹²

Fig.4 shows the experimental data and theoretical curves calculated from Eqn.(19). It is evident that the predicted S-shape of the kinetic curves is confirmed experimentally. There is quantitative agreement between the calculations and the experimental data.

SUMMARY

1. An equation has been obtained for the rate of attainment of a steady state in a rectification column (equation for the primary yield of the column under steady-state conditions).
2. The equation has been found to agree satisfactorily with experimental data.
3. An equation has been derived for the rate of attainment of a steady state in a column with stepwise variation of the concentration of the minor component in the feed mixture (transient conductivity function). In this case the kinetic curves have the more complicated S-shape.
4. The transient conductivity equation has been tested by distilling benzene-dichloroethane mixtures on a packed column. The equation agrees satisfactorily with experiment.

THE NATURE OF THE MAXIMUM ON DIFFERENTIAL CAPACITANCE CURVES

E. Shvarts, B. B. Damaskin,
and A. N. Frumkin

Curves showing the differential capacitance C as a function of the electrode potential ϕ , obtained in not too dilute solutions of inorganic acids and salts, have a characteristic maximum (hump)¹⁻⁵. The height and position of this maximum strongly depend on the nature of the anion and almost not at all on that of the cation. A common feature of the maxima observed with dilute solutions is that they all occur at potentials, close to the zero-charge point (z.c.p.), corresponding to a positive charge of the mercury surface, and that the height of the maximum decreases with increase in temperature.

Various theories have been proposed to explain the hump on the $C-\phi$ curves. Grahame⁶ believed that the maximum was associated with the formation on the mercury surface of a pseudocrystalline icelike layer, which "melts" both on increase in temperature and on increase in anodic polarisation. Watanabe and coworkers⁷ explained the hump on the $C-\phi$ curves by a minimum in the dielectric saturation of anions in the vicinity of the z.c.p., since under these conditions the polarisability of anions is a maximum, whereas at potentials distant from the hump the dielectric saturation is high. These authors suggested that the maximum is related to absolute electrode potential. Parsons⁸ pointed out that the maximum can be explained on the basis of Macdonald's theory⁹, if it is assumed that water molecules are at least partially oriented at the z.c.p. In this case it is necessary to assume that at the z.c.p. most of the water dipoles are oriented with their positive ends towards the electrode surface. This theory leaves open the question of the considerable increase in capacitance with increase in temperature at potentials more positive than that at the maximum. Finally, Watts-Tobin¹⁰ recently developed a theory of the electrical double layer according to which the hump on the $C-\phi$ curves in NaF solutions corresponds to the maximum effective dielectric constant of the water dipole monolayer, *i.e.* is related to the high polarisability of this layer at small positive surface charges. It is assumed that water dipoles at zero charge are oriented with their positive ends towards the metal, and when the potential is shifted towards positive values are reoriented with the formation of water molecule chains between anions and the metal surface. Further increase in capacitance with increase in positive polarisation is due to the appearance of a large number of dipoles formed by adsorbed mercury atoms and their mirror images in the metal phase.

The above theories do not provide a complete explanation of the nature of the maximum on differential capacitance curves and furthermore they involve certain inaccuracies. For example, Watts-Tobin's hypothesis¹⁰ of the existence of adsorbed mercury atoms on the liquid mercury surface is based on the experimental data of Grahame^{6,11} for NaF solutions, according to which there is a sharp rise in capacitance at potentials about 0.0 V with respect to the normal calomel electrode (n.c.e.). This result is contradicted by later capacitance measurements in 0.1 and 0.9 N NaF and CsF solutions¹², where there is no sharp rise in capacitance up to $\phi = 0.25$ V (n.c.e.). It is very probable that the rise in the $C-\phi$ curve observed by

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Institute of Chemistry and
Physicotechnical Institute at the
Lobachevskii Gorky State
University

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Grahame was associated not with the F^- ion but with the products of its interaction with glass. It is also impossible to agree with Watts-Tobin's assertion that the absence of maxima on $C-\varphi$ curves for KOH and K_2CO_3 solutions¹³ may be explained, by analogy with KI solutions, by specific adsorption of OH^- and CO_3^{2-} ions comparable with that of I^- .¹⁰

It was therefore of interest to continue the investigation of the maximum on $C-\varphi$ curves. For this purpose, in the present work we measured the capacitances of the electrical double layer in solutions of various salts at different temperatures.

EXPERIMENTAL

Method. The differential capacitance measurements were made by means of an impedance bridge, whose circuit has been described¹⁴. The frequency of the alternating current was 400 c/s in all experiments, the amplitude being 1.5 mV. The test electrode was a dropping mercury electrode symmetrically surrounded by a platinum cylinder which served as an auxiliary electrode. The time from the separation of the drop to bridge balance was determined by an electric stop watch PV-53L, which was automatically switched on and off by means of an electronic relay¹⁵.

For differential capacitance measurements at 25°, 50°, and 75°, the required temperature was maintained by circulating water from a thermostat through the measuring cell jacket. At 0° the cell was immersed in melting ice. The reference electrode was a normal calomel electrode at 20°, and in order to maintain a constant thermo-e.m.f., the electrolytic bridge was filled in all experiments (except for NaF) with 0.1 N KCl. The zero-charge points were determined under the same conditions by means of a streaming electrode with an accuracy of ± 1 mV. For KI and $K_4[Fe(CN)_6]$, the z.c.p. were calculated by the method of reverse integration¹⁶.

All the salts used were twice recrystallised from distilled water and, except for $K_4[Fe(CN)_6]$, ignited. Twice-distilled water was used to make up the solutions.

Results. We obtained $C-\varphi$ curves in 0.1 N solutions of KCl, KBr, KI, and $K_4[Fe(CN)_6]$ at 0°, 25°, 50°, and 75°. The data for 0° and 75° are shown in Fig. 1⁷. Fig. 2 compares the $C-\varphi$ curves for 0.1 N KCl at different temperatures. It is seen that the maximum is most pronounced in KCl and $K_4[Fe(CN)_6]$ at 0°, and gradually disappears with increase in temperature. On the other hand, capacitance measurements in 0.1 N solutions of LiCl, KCl, and CsCl at 0° show that the height and position of the maximum is practically independent of the nature of the cation. The disappearance of the maximum on increase in temperature and its negligible dependence on cations agrees with the literature data^{4,6,17}.

DISCUSSION

Let us consider what factors can in general result in the appearance of a hump on differential capacitance curves. For this purpose, we shall introduce the following notation:

† At 75° $K_4[Fe(CN)_6]$ undergoes irreversible decomposition in solution and as a result the $C-\varphi$ curves obtained under these conditions are not comparable with those at 0°, 25°, and 50°.

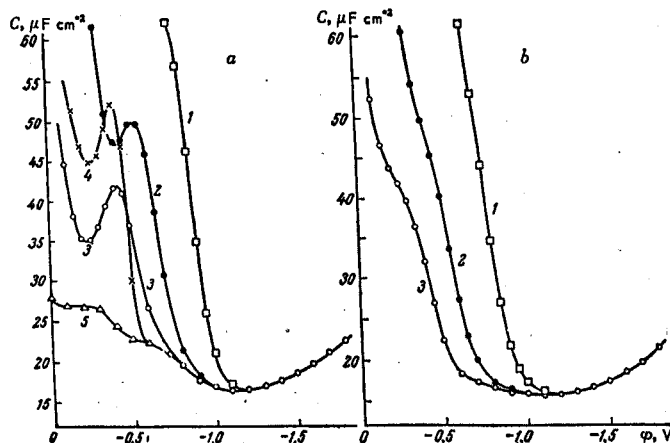


Fig. 1. Differential capacitance curves for 0.1 N solutions: 1) KI; 2) KBr; 3) KCl; 4) $K_4[Fe(CN)_6]$; 5) NaF; a) 0°; b) 75°.

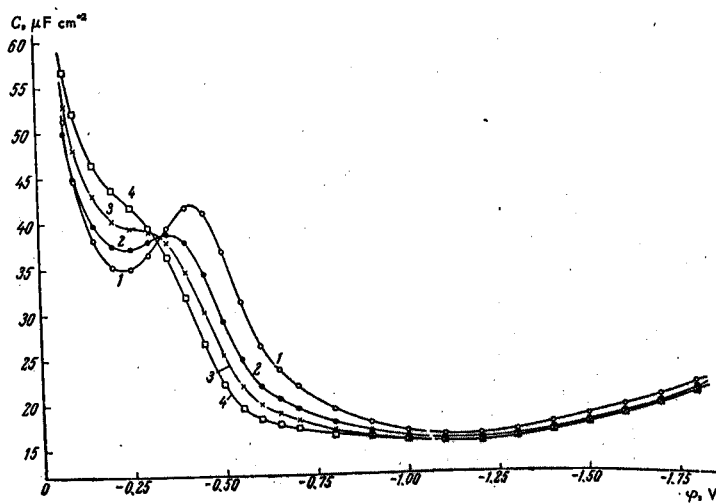


Fig. 2. Differential capacitance curves for 0.1 N KCl: 1) 0°; 2) 25°; 3) 50°; 4) 75°.

φ_a is the potential in relation to the z.c.p. in the given solution, ξ the zero-charge potential corresponding to that orientation of water dipoles which obtains at the given potential φ_a [thus $\xi = f(\varphi_a)$, and when $\varphi_a = 0$, we have $\xi = 0$], and K_0 the true integral capacitance defined by the equation

$$\epsilon = K_0 (\varphi_a - \xi), \quad (1)$$

where ϵ is the charge on the electrode surface given by

$$\epsilon = \int_0^{\varphi_a} C d\varphi. \quad (2)$$

By definition of differential capacitance, we obtain from Eqn. (1)

$$C = \frac{\partial \sigma}{\partial \varphi} = \frac{\partial K_0}{\partial \varphi} (\varphi_a - \xi) + K_0 \left(1 - \frac{\partial \xi}{\partial \varphi}\right), \quad (3)$$

whence

$$\frac{\partial C}{\partial \varphi} = 2 \frac{\partial K_0}{\partial \varphi} \left(1 - \frac{\partial \xi}{\partial \varphi}\right) + \frac{\partial^2 K_0}{\partial \varphi^2} (\varphi_a - \xi) - K_0 \frac{\partial^2 \xi}{\partial \varphi^2}. \quad (4)$$

The presence of a hump on the $C-\varphi$ curves (*i.e.* of the region where C decreases with increase in the positive value of φ) is in the general case due to a negative value of $\partial C/\partial \varphi$.

It is reasonable to suppose that $\partial K_0/\partial \varphi \geq 0$ and also that $|\xi/\varphi_a| < 1$ and $|\partial \xi/\partial \varphi| < 1$. It is evident from Eqn. (4) that in these conditions the appearance of a region in which $\partial C/\partial \varphi < 0$ may be explained either by a negative value of $\partial^2 K_0/\partial \varphi^2$ or a positive value of $\partial^2 \xi/\partial \varphi^2$. In order to establish to what extent the shape of the $C-\varphi$ curves may be determined by the nature of the variation of K_0 with φ , we calculated the formal integral capacitances K in 0.1 *N* solutions of KCl, KBr, KI, and $K_4[\text{Fe}(\text{CN})_6]$ at 0°, 25°, 50°, and 75° according to the formula

$$K = \frac{\sigma}{\varphi_a}, \quad (5)$$

and also the integral capacitances of the dense layer K_h in NaF solutions at 0° and 25° according to the formula

$$K_h = \frac{\sigma}{\varphi_a + \psi_1}, \quad (6)$$

where ψ_1 is the potential of the outer Helmholtz plane, defined in the kinetic theory of the diffusion layer¹³. The magnitude of the charge in Eqns. (5) and (6) is found by numerical integration of the differential capacitance curves according to Eqn. (2).

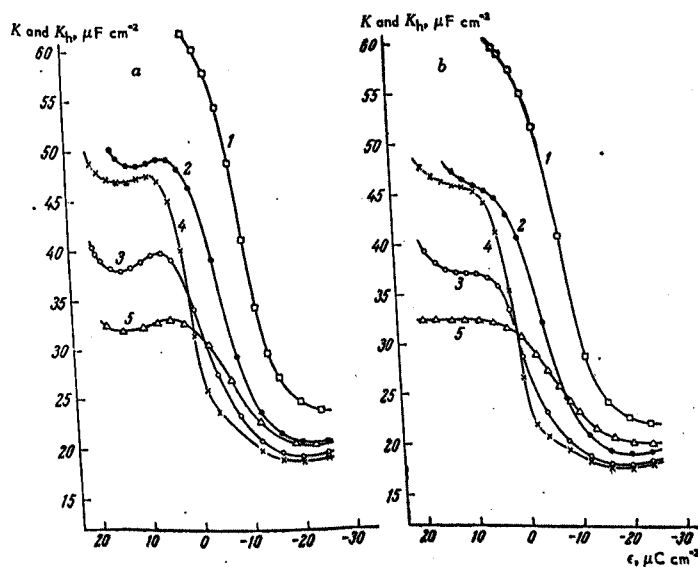


Fig. 3. Integral double layer capacitance curves for 0.1 *N* solutions: 1) KI; 2) KBr; 3) KCl; 4) $K_4[\text{Fe}(\text{CN})_6]$; 5) integral dense double layer capacitance curve for NaF solution; a) 0°; b) 25°.

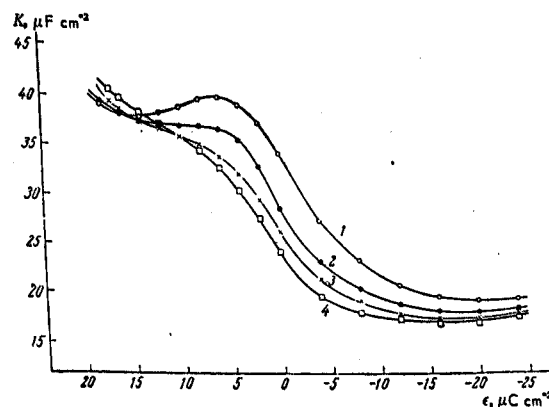


Fig. 4. Integral double layer capacitance curves for 0.1 *N* KCl: 1) 0°; 2) 25°; 3) 50°; 4) 75°.

The variation of K and K_h with ϵ is shown in Figs. 3 and 4. It is seen from the data obtained that the maxima on the $K-\epsilon$ and $K_h-\epsilon$ curves are absent for all the anions investigated when $t \geq 25^\circ$. Regions of adsorption of cations and anions as well as a transition region can be observed on the $K-\epsilon$ curves at 25°. It may be assumed that the region of adsorption with an approximately constant integral capacitance corresponds to a structure of the electrical double layer in which anions are partially hydrated on the solution side, whereas the subsequent rise in capacitance at high positive polarisations corresponds to complete dehydration of the anions. It is in these conditions that the double layer capacitances are closely related to the solubility of the corresponding mercury salts⁵. On increase in temperature, the link between ions and the hydrate shell weakens, the $K-\epsilon$ curve showing a continuous transition from the region of cation adsorption to one where completely dehydrated anions are adsorbed.

However, this interpretation of the variation of the double layer capacitance with the electrode potential (or its charge) is incomplete since at 0° there are four maxima on the $K-\epsilon$ and $K_h-\epsilon$ curves (Fig. 3a). The hump on integral capacitance curves in the presence of specifically adsorbed ions becomes even more pronounced if the charge is plotted not against the integral capacitance but against a capacitance K_h' , formally defined by the equation

$$\frac{1}{K_h'} = \frac{1}{K} - \frac{1}{K_d}, \quad (7)$$

where K_d is the integral capacitance of the diffusion layer. We have calculated the variation of K_h' with ϵ by the Grahame-Soderberg method¹⁹ from differential capacitance data in 0.053 and 0.15 *N* KCl solutions at 0° (Fig. 5). In view of the maxima on the $K-\epsilon$, $K_h-\epsilon$, and $K_h'-\epsilon$ curves, the humps on the differential capacitance curves cannot be entirely explained by a change in the formal integral capacitance according to the equation

$$C = K + \varphi_a \frac{\partial K}{\partial \varphi}, \quad (8)$$

by analogy with adsorption maxima on $C-\varphi$ curves obtained in solutions containing various organic substances^{2,18}. It follows from Eqns. (1) and (5) that

$$K = K_0 \left(1 - \frac{\xi}{\varphi_a}\right). \quad (9)$$

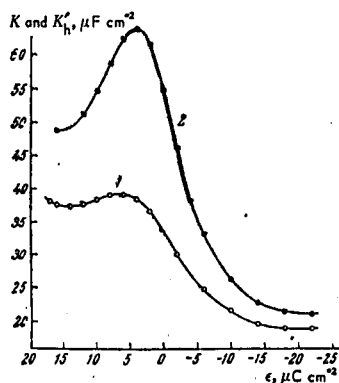


Fig. 5. Integral capacitance curves for 0.1 N KCl at 0°: 1) overall integral capacitance; 2) integral capacitance calculated from Eqn. (7).

Hence

$$\frac{\partial K}{\partial \varphi} = \frac{\partial K_0}{\partial \varphi_0} \left(1 - \frac{\xi}{\varphi_a}\right) + \frac{K_0}{\varphi_a^2} \xi - \frac{K_0}{\varphi_a} \frac{\partial \xi}{\partial \varphi}. \quad (10)$$

The maxima on the $K-\epsilon$ or $K-\varphi$ curves, *i.e.* the regions with negative values of $\partial K/\partial \varphi$, indicate either a negative value of ξ at positive φ_a ,¹⁰ or a positive value of $\partial \xi/\partial \varphi$, and in any case require the hypothesis that the orientation of water molecules changes.

According to Watts-Tobin¹⁰, the negative value of $\partial C/\partial \varphi$ is mainly due to the term $\partial^2 K_0/\partial \varphi^2 < 0$ and apparently to the positive value of $\partial^2 \xi/\partial \varphi^2$ at $\xi < 0$ [see Eqn. (4)] corresponding to complete reorientation of water molecules. However, another interpretation of the maxima on differential capacitance curves is possible, based on the assumption that water dipoles are oriented with the negative ends towards the electrode surface at the z.c.p. and that the values of ξ , $\partial \xi/\partial \varphi$, and $\partial^2 \xi/\partial \varphi^2$ are positive when $\varphi_a > 0$. We shall now examine in greater detail the interpretation which assumes a change in the orientation of adsorbed water dipoles when specifically adsorbed anions enter the electrical double layer.

Comparison of Figs. 3a and 5 shows that the maximum on the $K_h'-\epsilon$ curve in KCl solution at 0° is much higher than the analogous maximum on the $K_h-\epsilon$ curve in NaF solution also at 0°. According to Grahame²⁰, the capacitance of the dense layer (both differential and integral), which is related to the electronic surface charge (*i.e.* the capacitance when the charge ϵ_1 due to specifically adsorbed anions is constant), is to a first approximation independent of ϵ_1 and the same for different anions. Consequently, the considerable difference between the $K_h-\epsilon$ and $K_h'-\epsilon$ curves for NaF and KCl solutions respectively at 0° is due in the first place to the considerable specific adsorption of the Cl^- anions. On the other hand, the presence of a weak maximum on the $K_h-\epsilon$ curve in the NaF solution at 0° may possibly be due to the low specific adsorption of the F^- anion at this relatively low temperature, at 25° the specific adsorption of F^- being completely absent as a result of which there is no maximum on the

$K_h-\epsilon$ curve (Fig. 3b). This fact justifies the postulate that the orientation of water dipoles in the electrical double layer changes with specific adsorption of anions.

Fig. 6 shows the variation of the differential capacitance, due to cations (C_+) and anions (C_-), with the electrode potential, which we calculated by the Grahame-Soderberg method¹⁹ for 0.1 N KCl solution at 0° from differential capacitance data for 0.053 and 0.15 N KCl solutions. It is evident that in the potential range between -0.2 and -0.4 V (n.c.e.) the $C_- - \varphi$ and $C_+ - \varphi$ curves have inflections which correspond to arrests in the adsorption of Cl^- ions on increase of positive polarisation, this in turn resulting in a decrease of the total differential capacitance and hence in an appearance of a hump on the $C-\varphi$ curves. An arrest in the adsorption of anions is also possible when the shift of the potential towards positive values is partly due to a change in the orientation of dipoles (in this case water) in which the positive end is turned towards the electrode surface ($\xi > 0$). A similar phenomenon is well known in the case of oxygen adsorption on the surface of a platinum electrode²¹. However, in the case of a mercury electrode such adsorption of water dipoles is prevented by the positive surface charge. On the other hand, an arrest in the adsorption of anions on increase in positive polarisation may also be due to a decrease in the number of water dipoles adsorbed at the z.c.p. with the negative end turned towards the mercury surface; the inequality $\xi > 0$ will obviously hold in this case too. Such an effect is possible in the adsorption of anions having a sufficiently high polarising power (capable of forming a hydration shell), as is evident from the schematic diagram in Fig. 7. Thus in order that there may be an arrest in the adsorption of anions with increase in positive polarisation, and hence that a maximum may appear on the double layer capacitance curves, two conditions are necessary in the given case: (1) hydration of the anion and (2) its incorporation in the dense part of the electrical double layer (*i.e.* specific adsorption as defined by Devanathan²²).

The adsorbability of anions increases in the series from F^- to I^- , but their polarising power (capacity for hydration) decreases, as a result of which the height of the

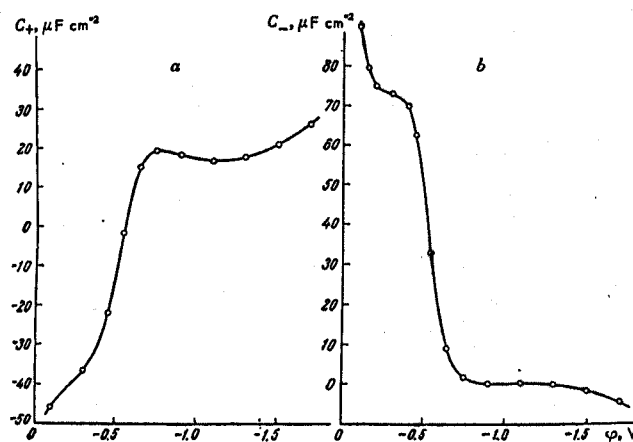


Fig. 6. Differential capacitance curves for 0.1 N KCl at 0°: a) due to cations; b) due to anions.

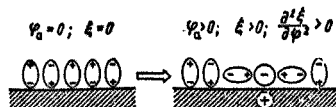


Fig. 7. Change in the orientation of water dipoles in the electrical double layer on adsorption of an anion.

hump on the $C-\varphi$ curves passes through a maximum. Indeed, in the case of the F^- ion, despite its extensive hydration, the adsorbability is low and the small hump on the $K_h-\epsilon$ curves occurs only at 0° , a small amount of the F^- ions being able to penetrate the dense layer at this temperature. In the case of the I^- anion, on the other hand, the adsorbability is high but the capacity for hydration is low, so that even at 0° there is no hump on the $K-\epsilon$ and $C-\varphi$ curves. In the presence of Cl^- anions, which have fairly high adsorbability and polarising power, the maxima on the double layer capacitance curves are quite pronounced.

The $[Fe(CN)_6]^{4-}$ anion possesses appreciable adsorbability at positive surface charges, which, however, decreases sharply on passing through the z.c.p. because of the high negative charge of the anion. On the other hand, the anion is strongly hydrated. As a result, the hump on the $C-\varphi$ curves for $K_4[Fe(CN)_6]$ is particularly high. Capacitance measurements for $1 N K_4[Fe(CN)_6]$ reveal a high ($C_{max} = 59.0 \mu F cm^{-2}$) and relatively narrow maximum; at the potential of the maximum a polarisation resistance of $0.31 \Omega cm^2$ is observed, and apparently corresponds to a change in the structure of the electrical double layer following incorporation of the $[Fe(CN)_6]^{4-}$ anions.

Increase in temperature reduces the extent of hydration of the ions as well as their adsorbability on the mercury surface. Since according to our ideas both these factors lead to a reduction of the arrest in the adsorption of anions when positive polarisation is increased, it is to be expected that higher temperatures should result in the disappearance of the hump on the double layer capacitance curves. The present and literature^{6,17} data are consistent with this conclusion. However, we believe that the final explanation of the hump on the $C-\varphi$ curves will only be possible after numerous experimental data have been accumulated on differential capacitance curves for different non-aqueous solvents.

SUMMARY

1. Differential capacitance curves have been obtained for $0.1 N$ solutions of KCl , KBr , KI , and $K_4[Fe(CN)_6]$ at 0° , 25° , 50° , and 75° , and for $0.1 N NaF$ solution at 0° and 25° . Zero-charge potentials have been determined for all the above solutions and the integral capacitances have been calculated as a function of the electrode charge.
2. The variation of the maxima on the $C-\varphi$ curves with change in the integral double layer capacitance has been examined. It has been shown that, in order to explain the maxima on the integral capacitance curves, it is necessary to postulate a change in the orientation of water molecules in the double layer.

3. The possibility has been examined of a change in the orientation of adsorbed water molecules on incorporation into the dense double layer of anions possessing fairly high polarising power, on the assumption that at the zero-point charge these dipoles are oriented with their negative ends towards the mercury surface.

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Lomonosov Moscow
State University

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NERNST'S HEAT THEOREM AND THE SECOND LAW OF THERMODYNAMICS

V.N.Masyukov

Ever since Nernst's discovery of his theorem attempts have been made to derive it from the second law of thermodynamics. Thus Vukalovich and Novikov write: "The unattainability of the absolute zero of temperature follows also from the second law of thermodynamics...".¹ To prove this postulate, they consider a Carnot cycle in which $T_2 = 0$ and $S = S_0 = \text{const}$ (Fig.1). Since the lower isotherm