U.D.C. 541.113;541.135

Heat Capacity of Aqueous Solutions of Electrolytes

V.A.Latysheva

The present review deals with studies of the heat capacity of aqueous solutions of electrolytes. The material has been selected to show the extent to which the studies which have been carried out reveal the relationship between the heat capacity of the solutions and their internal chemical character, with reference to the dependence of the heat capacity of solutions on their structure, the hydration and hydrolysis of ions, the formation of acido-complexes, etc. Some promising possibilities provided by the study of the heat capacity of aqueous solutions of electrolytes have been noted. The bibliography contains 264 references.

CONTENTS

I. Introduction	803
II. Some theoretical ideas	803
III. Partial molar heat capacities of electrolytes at infinite dilution $\overline{C}^0_{p_2}$	806
1. Experimental determination of $\overline{C}^0_{p_2}$	806
2. Semi-empirical methods for separating $\overline{C}^0_{p_2}$ into ionic components $\overline{C}^0_{p_i}$ and the calculation of $\overline{C}^0_{p_i}$ for different temperatures	807
IV. The relation of the heat capacity of solutions to the various types of reaction occurring in them	809
1. Heat capacity and the hydration of ions	809
2. Heat capacity and the hydrolysis of ions	811
3. Heat capacity and the formation of acido-complexes	813
4. Change in heat capacity on the formation of ternary and multi-component solutions	814
5. Sharp change in heat capacity within narrow ranges of temperature and concentration	814
6. Heat capacity of activation	815
V. Heat capacity at constant volume C_v	816

I. INTRODUCTION

The study of the heat capacity of aqueous solutions of electrolytes is being initiated in various spheres of theoretical and practical research. In the period 1960–1971, heat capacity was studied in connection with the development of efficient adsorption refrigerating machines [1], the technology of wet spinning [2], methods of distilling and processing sea water [3–8], and the rationalisation of the production of alumina [9–17] and other materials [18–28]. In most of the works cited, narrow problems of a practical character were resolved, but an incomparably greater number of studies were aimed at determining the relationship between heat capacity and the nature of solutions. This tendency is natural, since the search for general regular features, directed in the final analysis towards the development of a theory of solutions, should be much more effective than utilitarian studies in leading to the rapid elimination of the marked inadequacy of data on the heat capacity of solutions, which makes itself felt everywhere—from the non-ferrous metal industry [29] to the study of the functions of nucleic acids [30].

II. SOME THEORETICAL IDEAS

Essentially no development of fundamentally new theories of the heat capacity of solutions has taken place in recent years. We can only say that attempts have been made to develop, verify, or discuss the theoretical ideas previously put forward by Born [31] and Webb [32], Everett and Wynne-Jones [33], Everett and Coulson [34], Eley [35], Frank and Evans [36], Frank and Wen [37], Eucken [38–40], Kapustinskii [41,42], and others.

The application of the Born–Webb theory invariably encounters difficulties, associated with the fact that this theory does not take account of the molecular nature of the solvent [35,43–48]. Thus for example it has been shown convincingly [43,44] that the equation for the dependence of the partial molar heat capacity of ions at infinite dilution $\overline{C}^0_{p_2}$ on the radius of the ion:

$$\overline{C}^0_{p_2} = f_1\left(\frac{e^2}{r}\right) + f_2(e) \qquad (1)$$

where e is the charge and r the radius of the ion, derived by Kapustinskii [41,42] using only the Born equation, does not show even qualitative agreement with experiment. The slope of the theoretical curve is the opposite of that observed experimentally. Agreement with experiment can be obtained only by taking account of "the effect of the long-range action of ions on water, which should be negative and should increase with increase in the ionic radius and with increase in the complexity of the configuration of the ion" [43]. Eqn.(1) should then be replaced by:

$$\overline{C}^0_{p_2} = f_1\left(\frac{e}{r}\right)^2 + f_2(e) + f_3(r\varkappa), \qquad (2)$$

where $\varkappa$ is a coefficient characterising the configuration of the ion.

At the present time the Born–Webb theory is sometimes used only as a means of estimating the electrostatic components of the thermodynamic characteristics of ions in solution. The use of this method in practice is based on the need to know the effective dielectric constant of water in solutions, and its derivatives with respect to temperature. Thus some authors start from the converse;

they use some independent method of estimate these electrostatic components, and then calculate the effective dielectric constant and its derivatives[49]. In the case of heat capacity, compressibility, and thermal expansion, however, the attempts to carry out these estimates appear unsuccessful, partly because of the lack of accurate data[49], but chiefly because of the complexity of the interpretation of these properties[45,46]. The significant correction which was introduced into the electrostatic theory by Everett and Coulson[34] and which takes account of the unique state of the water molecules closest to the ion, did not lead to agreement with experiment[34,45]. Conway and coworkers[45] showed that the change in heat capacity ΔC associated with the effect of the restriction of the liberations of the water molecules closest to the ion is relatively small in magnitude and has the same sign as the change in entropy ΔS in the corresponding process, and that ΔC and ΔS should change in the same sense on going from one system to another. At the same time the order of change in the values of $\bar{C}_i^0$ for the ions of the alkali and alkaline earth metals and the halogens, and also the values of ΔC_V (the changes in heat capacity at constant volume) for the ionisation of methylammonium ions, obtained from the experimental data, are opposite to the corresponding orders for $\bar{S}_i^0$ and ΔS, and the signs of the quantities $\bar{C}_i^0$ and ΔC may be the opposite of the signs of $\bar{S}_i^0$ and ΔS (Fig.1). On this basis, Conway and coworkers[45] exclude the effect indicated by Everett and Coulson from the factors determining the magnitude of $\bar{C}_{pi}^0$ and give preference to the influence of ions on the structure of water. They assume that the positive values of $\bar{C}_{pi}^0$ for cations and the negative values for anions may be due to the structure-forming influence of cations and the destructive influence of anions.

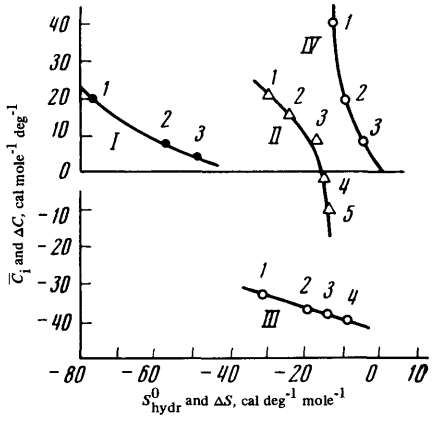


Figure 1. Comparison of the partial g-ion heat capacity of monatomic ions $\bar{C}_i$ (curves I–III) and the change in heat capacity in the protolytic dissociation of alkylammonium ions ΔC (curve IV) respectively with the entropy of hydration of the monatomic ions S^0_{hydr} and the change in entropy ΔS in the protolytic dissociation: I) Mg^{2+} (*1*), Ca^{2+} (*2*), Ba^{2+} (*3*); II) Li^+ (*1*), Na^+ (*2*), K^+ (*3*), Rb^+ (*4*), Cs^+ (*5*); III) F^- (*1*), Cl^- (*2*), Br^- (*3*), I^- (*4*); IV) $(CH_3)_3NH^+$ (*1*), $(CH_3)_2NH_2^+$ (*2*), $(CH_3)NH_3^+$ (*3*).

It should however be noted that Conway and coworkers use the values of $\bar{C}_{pi}^0$ on Eucken's scale, without justifying its use in preference to other scales. It is quite possible that scales in which the values of $\bar{C}_{pi}^0$ for cations are not positive but negative will prove more correct (this will be discussed later). Moreover, the changes in the opposite sense noted by the authors cited for $\Delta\bar{S}_i^0$ and $\bar{C}_{pi}^0$ may indicate merely that the effect of partial freezing of the degrees of freedom of the water on hydration overlaps the effect of change in structure, but not complete absence of the first effect.

In order to reveal the existence of the first effect, it is necessary to compare the heat capacities of ions not within the vertical groups of the periodic system but along the horizontal periods of elements with similar steric and electrostatic parameters (d or f elements). This approach has been made by a number of authors[50-55]. Study of the heat capacity of aqueous solutions of the perchlorates of the 3d metals (Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn) showed that the values of $\bar{C}_p^0$ for these electrolytes, on going from one ion to another, change in the same sense as the values of ΔH, ΔG, and ΔS for the hydration of the cations (Fig. 2).[50-53] Thus the strength of binding of water by the ions still has significant importance for the heat capacity. The study of the heat capacity of solutions of salts of the rare earth elements led to similar conclusions[54,55]. The concept of the influence of ions on the structure of water has attracted the greatest attention from research workers[35-37,56-58]. In particular, the ideas of Frank and coworkers[37] on the cluster structure of water and solutions have provided the basis for several recent theoretical and experimental studies[59-70]. Nemethy and Scheraga[59] suggest that the water molecules inside the clusters, on the surface, and outside the clusters differ from one another in the number of hydrogen bonds which they form and in the changes which they bring about in the vibrational spectrum of water. On the basis of this premise, Nemethy and Scheraga developed a statistical method for calculating the concentration and size of the water clusters and the thermodynamic properties of water from data on the vibrational spectra. The calculations do not show complete agreement with experiment for pure water (the method has not been used for aqueous solutions of electrolytes); in the opinion of Vand and Senior[60], this is due to underestimating the number of straight and branched chains in the structure of water. Attempts have been made to develop a theory of aqueous solutions of electrolytes from the semi-empirical theory of Eucken[38-40,71,72], based on the view that in solutions an equilibrium is established between monomers, dimers, tetramers, and octamers of water molecules and hydrated ions. Wicke compared new experimental data on the heat capacity of aqueous solutions of a number of alkali metal halides, alkylammonium salts, and aliphatic acids and their salts at temperatures in the range 0–130°[61,73] with the results of studies of other properties of the solutions carried out by different authors, and concluded that Eucken's theory is inadequate and that it is necessary to take into account the existence, in water and aqueous solutions, of structural units of the "flickering cluster" type, in Frank's terminology[37]. However, in the opinion of Wicke (and many others[46,61,74-76]) Frank's two-structure model is inadequate for a satisfactory description of the heat capacities of solutions. Wicke puts forward the so-called combined model of the structure of water, which as it were combines elements of the models of Eucken and Frank.

On the basis of this model, Wicke[61] and Rueterjans and coworkers[69] put forward an explanation of the form of the

temperature dependence of $\bar{C}_p^0$ for a number of simple halides (the existence of a maximum at temperatures in the range 50–90°) and the characteristic features of the heat capacity of solutions of tetra-alkylammonium halides ($\Phi C > 0$).

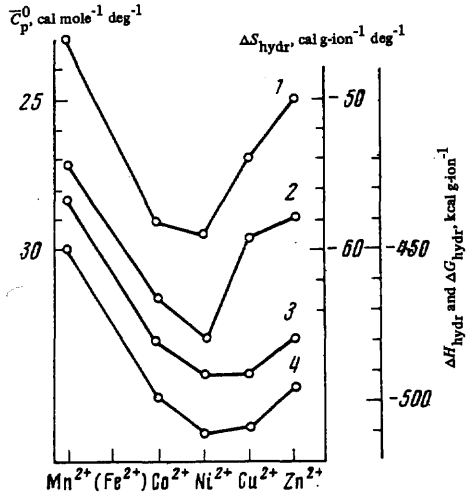


Figure 2. Comparison of the values of $\bar{C}_p^0$ for the perchlorates of the 3*d* metals (*1*) with the entropy ΔS_{hydr} (*2*), free energy ΔG_{hydr} (*3*), and enthalpy ΔH_{hydr} (*4*) of hydration of the corresponding cations.

The theoretical studies of Lovett and Ben-Naim [77], devoted to solutions of the inert gases in water, have proved of interest in the elucidation of the nature of the structure-forming influence of the non-polar parts of electrolytes on water. The one-dimensional model of aqueous solutions of the inert gases put forward in the work cited, and statistical calculations using this model, lead to the unambiguous conclusion that the introduction of inert gas molecules into heavy water (D_2O) should lead to less stabilisation of the structure than their introduction into ordinary water (which is less structured than heavy water). This difference is in fact observed and is based on the fact that (according to the model) the inert gas can stabilise the structure only when the water contains open cavities into which the gas can penetrate. The less structured water has more of these cavities.

Krestov and coworkers [78,79] approached the problem of heat capacity from the viewpoint of the theory of positive and negative hydration, developed by Samoilov [80]. Like Noyes [49], Krestov and coworkers [79] assume that the change in heat capacity accompanying the hydration of ions ΔC_p hydr can be broken down into two parts, one of which, ΔC_{pI}, is not related to the electrostatic parameters of the ion and is equal to the effect of the hydration of an inert gas atom having the same radius as the ion, whereas the other, ΔC_{pII}, depends on the nature of the effect of the electrostatic field of the ion on the structure of the surrounding water. Arguing within the framework of Samoilov's theory, the authors cited represent the quantity ΔC_{pII} as resulting from the partial compensation of two effects of the influence of ions on water: 1) the orientation of the nearest molecules in the field of the ion, and 2) the breakdown of the bonds between further-removed water molecules. The first effect should be accompanied by a decrease in heat capacity as a consequence of the decreased mobility of the molecules, and the second should be accompanied by an increase, since the water molecules become more mobile. Since the first effect predominates for ions with positive hydration, and the second effect predominates for ions with negative hydration, it is to be expected that for the former $\Delta C_{pII} < 0$, whereas for the latter $\Delta C_{pII} > 0$. The results of calculations carried out by Krestov and Klopov [79] confirm these suggestions, but they contradict the widely held opinion that the rupture of bonds in the structure of water should lead not to an increase in heat capacity but to a decrease; this is confirmed by the experimentally observed decrease in the values of $\bar{C}_p^0$ for alkali and alkaline earth metal salts and for the halides of the sub-groups with increase in the size of the ions [43,81]. On examination it was found that the contradiction was due to errors in the calculation of ΔC_{pI}, [79] carried out using data on the solubility of the inert gases in water [82]. The correct calculation leads to positive values of ΔC_{pI}, which within the limits of error are the same for all the inert gases (~40 cal mole^{-1} deg^{-1}) and to values of $\Delta C_{pII\,corr}$ which in all cases are negative and decrease with increase in the size of the ions in the sub-groups (column 4 of Table 1).

Table 1. Values of ΔC_{pI} and ΔC_{pII} for various ions (cal g-ion^{-1} deg^{-1}).

Ion	ΔC_{pI} [79]	ΔC_{pII} [79]	$\Delta C_{pII\,corr}$ (for $\Delta C_{pI} = 40$)
Li^+	−4.8	−3.7	−48.5
Na^+	−17.8	+4.1	−53.7
K^+	−25.2	+5.8	−59.4
Rb^+	−35.0	+14.8	−60.2
Cs^+	−48.6	+27.6	−60.8
Mg^{2+}	−18.4	−23.5	−81.9
Ca^{2+}	−25.6	−18.1	−83.7
Sr^{2+}	−39.6	−8.0	−87.6
Ba^{2+}	−49.2	−1.7	−90.9
F^-	−15.2	−3.3	−58.5
Cl^-	−23.6	+4.8	−58.8
Br^-	−37.8	+17.6	−60.2
I^-	−47.9	+27.1	−60.8

If in addition we take account of the tendency, noted by some authors (see, for example, Ref. 82), for ΔC_p to increase from He to Xe, we obtained an even greater decrease in ΔC_{pII} with increased size of the ions in each sub-group.

This result confirms the view [43,83] that Samoilov's theory does not provide an understanding of the heat capacity of solutions, since "the thermostatics of solutions is related not to fluctuations in the structure, produced by the translational movements of the molecules, but to the average statistical characteristics of the systems".

The results of theoretical studies of the influence of the concentration of an electrolyte on $\bar{C}_p^0$ (in the range of medium and high concentrations) have been published by Mikulin (p. 44 of Ref. 23). In Mikulin's opinion, the nature of the dependence of the partial molar heat capacity of the electrolyte on concentration in concentrated solutions is determined by the form of the concentration dependence of the so-called electrostatic component of the free energy of the solution G^{el}. The latter is related to "the nature and magnitude of the electrostatic forces" (the interaction of the ions and the polarisation of the water molecules) which

lead to the formation of the "ionic atmosphere" and bring about a change in the properties of the solvent close to the ion" (p. 49 of Ref. 23). It has the form:

$$G^{el} = -RTm(a + b\sqrt{c}) \quad (3)$$

where C is the molarity of the electrolyte, and a and b are constants which are characteristic of each electrolyte and which depend on temperature and pressure.

An extremely interesting feature of Mikulin's approach is the model of the hydrated ion, which takes account of the possibility that around the primary hydrated ion there is a layer of water molecules for which the dielectric constant value is greater than that for pure water (p. 126 of Ref. 23). The magnitude of the increase in the dielectric constant of this layer depends on the individual nature of the ions, and this is responsible for the specific character of the values of a and b in the equation for concentrated solutions. This unique layer is limited to a distance of 10–12 Å from the centre of the ion, so that in the range of highly dilute solutions it does not determine the form of the concentration dependence of G^{el}, which becomes the same for all electrolytes of the same valency type, in accordance with the Debye–Hückel theory.

Mikulin's theory has been critically reviewed[43]. The work cited also summarises the theoretical ideas previously developed by Mishchenko and coworkers on the factors determining the concentration and temperature dependence of the partial molar heat capacities of water and electrolytes in solution.

Drakin and coworkers[84] suggested that there is a linear relationship between the heat capacity of the hydration of ions ΔC_h on the one hand and the charge of the ion z and its hydrate coordination number n on the other

$$\Delta C_h = -Azn, \quad (4)$$

where A is a proportionality coefficient, the magnitude of which is determined empirically, and ΔC_h is the difference between the partial molar heat capacity of the ion at infinite dilution and the heat capacity of the ion in a vacuum.

This dependence is based on the idea that each of the n water molecules surrounding the ion can be bound by hydrogen bonds to two other molecules and hence can act as the starting point for a chain of hydrogen-bonded water molecules. The ion, which possesses a charge, will influence the vibrations of the chain. The total effect of the ion should be proportional to nz. This idea is attractive for its simplicity, and at first sight it might seem to provide a basis for a new method for determining the coordination numbers of ions in solution. As shown below, however, not all of the ions studied by these authors[84-87] obey this relationship, and the authors themselves conclude that it is only approximate[87]. We doubt whether all the change in heat capacity when ions pass into solution can be attributed to the formation of the hydration sheaths of the ions.

The results of these theoretical studies show clearly that the heat capacity of solutions is sensitive to the most varied characteristics of the interaction between the components of solutions. Thus in order to develop a general theory it is necessary first of all to accumulate sufficiently extensive and reliable experimental data on the relationship between heat capacity and the various forms of interaction in solution, such as the hydration of ions, their association, their action on the structure of water, hydrolysis, complex formation, etc.

Data on the partial molar heat capacities of electrolytes in highly dilute solutions are of exceptional importance for the development of the theory.

III. THE PARTIAL MOLAR HEAT CAPACITIES OF ELECTROLYTES AT INFINITE DILUTION $\bar{C}^0_{p_2}$

1. Experimental Determination of $\bar{C}^0_{p_2}$

The values of $\bar{C}^0_{p_2}$ are usually determined by extrapolating the apparent molar heat capacities of the electrolyte ΦC_{p_2} to zero concentration. For this extrapolation to be successful, the experimental data on the specific heat capacity of the solutions c_p should be as accurate as possible[88].

In recent years there has been an increase in the number of laboratories in which precision heat capacity measurements are being made. There has been an increased number of materials for which accurate c_p values have been obtained for the first time or for which earlier inaccurate values have been accurately determined[84-87,89-128]. Only a few papers[106], however, cover the range of solutions with concentrations less than 0.1 m. This means that the values of $\bar{C}^0_{p_2}$ obtained by extrapolation are still unreliable, since at lower electrolyte concentrations a change in the slope of the plot of ΦC_{p_2} against $\sqrt{m}$ is still quite possible[43,51,53,87,113,118,119,122,129].

Parker[130] proposed a way out of situations of this kind; in this approach, the slope for very dilute solutions is calculated from the Debye–Hückel theory, after which the ordinate of the initial point of the calculated section is determined by assuming that the change from the calculated straight line to the experimental line should take place along the smoothest and shortest curve. This method was used to calculate $\bar{C}^0_p$ for a number of uni-univalent electrolytes, and also to estimate the heat capacities of various solutions of electrolytes which have been little studied (NH_4Br, NH_4I, RbI, and MX, where M = Rb or Cs, and X = OH, Cl, Br, or NO_3). The application of Parker's method to electrolytes of the 1:1 valency type, which are chemically relatively "simple", is apparently justified at present, but it can hardly be used in the case of electrolytes with highly charged ions, which often tend to undergo hydrolysis, or, by strongly polarising the nearest water molecules, bring about structural effects in dilute solutions, not taken into account by the Debye–Hückel theory. A number of authors who have carried out the precise determination of the heat capacity of aqueous solutions of the chlorides of the elements of the beryllium side group at 25°[90-94] suggest that $\bar{C}^0_{p_2}$ be determined by use of interpolation equations giving the concentration dependence of the specific heat capacity. This method has some advantages over graphical extrapolation, but it also is unreliable in the absence of data for dilute solutions.

Work devoted specifically to the question of the extrapolation of the values of ΦC_p to $m = 0$ [113] has shown that even such a relatively "simple" 1:1-valent electrolyte as NaI can show quite unexpected behaviour in the range of low concentrations.

The difficulties associated with the extrapolation of ΦC_{p_2} to $m = 0$ have led to the search for new methods of determining $\bar{C}^0_{p_2}$. One of these is known as the "method of integral heats", due to Cobble[131]. In this method, the values of $\bar{C}^0_{p_2}$ are determined from data on the heat capacity of an individual electrolyte C_{p_2} and the change in heat

capacity on dissolution ΔC^0_{pS}. The latter are found by differentiating, with respect to temperature, the first heats of dissolution of the electrolyte in water ΔH^0_S, found by extrapolating the integral heats of dissolution ΔH_S to zero concentration using the extended Debye–Hückel equation [132]. An advantage of this method is the greater reliability of the extrapolation of ΔH_S to $m = 0$ (m = molality) compared with the usual extrapolation of the apparent molar heat capacities of the electrolyte Φ_{C_2}, since the function which Criss and Cobble use in the extrapolation is linearly dependent on the molality. Nevertheless, even this extrapolation does not always give good results, as apparently indicated by the insufficiently "smooth" temperature dependence of ΔH^0_S, observed by these authors in a number of cases. The artificial smoothing of this dependence, undertaken by Criss and Cobble, is hardly justified for all systems, since the existence of an incompletely smooth temperature dependence for ΔH^0_S is apparently possible in principle (see p. 1779).

If in addition we take into account the unavoidability of error in the determination of the heat capacity of an individual electrolyte C_{p_2}, which sometimes reaches several cal mole^{-1} deg^{-1}, we can understand why the accuracy of the measured values of $\overline{C}^0_{p_2}$ obtained by Cobble's method in a number of cases differs little from that for the values of $\overline{C}^0_{p_2}$ obtained by extrapolating the Φ_{C_2} values (Table 2).

Table 2. Comparison of the values of $\overline{C}^0_{p_2}$ (cal mole^{-1} deg^{-1}) obtained by the method of integral heats (m.i.h.) and by measurement of the heat capacity of the solutions (m.h.c.s.). $t° = 25°$.

Electrolyte	$-\overline{C}^0_{p_2}$ (m.i.h.)	References	$-\overline{C}^0_{p_2}$ (m.h.c.s.)	References
HCl	30.5	96	29.2	88,138
			30.0	(pp.400 and 652 of Ref.132)
			32.6	139
NaCl	18.9	131	23.3	140
			21.6	141
$BaCl_2$	72.6	131	73.5	141
			73	142
			74.36	138
Na_2SO_4	46.7	101	50	140
CsI	36.6	98	31.02	42
			31.6	141

The method of integral heats is being used in many studies at the present time [65,68,69,95–103,121,126,133–137]. The lack of reliable data on the heat capacity of most individual electrolytes (particularly crystal hydrates), however, restricts the possibilities provided by the use of this method.

2. Semi-empirical Methods for Separating $\overline{C}^0_{p_2}$ into Ionic Components $\overline{C}^0_{p_i}$ and the Calculation of $\overline{C}^0_{p_i}$ for Different Temperatures

The problem of separating the heat capacity of an electrolyte into ionic components is even further from solution than the analogous problems of resolving into components the heats of hydration, volumes, and various other properties. There coexist ionic heat capacity scales which differ considerably from one another not only in the absolute values but also sometimes in the signs of the heat capacities [43,81]. In the resolution of heat capacities it may be necessary to use criteria different from those used in the separation of the enthalpy of hydration, since the heat capacity, which is the derivative of the enthalpy with respect to temperature, may be distributed between the ions in a way which is quite different from that for the actual integral heat [43]. The method of resolving the heat capacities proposed by Mishchenko and coworkers is based on the relationship between the heat capacities and the volumes of the solutions. The authors cited assumed that the values of $\overline{C}^0_p$ are equal for those ions for which Fajans and Johnson established that the partial molar volumes are equal, namely NH_4^+ and Cl^-. The scale of ionic heat capacities obtained on this basis is given in Table 3. Drakin and coworkers [84] suggested that the separation of $\overline{C}^0_{p_2}$ into ionic components be based on the assumption that $\overline{C}^0_{pCl^-} = -8$. [84] The authors cited obtained this quantity by selecting a value which would satisfy the equation (4) which they put forward for the relationship between the heat capacities and the hydration coordination numbers of ions.

Table 3. Values of $\overline{C}^0_{p_i}$ for various ions (cal mole^{-1} deg^{-1}) on different scales. $t° = 25°$.

Ions	Ref.43	Ref.143	Ref.145	Ref.81	Ref.130	Ref.146
H^+	—23.4	—3	—21	—20.5	0	+28
Li^+	—9.9	+12	—4.0	—8.0	+16.4	+41
Na^+	—15.0	+2	—9.9	—12	+11.1	+37
K^+	—21.6	—3	—17.5	—18	+5.2	+31
Rb^+	—	—	—20.3	—19	+3.3	+30
Cs^+	—	—	—22.7	—23	+1.9	+26
Be^{2+}	—	—	+16.3	—22	—	+76
Mg^{2+}	—51.3	—	—23.6	—36	—	+62
Ca^{2+}	—54.3	—	—39.5	—44	—	+54
Sr^{2+}	—57.0	—	—48.6	—46	—	+52
Ba^{2+}	—60.3	—	—54 4	—54	—	+44
F^-	+26.9	—	+3.6	—8	—25.5	—57
Cl^-	—6.6	—26	—11.8	—10	—32.6	—59
Br^-	—9.6	—26	—15.2	—12	—33.9	—61
I^-	—10.3	—27	—19.6	—13	—34.0	—62
NO_3^-	3.8	—15	—	—7	—20.7	—56
NH_4^+	—6.6	+12	—	—	+19.1	—
OH^-	—8.6	—29	—	—8	—35.5	—57

De Ligny and coworkers [143] put forward an original method for finding the heat capacity for the individual hydrogen ion, involving the determination of ΔC_p for the hydration of the H^+ ion from the cycle:

$$\begin{array}{ccc} H^+(aq) + Foc(aq) & \longrightarrow & Fic^+(aq) \xrightarrow{1} {}^1/_2 H_2(gas) \\ \uparrow 4 & & \downarrow 2 \\ H^+(gas) + Foc(gas) & \xleftarrow{3} & Fic^+(gas) + H^+(gas) + \bar{e}(gas) \end{array} \qquad (5)$$

where Fic^+ represents the ferrocinium ion $(C_5H_5)_2Fe^+$, and Foc represents ferrocene.

In the calculation of this cycle it is assumed that the heat capacity of the hydration ΔC_p hydr of large ions of the type Fic^+ ($r = 3.8$ Å) is additively made up of electrostatic and non-electrostatic components, so that the difference ΔC_p hydr $Fic^+ - \Delta C_p$ hydr Foc is equal to the electrostatic component of the hydration of Fic^+ and can be calculated

from the Born equation. The other quantities are determined rigorously. This gave $\Delta C_{hydr\,H^+} = -8 \pm 8$ and $\overline{C}^0_{p\,H^+}(aq) = -3 \pm 8$. The values of the heat capacities of other ions calculated on this basis are given in Table 3.

Latysheva[81] proposes a method for estimating ionic heat capacities which is based on the analysis of vibrational spectra of hydroxonium and hydroxyl ions in aqueous solutions. The results of such an analysis have shown that the nature of motion of particles in hydrate shells, and also the characteristics of hydration of H_3O^+ and OH^- ions, are very similar[144]. Latysheva therefore assumes that $\overline{C}^0_{p\,H_3O^+}$ will differ from $C_{p\,OH}$ only by an amount equal to the difference between the internal specific heats of non-hydrated ions, and separates $\overline{C}^0_{p_2}$ into ionic components. The starting values of $C^0_{p_2}$ are taken from the work of Criss and Cobble[146]. The resulting scale is shown in Table 3.

In papers by Cobble[146,147], Naumov and coworkers[148-152], and Krestov and coworkers[135,145,153], the question of the separation of $\overline{C}^0_{p_2}$ into ionic components is examined at the same time as, and in relation to, the temperature dependence of the entropies and heat capacities of ions.

Criss and Cobble[146,147] took as a basis the possibility of calculating rigorously the mean partial molar heat capacity of an electrolyte $\overline{C}^0_{p_2}]_{t_1}^{t_2}$ in the temperature range t_1-t_2 using the thermodynamic relationship

$$\overline{C}^0_p]_{t_1}^{t_2} = \frac{\overline{S}^0(t_2) - \overline{S}_0(t_1)}{\ln T_2/T_1}. \qquad (6)$$

The authors cited took account of the lack of the necessary experimental values of $S^0(t)$, and tried to establish a quantitative relationship between the values of $\overline{S}^0$ at different temperatures for individual groups of ions, classified according to structural type (simple or complex) and sign of charge (cations or anions). As a result, Criss and Cobble formulated the correspondence principle: "A standard state can be chosen at every temperature such that the partial molar entropies of one class of ions at this temperature are linearly related to the corresponding entropies at some reference temperature":

$$\overline{S}^0(t_2) = a(t_2) + b(t_2)\,\overline{S}^0(t_1) \qquad (7)$$

where $a(t_2)$ and $b(t_2)$ are empirical constants for a given class of ion†. By choice of standard state at each temperature is meant the specification of $\overline{S}^0$ for the hydrogen ion at this temperature. Having assumed that at 25° $S^0_{H^+} = -5.0$ e.u. (in accordance with published data), Criss and Cobble had to assume that at 60, 100, and 150° this quantity had the values −2.5, 2.0, and 6.5 e.u. respectively, otherwise the simple linear correspondence principle was not obtained.

The authors cited showed that with this choice of conditions, for simple ions, the principle applies with a range of ±0.5 cal mole^{-1} deg^{-1} up to 150°, and on this basis they assumed that extrapolation to 200° is possible. The use of the correspondence principle makes it possible to estimate, simply and rapidly, unknown entropies of electrolytes at different temperatures, and average heat capacities within the temperature ranges indicated. The values of the entropies and heat capacities of individual ions obtained by this calculation can hardly be the true values, however, since it has not been proved that the form of the correspondence principle is necessarily linear.

† It is obvious that the analytical form of the expression of the correspondence principle corresponds to one of Karapet'yants' comparative calculation methods.

It is therefore not accidential that the values of $\overline{C}^0_{p\,H^+}$ at 25°, obtained by differentiation of the curve giving the dependence of $\overline{S}^0_{H^+}$ on T and equal to 28 cal mole^{-1} deg^{-1}, and also the complete scale of ionic heat capacities based on this value by Criss and Cobble (see Table 3), have been criticised by a number of authors[81,135,153]. The high positive values of $\overline{C}^0_p$ for cations, and the large negative values of $\overline{C}^0_p$ for anions appear unjustified, if we take into account the more energetic binding, on the average, of water molecules by cations, and their larger hydration numbers. The increase in the values of $\overline{S}^0_{H^+}$ with increase in temperature also appears unnatural, since for a positively hydrated cation, such as the H^+ ion, the effect of the ordering of the structure when the ion is placed in water should predominate over the destructive influence to a still greater extent at higher temperatures[43].

Khodakovskii and coworkers[148-152] critically reviewed available published data on the equilibrium constants of processes involving the participation of different ions at different temperatures, calculated the heat capacities of many ions over a wide range of temperatures, and concluded that the temperature dependence of $\overline{C}^0_{p_2}$ is described satisfactorily by the equation

$$\overline{C}^0_{p_2} \cong bT. \qquad (8)$$

This approximation is applicable only for calculations in the temperature range 200−300°, that is at temperatures at which most of the hydrothermal processes in which these authors were interested took place, but it does not describe the extremal form of the dependence of $\overline{C}^0_{p_2}$ on $t°$ in the temperature range from 20° to 80°.[135] Having shown convincingly that the values of $\overline{S}^0_2$ obtained by Cobble and Criss are not absolute, the authors cited proposed new equations for the relationship between $\overline{C}^0_{p_2}$ and $\overline{S}^0_2$ for ions. These equations are not rigorous either, however, since they are based on the approximation $\overline{C}^0_{p_2} \simeq bT$ examined above.

An interesting attempt to obtain consistent values of the partial molar heat capacities and entropies of ions in infinitely dilute solutions in the temperature range 0−100° was described by Krestov and Kobenin[135,145,153]. On the basis of the concepts of the electrostatic and non-electrostatic contributions to the entropy and heat capacity of hydration of ions, developed by Krestov and coworkers[78,79,155-158], Krestov and Kobenin derived an equation for the partial molar entropy of the hydrated ion‡ at a temperature T, $S^T_{aq.i}$

$$\overline{S}^T_{aq\ i} = S^{298}_{aq\ i} + 45.7 \ln T/298 + \Delta a_T + \Delta b_T |z| + \Delta d_T \frac{|z|}{r_{aq}} \qquad (9)$$

and from this, by appropriate differentiation, they obtained the relationship

$$(C_p)^T_{aq\ i} = 45.7 + \left(\frac{\partial \Delta a_T}{\partial T} + \frac{\partial \Delta b_T}{\partial T}|z| + \frac{\partial \Delta d_T}{\partial T}\frac{|z|}{r_{aq}}\right) T \qquad (10)$$

where $S^{298}_{aq.i}$ and $(C_p)^T_{aq.i}$ are respectively the partial molar entropy at 298°K and the partial molar heat capacity at T for the ion in an infinitely dilute solution; z is the charge of the ion; r_{aq} is the radius of the hydrated ion, equal to $r_{crystallographic}$ + an increment q; and Δa_T, Δb_T, and Δd_T are constants at a temperature T.

‡ In the works cited, the quantities $\overline{C}^0_{pi}$ and $\overline{S}^0_i$ are meant, although the corresponding terms are not introduced in the text.

To determine the constant coefficients, the authors cited wrote Eqn. (10) in the form

$$(C_p)'^{T}_{aq\ i} = 45.7 + \left(\frac{\partial \Delta a_T}{\partial T} + \frac{\partial \Delta b_T}{\partial T}|z| + \frac{\partial \Delta d_T}{\partial T}\frac{|z|}{r_{aq}}\right)T - (C_p)'^{T}_{H^+\,aq}\ z \quad (11)$$

and solved the system of equations (11) for several ions. Here, $(C_p)'^{T}_{aq.i}$ is a conditional quantity which is smaller than the "absolute" heat capacity of the hydrated ion by the "absolute" heat capacity of the hydrated proton at the temperature T, multiplied by the charge of the ion. The $(C_p)'^{T}_{aq.i}$ values were determined from experimental data on the heat capacity of the hydrogen halides and other halides, with the condition that $(C_p)'^{T}_{aq.H^+} = 0$. By integrating the temperature dependence of the coefficients in Eqn. (11), the authors cited calculated Δa_T, Δb_T, Δd_T, and $S^T_{H^+}$ in the range 0–100°.

The values of $\bar{C}^0_{p_i}$ for a large number of ions were obtained by this method [145]. Some of these values are given in Table 3. The values of $\bar{S}^0_{H^+aq}$ obtained by Cobble and by Krestov and Kobenin are compared in Table 4. It can be seen that with increase in temperature the values of $\bar{S}^0_{H^+}$ being compared change in opposite directions; there is a stronger physical justification for the direction of the change in $\bar{S}^0_{H^+}$ given by Krestov and Kobenin, so that more reliance can be placed on the value of $(C_p)^{298}_{H^+aq}$ obtained by Krestov and Kobenin. An interesting feature is that this value practically coincides with the corresponding value obtained by Latysheva [81] by a completely different method. The method of Krestov and Kobenin, unlike that of Cobble and Criss, does not require the artificial fixing of the values of $S^T_{H^+}$ at several temperatures, so that it appears more "absolute".

The only conditional quantity introduced into the calculation by Krestov and Kobenin is $\bar{S}^{298}_{H^+} = -2.1$ e.u. This method also, however, can only be regarded as approximate, since it is based on the assumption that the non-electrostatic components of the thermodynamic characteristics of the hydration of ions and inert gases are equal. This assumption is obviously incorrect for ions which are not of the noble gas type, as confirmed by the significant discrepancies between the calculated and experimental values of ΔC_p for the hydration of the chlorides of the rare earth elements (REE). [135]

In the case of ions of the noble gas type this assumption is of course more justified, but even in this case the calculation cannot be accurate, since it is known that a change in the charge of the nucleus can alter significantly the ratio of the electronic terms for the same number of electrons in the atom [159], and hence may influence the nature of the interaction of the ion with water.

To summarise, it may be stated that despite vigorous attempts to obtain real values of $\bar{C}^0_p$ for individual ions, this problem cannot yet be regarded as solved. The conditional scale of heat capacities ($\bar{C}^0_{pH^+} = 0$) therefore apparently has not lost its value completely, and it is still being used [43,130] (Table 3).

Table 4. Values of $\bar{S}^0_{H^+}$ at different temperatures.

t,°C	Ref.146	Ref.135	t,°C	Ref.146	Ref.135
25	−5.0	−2.1	100	+2.0	−6.0
60	−2.5	−4.3	150	+6.5	—

IV. THE RELATION OF THE HEAT CAPACITY OF SOLUTIONS TO THE VARIOUS TYPES OF REACTION OCCURRING IN THEM

1. Heat Capacity and the Hydration of Ions

The hydration of ions leads to changes in the state of not only the ions themselves and the nearest water molecules but also, in the great majority of cases, to a change in the structure of all the remaining water. The changes in heat capacity associated with the effects of the so-called short-range and long-range hydration may sometimes differ even in sign. In this connection, a number of papers emphasize one or other of these aspects of the phenomenon.

One of the most important characteristics of the short-range hydration of ions is the number of water molecules coordinated directly around the ion. Since the chemical binding of liquid water by salts on the formation of crystal hydrates [35,160] and even the covalent hydration of carbonyl groups [161] lead to a significant decrease in heat capacity, it was natural to expect the observation of a distinct relationship between the number of water molecules coordinated to the ions and the heat capacity of solutions. Attempts to find a quantitative relationship of this kind in analytical form were made by Drakin, Karapet'yants, and coworkers [84,86,87,122]. The relationship which they put foward was mentioned above [see Eqn. (4)]. To verify this equation, the heat capacities of aqueous solutions of a number of nitrates were studied. The values of n appearing in this equation for most cations were chosen on the basis of an analysis of the values of the coordination numbers in crystalline compounds of the corresponding elements [162,163] and for Cd^{2+} and Pb^{2+} by analogy with strontium and barium, in the same periods§. It was found that not all the ions are covered by this form of relationship. Apart all together from ions which do not have the inert gas structure, other ions such as Na^+ and Sr^{2+} are not covered. This may be due to insufficiently reliable estimation of the coordination numbers of the ions in solution and to the lack of justification for the view that the magnitude of the change in heat capacity on hydration is determined entirely by this single parameter. In actual fact, when the ions of elements belonging to different periods and sub-groups are compared, we can observe not only a change in the coordination numbers of the ions but also a change in the energy of the attachment of water molecules to the ions and in the extent to which ions influence the structure. The influence of the first of these factors was demonstrated in a study of the heat capacity of solutions of the perchlorates of the bivalent 3d elements, which have identical cation coordination numbers and similar structural parameters (see p. 1759). It is only for the ions of the REE, for which the structural similarity is even greater, that almost complete agreement is observed between the Φ_{C_p} values for their salts, if we consider the first and second halves of the REE series separately (Fig. 3). The difference between the Φ_{C_p} values for the two groups of elements in this case can in fact be attributed chiefly to the change in the coordination number of the cations [54,55]. The apparent absence of a correlation between the hydration energy of cations and the heat capacity of solutions in this case indicates the existence of some compensation effect, and

§ This analogy appears insufficiently justified in the case of Pb^{2+} and Ba^{2+}, in view of the marked difference in the electronic structure of these ions.

not that the heat capacity is independent of the binding energy of the water for the cations. This is possibly due to an intensification of the structure-forming action of the ions with increase in their field strength, particularly since the values of the standard entropy of the ions $\bar{S}_i^0$ decrease in the same direction, and in the alkali and alkaline earth metal series the action of the ions on the structure of water evidently becomes of primary importance (as already noted on p. 804).

Attempts have been made to consider heat capacity only in relation to structural changes. An original approach to the study of the influence of ions on the structure of water was made by Mrevlishvili and Privalov [164,165], who studied the temperature dependence of the heat capacity of frozen aqueous solutions of a number of electrolytes during heating, in order to estimate ΔS for the fusion of ice in the presence of various electrolytes. These values of ΔS differ significantly from the values of ΔS for the fusion of pure ice. In the opinion of the authors cited, this indicates a change in the structure of water under the influence of the ions. Thus for example it was found that Na^+ and Cl^- ions produce little change in the structure of water, whereas the K^+ ion destabilises it. The cations can be arranged in the following sequence of increasing ordering influence on water: $Mg^{2+} < Ca^{2+} < H^+ < Li^+ < Na^+$. A marked ordering influence on the structure is also shown by OH^- ions.

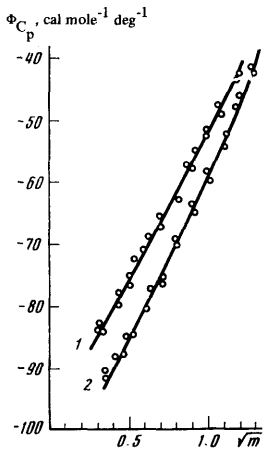


Figure 3. Dependence of ΦC_p for the chlorides of dysprosium, erbium, ytterbium (curve *1*), lanthanum, and neodymium (curve *2*) on the concentration of the solutions (m is the molality) at 25°. [54]

Papers by Mishchenko and coworkers, summarised in two reviews [43,116], emphasise the need to make simultaneous allowance for the binding of water in the hydrate sheaths of ions and the structural changes brought about in water, and examine the ratio of the contributions from these effects over a wide range of concentrations. In particular, it was shown that the role of structural changes is especially marked in dilute solutions and at low temperatures. At the same time the binding of water by ions becomes weaker at higher concentrations, as a consequence of the increase in the electrical viscosity in the solution, and this explains the increase in $\bar{C}_{p_2}^0$ with increase in concentration. In the region of the complete distribution boundary (CDB), a decrease in the energetic hydration of ions is possible, and this should lead to a further increase in $\bar{C}_{p_2}^0$. Further increase in concentration may be accompanied by a redistribution of the hydrate water in favour of the more hydrophilic partner. This should decrease the slope of the $\bar{C}_{p_2} = f(\sqrt{m})$ isotherm and may even lead to the production of a maximum. The possibility of the production of maxima in the range of "extremely high concentration" in the solutions was also predicted by Drakin and coworkers [166], who suggested that the production of maxima should be due to association in solution. In actual fact, maxima on the $\bar{C}_{p_2} = f(\sqrt{m})$ isotherms were observed for the salts of various REE. [54] Spedding and Jones attribute this to the possible formation of acido-complexes in concentrated solutions. In the section on heat capacity and complex formation it will be shown that this explanation is erroneous. The observation being discussed apparently corresponds more closely to the prediction of Mishchenko and coworkers.

The relative decrease in the role of the disruption of the water structure with increase in temperature and concentration was also demonstrated by Mashovets, Puchkov, and coworkers [9-17]. Mishchenko and Stagis were the first to study the heat capacity of solutions at the complete distribution boundary [167,168].

In an examination of the heat capacity of comparatively simple electrolytes (consisting of inorganic, generally monatomic, ions), only the breakdown of the intrinsic structure of water on the hydration of ions is discussed, whereas in the study of solutions of electrolytes including organic ions there is frequently encountered a phenomenon which is attributed to a strengthening of the intrinsic structure of water under the influence of the ions (see p. 805).

Ahluwalia and coworkers [65-67] determined the values of ΔC_p^0 of dissolution and $\bar{C}_{p_2}^0$ for a number of tetra-alkylammonium halides at 25° and 35°, and found that the ΔC_p^0 values increase in the order:

Me_4NI	$<$	Me_4NBr	$<$	Et_4NBr	$\simeq$	Et_4NI	$<$	Pr_4NBr	$\leqslant$	Pr_4NI	$<$	Bu_4NBr
-10.5 ± 6		-10.4 ± 4		33.0 ± 3		37.5 ± 4		112.5 ± 2		119 ± 4		179 ± 3

They conclude that Me_4N^+ cations break down the structure of water, and that the other cations strengthen it. The $C_p = f(T)$ and $\Delta C_p = f(T)$ curves are not monotonic [65] (Fig. 4). The minimum at 50° was explained in terms of "hydrophobic" interactions, and the maximum at 70° was explained on the assumption that the heat capacity of the structuring process decreases above 70°. The idea that large ions have a structuring action was confirmed by Boyd and coworkers [68], who studied the values of ΔC_p^0 for ion exchange by examining the temperature dependence of the values of ΔH^0 for the exchange of Na^+ and Bu_4N^+ on ion exchange resins.

Kresheck [169] determined $\bar{C}_p^0$ values for several amino-acids in infinitely dilute aqueous and heavy-water solutions at 25° and concluded that the non-polar side chains of methionine and norvaline promote structure formation in water, the effect being greater for light water than for heavy water, in agreement with the theoretical predictions of Lovett and Ben-Naim [77] (see p. 805). Kay and coworkers [62,63] compared the results of the study of many properties (thermodynamic and transport properties) of aqueous and non-aqueous solutions at several temperatures in terms of the theory of Frank and Wen; this enabled Kay

to divide ions into three classes: electrostrictional structure-forming (Li^+, F^-, Ca^{2+}), hydrophobic structure-forming (Bu_4N^+, Ph_4B^-, etc.), and structure-destroying (Cs^+, I^-, Me_4N^+).[62] The ion classification made by Kay leaves open the question of the possibility of an increased heat capacity due to the hydration of hydrophilic ions of inorganic character. Moreover, the opinion has grown in the literature that the dissolution of these electrolytes in water is always accompanied by a decrease in heat capacity[43,170]. Recently, however, it was found[171-175] that the temperature coefficient of ΔH for the dissolution of manganese and zinc perchlorate crystal hydrates is positive over an appreciable range of concentration, that is the ΔC_p values for the dissolution of these salts are positive and not negative. It was suggested that this effect is due to the formation, around the aquo-cations, of associates of water molecules, joined by hydrogen bonds. The formation of associates depends on the nature of the ions and the state of water in the corresponding aquo-complexes, and on this basis suggestions have been put forward regarding the cases in which ΔC_p for the dissolution of an electrolyte may be greater than 0 or less than 0. In the work cited, attention was drawn to the existence of characteristic features in the properties of dilute solutions, which can be understood qualitatively by assuming that the effect of the structuring of water by many ions is particularly marked in highly dilute solutions.

The question of the unique behaviour of heat capacity in the range of very dilute solutions was also dealt with in papers by Mishchenko and Novoselova[107-109,113], and agrees with studies of other properties of dilute solutions[129,176,177].

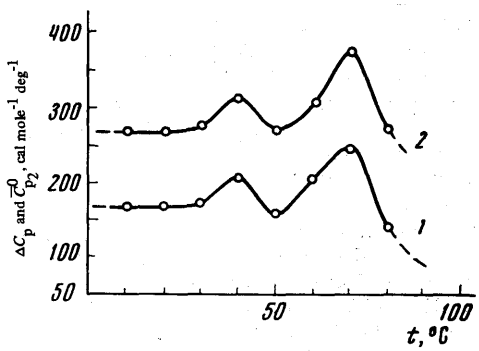


Figure 4. Temperature dependence of ΔC_p for the dissolution of tetraphenylborate in water (*1*) and $\overline{C}^0_{p_2}$ for tetraphenylborate (*2*).[65]

2. Heat Capacity and Hydrolysis of Ions

No special studies of heat capacity in relation to the hydrolysis of ions have been made in the period under review. It is possible only to try to estimate this effect from data on the change in heat capacity on the ionisation of water[178-180], ammonium ions and some of their derivatives[181,182], and acids[150,178,180-191], and also from the results of individual studies of the temperature dependence of the hydrolysis constants of metal cations[192-201].

Table 5 gives the values of ΔC_p for the ionisation of water for various acids and for the ammonium ion and its derivatives, obtained either as the temperature coefficients of ΔH for the reaction[178,180,181,186-188] or from the temperature dependence of the ionisation constants[150,181-185,190,191]. The values of ΔC_p for the hydrolysis of the anions formed on the dissolution of the uncharged acids listed in Table 5 are obviously equal to the difference between ΔC_p for the ionisation of water and ΔC_p for the protolytic dissociation of the acid. The corresponding values are given in column 5 of Table 5. It can be seen that the values of ΔC_p hydrol for the anions may be negative or positive.

Table 5. Values of ΔC_p for protolytic dissociation, ΔC_p p.d., for compounds, and values of ΔC_p for hydrolysis, ΔC_p hydrol, for the corresponding acid residues, at 25° (cal mole^{-1} deg^{-1}).

Proton donor	ΔC_p p.d.	References	Proton acceptor	ΔC_p hydrol
1	2	3	4	5
H_2O	−50 −52 −56.7	179 150 178	—	—
HNO_3	−36.9	150	NO_3^-	−13.1
HNO_2	−117	182, 183	NO_2^-	67
H_3PO_4	−37	181	$H_2PO_4^-$	−13
H_3PO_4	−43.5	150	$H_2PO_4^-$	−6.5
$H_2PO_4^-$	−54	181	HPO_4^{2-}	4
$H_2PO_4^-$	−49.7	150	HPO_4^{2-}	−0.3
HPO_4^{2-}	−169	150	PO_4^{3-}	119
H_3AsO_4	−37.2	150	$H_2AsO_4^-$	−12.8
$H_2AsO_4^-$	−65.6	150	$HAsO_4^{2-}$	15.6
$HAsO_4^{2-}$	−142	150	AsO_4^{3-}	92
H_2CO_3	−54.6	150	HCO_3^-	4.6
HCO_3^-	−54.6	150	CO_3^{2-}	4.6
H_2SO_3	−67.7	150	HSO_3^-	17.7
HSO_3^-	−68.5	150	SO_3^{2-}	18.5
HSO_4^-	−42.8	150	SO_4^{2-}	−7.2
$HSeO_4^-$	−99.3	150	SeO_4^{2-}	49.3
H_3BO_3	−460	150	$H_2BO_3^-$	410
H_4SiO_4	−35.3	150	$H_3SiO_4^-$	−14.7
$H_3SiO_4^-$	−135	150	$H_2SiO_4^{2-}$	85
H_4GeO_4	+686	150	$H_3GeO_4^-$	−736
H_6TeO_6	−13.9	150	$H_5TeO_6^-$	−36.1
$H_5TeO_6^-$	8.2	150	$H_4TeO_6^{2-}$	−58.2
HF	−28	150	F^-	−22
HCl	<0	191	Cl^-	>−50
H_2S	−68.5	150	HS^-	18.5
HS^-	−45	150	S^{2-}	−5
HCN	−36.2	185	CN^-	−13.8
HCN	−60	186	CN^-	10
CH_3COOH	−36	180	CH_3COO^-	−14
CH_3COOH	−34	187	CH_3COO^-	−16
$CH_2ClCOOH$	−36	187	CH_2ClCOO^-	−14
$CH_2BrCOOH$	−22	187	CH_2BrCOO^-	−28
CH_2ICOOH	−29	187	CH_2ICOO^-	−21
CH_2CNCO_2H (cyanoacetic)	−36	184	CH_2CNCOO^-	−14
$HO\cdot C_6H_4\cdot CO_2H$ (salicylic)	−45	188	$HOC_6H_4\cdot COO^-$	−5
$HOC_6H_4\cdot CO_2^-$	−33	188	$^-O\cdot C_6H_4CO_2^-$	−17
CH_3CHNH_2COOH (α-alanine)	−34	187	$CH_3CHNH_2CO_2^-$	−16
NH_2CH_2COOH (glycine)	−29 (−34.5)	187	$NH_2CH_2CO_2^-$	−21
$CH_3(CH_2)_2CH\cdot NH_2COOH$ (α-aminovaleric)	−30	187	$CH_3(CH_2)_2CH\cdot NH_2CO_2^-$	−20
NH_4^+	0	182	NH_3	—
$CH_3NH_3^+$	8; 7.5	181, 182	CH_3NH_2	—
$(CH_3)_2NH_2^+$	19.9	182	$(CH_3)_2NH$	—
$(CH_3)_3NH^+$	41.0	182	$(CH_3)_3N$	—
$OHNH_3$	−23	182	$OH\cdot NH_2$	—
$C_6H_5NH_3^+$	0.0	182	$C_6H_5NH_2$	—
$o\text{-}ClC_6H_4NH_3^+$	0.0	182	$o\text{-}ClC_6H_4NH_2$	—
(THAM) H^+	−17.4	178	THAM	—

The hydrolysis of metal cations involves essentially the protolytic dissociation of their aquo-complexes, so that subsequently we can try to estimate the values of ΔC_p for these processes by analysing the accumulated data for other acids.

Examination of the data in Table 5 reveals the following features.

1. The protolytic dissociation of uncharged molecules and anions is generally accompanied by a decrease in heat capacity, but the dissociation of positive ions almost always corresponds to an increase in heat capacity or to very little change.

2. The value of ΔC_p for the first stage of the dissociation of the uncharged molecules of many acids lies in the range between -22 cal mole^{-1} deg^{-1} and -38 cal mole^{-1} deg^{-1}. An exception is provided by acids which tend to decompose (HNO_2, H_2CO_3, H_2SO_3, H_2S) or polymerise (H_3BO_3, H_4GeO_4, H_6TeO_6), or which have a complex branched structure (THAM¶ or substituted carboxylic acids). It is also possible that some of these deviations are due to a large error in the determination of ΔC_p.

3. The value of ΔC_p for each successive stage of the step-wise dissociation of H_3PO_4, H_3AsO_4, and H_4SiO_4 is more negative than the previous one (Fig. 5).

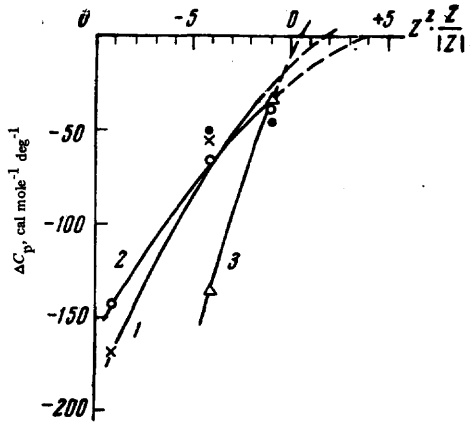


Figure 5. Values of ΔC_p for the successive stages of the acidic dissociation of H_3PO_4 (*1*), H_3AsO_4 (*2*), and H_4SiO_4 (*3*) as functions of the charge z of the conjugated base.

4. In the series of methylammonium ions, an increase in ΔC_p for the dissociation is observed with increase in the number of methyl groups.

The existence of several independent regular features, not to speak of the exceptions, indicates that the values of ΔC_p for the ionisation of protolytes are determined by various factors. One is the change in the electrostatic parameters of the particles in the dissociation process. This is obviously confirmed by the first three of the above regular features.

King[181] attempted to described ΔC_p for protolytic dissociation on the basis of Born's electrostatic model of hydration. He showed that, according to this model, ΔC_p for ionogenic reactions (corresponding to the dissociation of uncharged or anionic acids) should be negative, and should be more negative, the higher the charge of the anion. In the case of isoelectric reactions (for example the dissociation of NH_4^+), the absolute value of ΔC_p should be slightly greater, and possibly positive. Verification of the theory by experiment led King to the conclusion that the simple electrostatic model does not make it possible to predict ΔC_p quantitatively for protolytic dissociation[181]. It is necessary to take account of other factors influencing ΔC_p. Many authors consider that the most important of these factors is the hydration of the particles, including the rearrangement of the solvent as a result of the dissociation of the solute[180-184,186]. The temperature dependence of ΔC_p for the ionisation is particularly sensitive to these changes[180,182,184]. Thus if our aim is to estimate ΔC_p for the protolytic dissociation of the aquo-cations of metals

$$M(H_2O)_n^{z+} + H_2O \rightleftarrows MOH(H_2O)_{n-1}^{z-1} + H_3O^+$$

or in other words the hydrolysis of M_{aq}^{z+} cations, it is necessary to have not only the electrostatic parameters of the components of the reaction but also data (which are usually not available) on their hydration and action on the structure of the solution.

If we nevertheless assume that the electrostatic approach should be most applicable to metal ions of spherical shape, we may expect (following King's method[181]) for the hydrolysis of singly-charged metal ions ΔC_p close to zero, that for doubly-charged ions about 20–40 cal mole^{-1} deg^{-1}, and that for triply-charged ions 60–80 cal mole^{-1} deg^{-1}. It is difficult to verify this suggestion, since no direct calorimetric measurements of ΔC_p have been made. The known dependence of pK† for the hydrolysis of cations[192-201] on the reciprocal of the absolute temperature $1/T$ in most cases is linear, irrespective of the charge of the cation. Thus within the limits of error of the measurement of pK, the value of ΔC_p for the hydrolysis is equal to zero. The error in the measurement of pK, however, is nowhere less than ± 0.02 pK units; according to King's estimates[181], this would correspond to an error of several tens of cal mole^{-1} deg^{-1} in the determination of ΔC_p.

In a spectrophotometric study[191] of the hydrolysis of $FeCl_3$, $Fe(NO_3)_3$, and $Fe(ClO_4)_3$ it was found that ΔH for the reaction $Fe^{3+} + H_2O \rightleftarrows FeOH^{2+} + H^+$ in the temperature ranges from 21° to 50° and from 50° to 90° has the values 3.4 kcal mole^{-1} and 8.6 kcal mole^{-1} respectively. This gives the value $\Delta C_p \sim 150$ cal mole^{-1} deg^{-1}, which does not agree with the value -16.5 cal mole^{-1} deg^{-1} calculated on the basis of data on $\bar{C}_p^0$ for the components of the reaction, equal to -61 (Fe^{3+}), -39 ($FeOH^{2+}$), 18 (H_2O), and -20.5 (H^+) cal deg^{-1} mole^{-1}.[81]

From data on ΔS for the reaction $Al^{3+} + 2H_2O \rightleftarrows AlOH^{2+} + H_3O^+$,[201] the value of ΔC_p for this reaction can be estimated at about 30 cal mole^{-1} deg^{-1}. This value is also greater than the error in its determination, since it is found from the change in ΔS with temperature, which in this case is commensurate with the error in the determination of ΔS.

Thus the question of the values of ΔC_p for the hydrolysis of cations remains open. Nevertheless, it can hardly be assumed that the magnitude of this quantity has in fact the same zero value for all cations, since the state of the components of the solution changes quite markedly on

¶ THAM = tris(hydroxymethyl)aminomethane.

† $pK = \lg K$, where K is the hydrolysis constant.

hydrolysis and is different for different systems. This is indicated, for example, by the values of ΔS for hydrolytic processes, taken from a review by Arnek [202] (Table 6). The values of ΔS for the reactions of the same type involved in the formation of the complexes $CdOH^+$, $HgOH^+$, and $FeOH^{2+}$ vary from −2.7 e.u. to +23 e.u., those for complexes of the type $M_4(OH)_4^{4+}$ from −20.8 e.u. [for $Pb_4(OH)_4^{4+}$] to +14.0 e.u. [for $Ni_4(OH)_4^{4+}$], etc. It is difficult to believe that such marked differences in the entropy of the reaction are not associated with differences in the change in heat capacity. In actual fact, data on the measured heat capacity of aqueous solutions of the perchlorates of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} at 25° [50,51,81,171] showed that in the range of high concentrations there is a correlation between the degree of hydrolysis of the cations and the apparent (and partial) molar heat capacity of the salts in solution (Fig. 6).

Table 6. Change in entropy ΔS accompanying the hydrolysis of cations $qM^{n+} + pH_2O \rightleftharpoons M_q(OH)_p^{(nq-p)+} + pH^+$ at 25° in 3 M $NaClO_4$. [202]

Hydrolysis product	ΔS, e.u.	Hydrolysis product	ΔS, e.u.	Hydrolysis product	ΔS, e.u.	Hydrolysis product	ΔS, e.u.
Be_2OH^+	0.2	$Fe_2(OH)_2^{4+}$	20.0	$CdOH^+$	−2.7	Hg_2OH^{3+}	−2.1
$Be_3(OH)_3^{3+}$	11.3	$Fe_3(OH)_4^{5+}$	22.0	Cd_2OH^{3+}	−5.1	$Hg_2(OH)_2^{2+}$	18.8
$(UO_2)_2(OH)_2^{2+}$	4.3	$Ni_4(OH)_4^{4+}$	14.0	$Cd_4(OH)_4^{4+}$	−9.4	$Pb_3(OH)_4^{2+}$	−15.8
$(UO_2)_3(OH)_5^+$	6.0	$Cu_2(OH)_2^{2+}$	4.4	$HgOH^+$	7.9	$Pb_4(OH)_4^{4+}$	−20.8
$FeOH^{2+}$	23.0			$Hg(OH)_2$	4.6	$Pb_6(OH)_8^{4+}$	−27.0

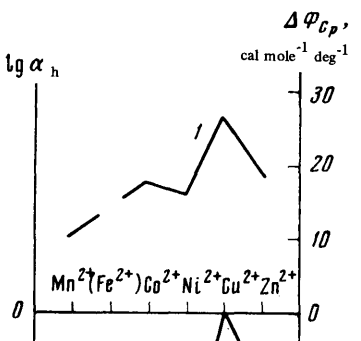


Figure 6. Correlation between the increase in the apparent molar heat capacity of the perchlorates of the 3*d* metals with increase in concentration from 0 to 4 *m*, $\Delta\Phi_{C_p}$ (*1*) and the logarithm of the degree of hydrolysis $\lg\alpha_h$ for the corresponding cations in concentrated solutions of their chlorides (*2*).

If this correlation is not accidential, it indicates a positive change in heat capacity in the hydrolysis of these electrolytes in concentrated solutions. In the works cited it was suggested that a positive change in heat capacity may accompany the localised hydrolysis and hydrolytic polymerisation of cations, that is the processes which take place preferentially at high concentrations of the salt.

3. Heat Capacity and the Formation of Acido-complexes

The question of the change in heat capacity on the formation of acido-complexes in solution has been examined many times [7,10,11,54,203-228]. In all the works cited, with some exceptions [54,209,212-216,223,226], an indirect method for determining ΔC_p for complex formation from the temperature coefficients of the values of ΔH and ΔG was used. The main results are given in Table 7. It can be seen that the values of ΔC_p for ion association ΔC_{pk} vary over a wide range, depending on the specific ions, but are always positive.

Table 7. Change in heat capacity ΔC_{pk} on formation of various acido-complexes (cal $mole^{-1}$ deg^{-1}).

Process	T, °C	Ionic strength of medium I	ΔC_{pk}, cal $mole^{-1}deg^{-1}$	Reference
$Ni^{2+}+Suc^{2-}$ [a] $\rightleftarrows NiSuc$	0—45	0.1	42±20	203
$Co^{2+}+Suc^{2-} \rightleftarrows CoSuc$	0—45	0.1	72±20	203
$Mn^{2+}+Suc^{2-} \rightleftarrows MnSuc$	0—45	0.1	62±15	203
$Ni^{2+}+C_2O_4^{2-} \rightleftarrows NiC_2O_4$	0—45	supersaturated solutions	35±12	203
$Co^{2+}+C_2O_4^{2-} \rightleftarrows CoC_2O_4$	0—45	ditto	20±10	203
$Mn^{2+}+C_2O_4^{2-} \rightleftarrows MnC_2O_4$	0—45	»	65±5	203
$Co^{2+}+A^-$ [b] $\rightleftarrows CoA^+$	0—45	0.1	35±13	204
$Ni^{2+}+A^- \rightleftarrows NiA^+$	0—45	0.1	31±6	204
$Ni^{2+}+Gl^-$ [c] $\rightleftarrows NiGl^+$	0—45	—	28±2	205
$NiGl^+ + Gl^- \rightleftarrows NiGl_2$	0—45	—	28±25	205
$Co^{2+}+Gl^- \rightleftarrows CoGl^+$	0—45	—	22±14	205
$CoGl^+ + Gl^- \rightleftarrows CoGl_2$	0—45	—	24±20	205
$Mn^{2+}+Gl^- \rightleftarrows MnGl^+$	0—45	—	16±10	205
$Ni^{2+}+Mal^{2-}$ [d] $\rightleftarrows NiMal$	0—45	—	46±20	206
$Co^{2+}+Mal^{2-} \rightleftarrows CoMal$	0—45	—	68±25	206
$Mn^{2+}+Mal^{2-} \rightleftarrows MnMal$	0—45	—	92±30	206
$Fe^{3+}+Cl^- \rightleftarrows FeCl^{2+}$	10	0	61±4	207
ditto	10	9.72 ($HClO_4$)	23±4	207
»	25	0	58±1	207
»	25	9.72 ($HClO_4$)	24±4	207
»	55	0	53±4	207
»	55	9.72 ($HClO_4$)	20±4	207
$Bi^{3+}+Cl^- \rightleftarrows BiCl^{2+}$	0	4 *M* $HClO_4$	36	208
ditto	10	4 *M* $HClO_4$	36	208
»	40	4 *M* $HClO_4$	32	208
$Bi^{3+}+Br^- \rightleftarrows BiBr^{2+}$	40	4 *M* $HClO_4$	32	208
$Zn^{2+}+4Cl^- \rightleftarrows ZnCl_4^{2-}$	25	2 *m* [$Zn(ClO_4)_2$—$CaCl_2$—H_2O]	70	209
ditto	25	3 *m* ditto	32	209
$Cd^{2+}+4Cl^- \rightleftarrows CdCl_4^{2-}$	25	2 *m* [$Cd(ClO_4)_2$—$CaCl_2$—H_2O]	60	209
ditto	25	3 *m* ditto	57	209

[a] Suc^{2-} = succinate anion; [b] A^- = β-alanite anion; [c] Gl^- = glycinate anion; [d] Mal^{2-} = malonate anion.

The large positive change in heat capacity on complex formation is also indicated by the study of ΔH for the formation of $FeBr^{2+}$ [210] and $CdBr^+$ [211] at different temperatures and by the study of heat capacity in the H_2SO_4—HNO_3—H_2O system [212]. In view of this characteristic

feature of the ΔC_{pk} values, it must be assumed that Spedding and Jones' conclusion that complex formation is responsible for the production of the maximum on the $\Phi Cp = f(m)$ curves for the REE chlorides at high concentrations is incorrect[54,55] (see p. 810).

The positive change in heat capacity on the formation of acido-complexes is attributed to the partial liberation of water from the hydrate sheaths of simple ions and to a reduction of the range over which ions affect the heat capacity of the surrounding water due to a decrease in the overall charge of the particles[209,213-216]. Vasil'ev[207,208,210,217-222] explains this phenomenon on the basis of the view that "icebergs" of water molecules are formed around simple and complex ions, and that these icebergs undergo rearrangement on complex formation.

An interesting feature is that the effect of temperature on ΔC_{pk} in the cases studied[207,208,217] is relatively small (Table 7); at $I = 0$, with increase in temperature from 0° to 50°, the value of ΔC_{pk} decreases by only a few calories. With increase in I the effect of temperature becomes even smaller. This suggests that the decrease in ΔC_{pk} with increase in temperature is due chiefly to the decrease in the heat capacity of the free water. With increase in the ionic strength, the quantity of free water becomes smaller, with a corresponding decrease in the effect of temperature on ΔC_{pk}.[223]

ΔC_{pk} has been determined by the direct calorimetric method for the $Zn(ClO_4)_2-CaCl_2-H_2O$ and $Cd(ClO_4)_2-CaCl_2-H_2O$ systems[209,214-216,226] for several values of the total electrolyte concentration and for different ratios of the quantities of complex-forming species and ligand. The values obtained are the overall values for a mixture of several species of complex, but at high ratios m_{Cl}/m_M they correspond almost completely to the formation of the complexes $ZnCl_4^{2-}aq$ and $CdCl_4^{2-}aq$. After analysing the dependence of ΔC_{pk} on m_{total}, on m_{Cl}/m_M, and on $[Cl^-]_{free}$, the authors cited concluded that the greatest increase in ΔC_{pk} corresponds to the formation of the neutral species, and that ΔC_{pk} is sensitive to the state of the species in the outer sphere.

4. Change in Heat Capacity on the Formation of Ternary and Multi-component Solutions

In addition to the paper already cited[3-6,9-12,15,16,22,23], work in this field has been published by Karapet'yants, Vasilev, and coworkers[91-94,229-237], Latysheva and Andreeva[209,214-216,223,226], and Anderson and coworkers[238,239].

The paper by Karapet'yants, Vasilev, and coworkers are devoted to the study and interpretation of those deviations from additivity which accompany the formation of ternary solutions from two binary solutions when these are isomolal (sometimes isopiestic). Most of the systems studied (mixtures of solutions of alkali and alkaline earth metal halides) do not contain acido-complexes, and the changes in heat capacity accompanying their formation from the binary solutions are extremely small. The authors cited attributed them to slight changes in the structure of the solution and to the redistribution of water between the ions. Work by Anderson and coworkers[238,239] has been carried out in approximately the same direction.

Latysheva and Andreeva[209,214-216,226] studied ΔC_p for the formation of the ternary non-complex-forming solutions $Ca(ClO_4)_2-Zn(ClO_4)_2-H_2O$, $Ca(ClO_4)_2-Cd(ClO_4)_2-H_2O$, and $CaCl_2-Ca(ClO_4)_2-H_2O$ from the corresponding (isomolal) binary solutions. The values obtained are small compared with ΔC_p for the formation of ternary complex-forming systems. The values of ΔC_p are slightly greater in the system formed by solutions of zinc and calcium perchlorates than in the other two systems; in the opinion of the authors cited, this indicates an appreciable redistribution of water between Zn^{2+} and Ca^{2+} cations, which differ significantly in their ability to undergo hydration. Nevertheless, it follows from these papers, and also from the others listed above, that the changes in heat capacity associated only with the redistribution of water between the dissolved electrolytes or with the structural changes in the system on the formation of the ternary solution from the binary solutions are generally small compared with the changes in heat capacity on the dissolution or ionisation of electrolytes, or the formation of acido-complexes. This is evidently related to the fact that the effect of the ions on the heat capacity of the more distant layers of water molecules is much less than that for the nearest molecules.

5. Sharp Change in Heat Capacity within Narrow Ranges of Temperature and Concentration

The few papers which have been published in this field[65,240-245] indicate the possibility of fairly sharp changes in the heat capacity of certain solutions within a narrow range of temperature or concentration. Smirnova and coworkers[240] observed the existence of a maximum on the $\Phi Cp = f(\sqrt{m})$ curve in the range of high concentrations (80–82%) of polyphosphoric acids, and attributed it to a change in the structural form. Latysheva and coworkers[241,242] studied the influence of heating through several degrees on the heat capacity of solutions of strontium perchlorate and manganese sulphate, saturated at temperatures close to the temperature of the change in the composition of the solid phase. The transformations studied were $Sr(ClO_4)_2.4H_2O \rightarrow Sr(ClO_4)_2.2H_2O + 2H_2O$ ($t° = 25.5°$) in the case of strontium perchlorate, and $MnSO_4.5H_2O \rightleftharpoons MnSO_4.4H_2O + H_2O$ ($t° = 27°$) in the case of manganese sulphate. Both systems showed sharp changes in heat capacity, but the form of the curve and the displacement of the temperature of the sudden change with change in concentration are specific for each system. Typical examples of curves for the two systems are shown in Fig. 7. With increase in concentration, the temperature of the sudden change increased in the $Sr(ClO_4)_2-H_2O$ system, and decreased in the $MnSO_4-H_2O$ system. The heat capacity isotherms for these systems also show sharp changes in heat capacity (within a narrow range of concentrations). The phenomena are attributed to a change in the structure of the solutions due to the partial dehydration of the cations, accompanied in the case of the $MnSO_4-H_2O$ system by the formation of acido-complexes. Labowitz and Westrum[243], in a study of the heat capacity of solutions of NH_4F in water at concentrations of 0.005 to 0.50 m and temperatures in the range 55–325°K, found that the heat capacity of the solutions varies very smoothly with temperature at some concentrations, whereas at other concentrations a heat capacity surge is observed at the eutectic temperature. The change from the first solutions to the second apparently corresponds to a significant rearrangement of the solutions within a finite range of concentrations.

In the cases examined, the heat capacity surges were observed at fairly high electrolyte concentrations, so that

they must have been due to changes in the structure of the solution as a whole. At the same time the possibility of a sharp rearrangement in only one component is not excluded. For example, in pure water, breakdown of the collective structure was observed close to 34°.[244] This effect increases when non-polar substances of the benzene type are dissolved in water: the curve giving the temperature dependence of ΔC_p for the dissolution of benzene shows a distinct maximum in the region of 30° (Fig. 8).[245]

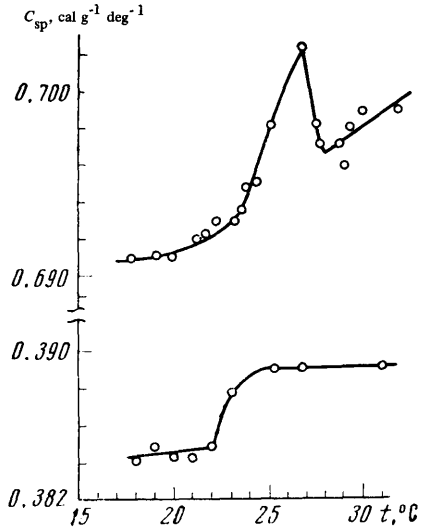


Figure 7. Examples of the form of the temperature dependence of the heat capacity of solutions of $Sr(ClO_4)_2$ (1) and $MnSO_4$ (2) under conditions close to those corresponding to the change in the composition of the solid phase in equilibrium with the solution.

In solutions of strong electrolytes this effect disappears, since the dissolution itself in this case leads to breakdown of the collective structure of water[244]. On the dissolution of substances with a strong ordering influence, on the other hand, the extremal values on the curves giving the temperature dependence of the heat capacity may become even sharper.

Solutions of polyribouridylic, polyriboadenylic, and deoxyribonucleic acids showed sharp heat capacity λ-surges at two temperatures[246]. The cause in this case is apparently the change in the collective hydrophobic interaction of the protein molecules. According to some estimates[247], the hydrophobic interaction between two protein side chains in solution at 25° is characterised by values of ΔC_p in the range from −10 cal mole^{-1} deg^{-1} to −50 cal mole^{-1} deg^{-1}. Berendsen even suggests that hydrophobic bonds are a more important factor in the stabilisation of the native conformation of a protein than intermolecular hydrogen bonds[247]. Breakdown of the hydrophobic interaction is associated with a sharp change in the structure of the surrounding water.

The marked contribution of changes in structure to the value of the heat capacity of solutions may be related to the heat capacity of activation, and moreover it must obviously have a decisive influence on the difference between the isobaric and isochoric heat capacities.

6. Heat Capacity of Activation

This problem was studied by Cobble[248-250], who showed that for the successful development of the theory of reaction rates in aqueous solution there is an extreme lack of data on the relationship between the nature and structure of the activated complexes on the one hand and the values of the energy $\Delta E^{\neq}$, enthalpy $\Delta H^{\neq}$, and entropy $\Delta S^{\neq}$ of activation on the other.

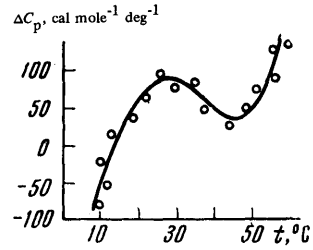


Figure 8. Temperature dependence of ΔC_p for the dissolution of benzene in water.

Cobble assumes that this gap can be filled by studying the heat capacity of activation $\Delta C_p^{\neq}$, which can be determined experimentally (as the temperature coefficient of $\Delta H^{\neq}$) or calculated for an activated complex with a given structural model using the principles of statistical thermodynamics. Additional verification of the description of the symmetry and internal motion in the activated complex is possible by means of a statistical calculation of the $\Delta S^{\neq}$ values, which are related to $\Delta C_p^{\neq}$ by the familiar equation

$$\left(\frac{\partial \Delta S^{\neq}}{\partial T}\right)_p = \frac{\Delta C_p^{\neq}}{T}. \qquad (12)$$

On the other hand, in Cobble's opinion, $\Delta C_p^{\neq}$ can be extimated from experimental data on $\Delta S^{\neq}$ by means of the correspondence principle (p. 808). The results of this estimate for a number of reactions are given in Table 8.

Table 8. Estimated values of $\Delta C_p^{\neq}$ for various reactions[249] at 25°.

Rate-determining reaction	$\Delta C_p^{\neq}]_{25}^{100}$, cal mole^{-1} deg^{-1}
$OCl^- + OCl^- \rightarrow [OClOCl]^{2-\neq}$	98
$[S\dot{O}_3]^{2-} + [S_2O_3]^{2-} \rightarrow [O_3S\dot{O}_2S_2]^{4-\neq}$	75
$[Fe^{\cdot}(CN)_6]^{4-} + [Fe(CN)_6]^{3-} \rightarrow [Fe^{\cdot}(CN)_6\,Fe(CN)_6]^{7-\neq}$	52
$HO_2^- + Co^{3+} \rightarrow [HOCo]^{2+\neq}$	$\leqslant 0$
$[Pu^{\cdot}(OH)]^{3+} + Pu^{3+} \rightarrow [Pu^{\cdot}(OH)\,Pu]^{6+\neq}$	−29
$[Fe^{\cdot}(OH)]^{2+} + Fe^{2+} \rightarrow [F\ddot{e}(OH)\,Fe]^{4+\neq}$	−35
$Cr^{2+} + [(H_2O)\,Co(NH_3)_5]^{3+} \rightarrow [Cr(H_2O)\,Co(NH_3)_5]^{5+\neq}$	~−40
$H^+ + VO_2^+ + Fe^{2+} \rightarrow [HVO_2Fe]^{4+\neq}$	−53

Unlike reactions in gases, reactions in aqueous solutions may have very large $\Delta C_p^{\neq}$ values, which may be

either positive or negative. In the last case it is possible in principle that above a certain inversion temperature the activation energy will be not positive but negative, since

$$\Delta H^{\neq}_{(T_1)} = \Delta H^{\neq}_{(T_1)} + \Delta C^{\neq}_p (T_2 - T_1) \qquad (13)$$

and the kinetics will become retrograde. The problem of retrograde kinetics is now being studied in Cobble's laboratory.

In the opinion of Arnett and coworkers [251], the fluctuations and irregularity in the experimentally determined values of $\bar{C}^0_{p_2}$ for some substances may be due to fluctuations in the values of $\Delta C^{\neq}_p$.

V. HEAT CAPACITY AT CONSTANT VOLUME C_V

Kozhevnikova and Latysheva [50,171,252] determined C_V and $C_p - C_V$ for aqueous solutions of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} perchlorates. Contrary to the previously held opinion, the difference $C_p - C_V$ was found to be fairly large. In addition, the form of the dependence of $\Phi C_p - \Phi C_V$ on the concentration, previously unknown for electrolytes, was determined. All the perchlorates are characterised by a maximum on the $\Phi C_p - \Phi C_V = f(m)$ curve (Fig. 9). To explain the results obtained, these authors put forward a model of the structure of these solutions at different concentrations.

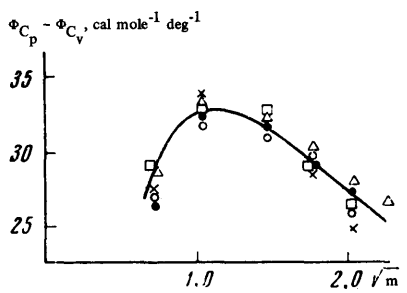


Figure 9. Dependence of the difference $\Phi C_p - \Phi C_V$ for the perchlorates of doubly-charged 3*d* metals (Mn, Co, Ni, Cu, and Zn) on the concentration of the solution.

The determination of C_V has been carried out by Gucker [105,253], but the numerical data [253] are unfortunately not yet available to Soviet readers.

C_V values for solutions of several electrolytes at 25° and 230° have been determined under the direction of Galinker [254,255]. An interesting observation is the marked increase in the difference $C_p - C_V$ with increase in temperature. At the same time there is a sharp decrease in the difference between water and electrolyte solutions. The magnitude of $C_p - C_V$ decreases with increase in concentration at high temperatures, in contrast to the behaviour at low temperatures. The authors cited assume that $C_p - C_V$ is related to the sharp increase in the entropy of the liquid at constant pressure, that is "it is found that a small decrease in the volume of the liquid brings about a marked decrease in the freedom of the thermal motion of the molecules".

---o0o---

The material reviewed demonstrates the deep and complex relationship between the heat capacity of aqueous solutions of electrolytes and the chemical character of the dissolved ions and the solvent. Without establishing the essential features of this relationship we cannot hope to develop the theory of the problem and solve the corresponding applied problems. At the same time the most rigorous route—from the quantum-mechanical description of the ion–molecule interactions to the macro-properties of solutions via statistical thermodynamics—is as yet too difficult. A method which is more accessible at the present time and therefore more promising (the establishment of the relationship between the chemistry of the micro-reactions in solutions and their properties) involves the search for and the thorough analysis of the regular features of the change in properties from one solution to another on the basis of the periodic classification of the elements. It is the (temporary) impossibility of predicting theoretically all the contributions to the heat capacity of a solution with a given composition which makes necessary an analysis of the regular features for a number of systems related to one another by the periodic classification, since in an analysis of this kind the probability that one of the constituent macro-properties will be missed is decreased sharply [129]. For example, the important contribution of the destructive influence of ions to the heat capacity was detected only in analysis of the regular features of the change in the values of $\bar{C}^0_p$ for series of ions of the alkali and alkaline earth metals and the halogens [36,37,50,171], and not from the heat capacity of solutions of any single electrolyte. The addition of the series of 3*d* metal ions [50–53,81,129,171,175,252,256,257] to these series revealed the effect of the interaction energy of the ions with water on heat capacity, and the study of REE ions revealed the influence of the coordination number of the cations [54,55]. A comparative study of the heat capacity of solutions of the chlorides and perchlorates of the elements of the second main group and side group provided further information on the relationship between heat capacity and the formation of acido-complexes in solution [209,213–216,226].

Thus in order to develop the theory of the heat capacity of solutions, the studies must not be restricted to solutions of the simplest salts, that is the alkali halides, and it is necessary to extend the range of materials studied even further, using the logic of the periodic classification. The fruitful results to be obtained from the use of the periodic classification for practical purposes by the method of comparative calculation have been proved convincingly in a large number of papers [124,154,231,232,258,259]. The method makes it possible in many cases to predict the properties of solutions of compounds which are difficult to obtain.

Nevertheless, the problem of increasing the accuracy of experimental methods for the determination of heat capacity, particularly in dilute solutions, remains urgent. The lack of accurate heat capacity data is at present holding back its theoretical analysis. In view of the exceptional complexity of the interpretation of the heat capacity of solutions, it would be extremely useful to have the results of investigations combining a study of heat capacity with an examination of other properties over a wide range of temperatures and pressures [254,255,260].

The development of new methods for estimating individual contributions to the heat capacity of solutions from the results of spectroscopic measurements of different kinds would be extremely useful. Spectra characterising the weak intermolecular interactions and rotations of molecules would be highly important, since the change in intramolecular vibrations as a result of interactions in aqueous solutions of electrolytes makes only a relatively small contribution to the heat capacity [181]. We can also apparently expect to obtain interesting information from studies of the changes in heat capacity in non-equilibrium processes, for example the so-called heat capacity of transfer C^*, determined in the study of the Soret effect [261-264]. In the opinion of Kennerley and coworkers [262], the effect of transfer makes it possible to obtain a pecture of the state of water which is external with respect to the moving particle, that is the hydrated molecule or ion, whereas an overall property of the solution includes the characteristics of all the particles simultaneously.

One of the most important problems related to the study of the heat capacity of aqueous solutions of electrolytes undoubtedly remains the problem of the development of the theory of the liquid state of water.

REFERENCES

1. T. Uemura and S. Hasaba, Technol. Rept. Kansai Univ., 6, 31 (1964).
2. H. Ohe, Y. Ichikawa, K. Kawamura, I. Kajima, and M. Ishiwara, Seni-Gakkaishi, 23, 368 (1967).
3. L. A. Bromley, V. A. Desaussure, J. C. Clipp, and J. S. Wright, J. Chem. Eng. Data, 12, 202 (1967).
4. L. A. Bromley, J. Chem. Eng. Data, 13, 60 (1968).
5. L. A. Bromley, A. E. Diamond, E. Salami, and D. G. Wilkins, J. Chem. Eng. Data, 15, 246 (1970).
6. D. T. Jamieson, J. S. Tudhope, R. Morris, and G. E. Cartwright, Desalination, 7, 23 (1969).
7. W. L. Marshall, J. Phys. Chem., 71, 3584 (1967).
8. D. W. Faletti, I. W. Herrick, and M. F. Adams, J. Electrochem. Soc., 116, 698 (1969).
9. G. Z. Mal'tsev and V. P. Mashovets, Zhur. Prikl. Khim., 38, 92 (1965).
10. V. P. Mashovets, L. V. Puchkov, R. P. Matveeva, and T. A. Baranova, Tsvetn. Metal., 42, 60 (1969).
11. V. P. Mashovets, N. V. Penkina, L. V. Puchkov, and R. P. Matveeva, "Trudy Vsesoyuznoi Nauchno-tekhnicheskoi Konferentsii po Termodinamike Leningradskogo Tekhnologicheskogo Instituta Kholodil'noi Promyshlennosti, Leningrad, 1970" (Proceedings of the All-Union Scientific and Technical Conference on Thermodynamics, Leningrad Technological Institute for the Refrigeration Industry, Leningrad, 1970), p. 248.
12. V. P. Mashovets, N. V. Penkina, L. V. Puchkov, and R. P. Matveeva, "Tezisy Dokladov Vsesoyuznoi Nauchno-tekhnicheskoi Konferentsii po Termodinamike Leningradskogo Tekhnologicheskogo Instituta Kholodil'noi Promyshlennosti, Leningrad, 1968" (Summaries of Papers Presented at the All-Union Scientific and Technical Conference on Thermodynamics, Leningrad Technological Institute for the Refrigeration Industry, Leningrad, 1968), p. 8.
13. V. P. Mashovets, R. P. Matveeva, and L. V. Puchkov, "Tezisy Dokladov 4-i Vsesoyuznoi Konferentsii po Kalorimetrii, LGU, Leningrad, 1968" (Summaries of Papers Presented at the Fourth All-Union Conference on Calorimetry, Leningrad State University, Leningrad, 1968), p. 15.
14. V. P. Mashovets and L. V. Puchkov, "Tezisy Dokladov 2-i Vsesoyuznoi Konferentsii po Teorii Rastvorov" (Summaries of Papers Presented at the Second All-Union Conference on the Theory of Solutions), Izd. Nauka, Alma-Ata, 1968, p. 67.
15. N. V. Penkina and L. V. Puchkov, Zhur. Prikl. Khim., 44, 1554 (1971).
16. N. V. Penkina, L. V. Puchkov, and T. A. Baranova, Zhur. Prikl. Khim., 44, 1890 (1971).
17. L. V. Puchkov, T. A. Baranova, and M. E. Lapidus, Zhur. Prikl. Khim., 43, 455 (1970).
18. V. N. Popov, in Ref. 12, p. 19.
19. V. N. Popov, in Ref. 11, p. 371.
20. S. P. Sukhatme and N. Saikhedkar, Indian J. Technol., 7, 1 (1969).
21. I. A. Parshikov, Zhur. Prikl. Khim., 34, 2649 (1961).
22. V. V. Korchagin, Trudy VNIIG, No. 52, 37 (1967).
23. G. I. Mikulin, in collected papers, "Voprosy Fizicheskoi Khimii Rastvorov Elektrolitov" (Problems in the Physical Chemistry of Electrolyte Solutions), Izd. Khimiya, Leningrad, 1968, p. 401.
24. A. B. Zdanovskii, "Trudy Solyanoi Laboratorii Akademii Nauk SSSR" (Proceedings of the Salt Laboratory of the Academy of Sciences of the USSR), No. 6, 1938.
25. A. B. Zdanovskii, Byull. VNIIG, No. 4, 1 (1938).
26. E. I. Chernen'kaya, "Tezisy Dokladov 4-i Vsesoyuznoi Konferentsii po Kalorimetrii" (Summaries of Papers Presented at the Fourth All-Union Conference on Calorimetry), Izd. Leningrad. Gos. Univ., Leningrad, 1968, p. 47.
27. E. I. Chernen'kaya, Zhur. Prikl. Khim., 44, 1543 (1971).
28. E. I. Chernen'kaya, Zhur. Prikl. Khim., 44, 1721 (1971).
29. H. H. Kellogg, Chem. Abs., 68, 62190z (1968).
30. R. M. Izatt, J. J. Christensen, and J. H. Rytting, Chem. Revs., 71, 439 (1971).
31. M. Born, Ztschr., Phys., 1, 45 (1920).
32. T. J. Webb, J. Amer. Chem. Soc., 48, 2589 (1926).
33. D. H. Everett and W. F. K. Wynne-Jones, Trans. Faraday Soc., 35, 1380 (1939).
34. D. H. Everett and C. A. Coulson, Trans. Faraday Soc., 36, 633 (1940).
35. D. D. Eley, Trans. Faraday Soc., 40, 184 (1944).
36. H. S. Frank and M. W. Evans, J. Chem. Phys., 13, 507 (1945).
37. H. S. Frank and W. Y. Wen, Disc. Faraday Soc., 24, 133 (1957).
38. A. Eucken, Nachr. Ges. Wiss. Göttingen, 1, 36 (1946).
39. A. Eucken, Nachr. Akad. Wiss. Gött., Math-Phys. KI, 1947, H. 2, 33.
40. A. Eucken, Z. Elektrochem., 52, 255 (1948).
41. A. F. Kapustinskii, Zhur. Obshch. Khim., 12, 186 (1942).
42. A. F. Kupustinskii, Acta chimica acad. Sci. Hung., 15, 4 (1958).
43. K. P. Mishchenko and G. M. Poltoratskii, "Voprosy Termodinamiki i Stroeniya Vodnykh i Nevodnykh Rastvorov Elektrolitov" (Problems of the Thermodynamics and Structure of Aqueous and Non-aqueous Solutions of Electrolytes), Izd. Khimiya, Leningrad, 1968.

44. K. P. Mishchenko and A. M. Ponomareva, Zhur. Fiz. Khim., 26, 998 (1952).
45. B. E. Conway, R. E. Verrall, and J. E. Desnoyers, Ztschr. Physik. Chem., 230, 157 (1965).
46. J. E. Desnoyers and C. Jolicoeur, in "Modern Aspects of Electrochemistry", Plenum, Vol. 5, New York, 1969.
47. C. A. Coulson, Proc. Roy. Soc., A255, 69 (1960).
48. D. Feakins and P. Watson, J. Chem. Soc., 4734 (1963).
49. R. M. Noyes, J. Amer. Chem. Soc., 86, 971 (1964).
50. V. A. Latysheva and O. A. Kozhevnikov, in "Termodinamicheskie i Termokhimicheskie Konstanty" (Thermodynamic and Thermochemical Constants), Izd. Nauka, Moscow, 1970, p. 146.
51. O. A. Kozhevnikov, Summary of Candidate's Thesis, Leningrad State University, Leningrad, 1969.
52. O. A. Kozhevnikov and V. A. Latyshev, "Tezisy Dokladov 1-i Mendeleevskoi Diskussii" (Summaries of Papers Presented at the First Mendeleev Discussion), Izd. Khimiya, Leningrad, 1968, p. 52.
53. O. A. Kozhevnikov and V. A. Latysheva, "Tezisy Dokladov 3-i Vsesoyuznoi Konferentsii po Kalorimetrii" (Summaries of Papers Presented at the Third All-Union Conference on Calorimetry), Izd. Moskov. Gos. Univ., Moscow, 1966, p. 75.
54. F. H. Spedding and K. C. Jones, J. Phys. Chem., 70, 2450 (1966).
55. J. P. Walters and F. H. Spedding, Nuclear Sci. Abstr., 23(8), 13 689 (1969).
56. M. S. Vrevskii, Zhur. Russ. Fiz.-Khim. Obshch., 31, 164 (1899).
57. F. Urban, J. Phys. Chem., 36, 1110 (1932).
58. A. G. Samoilovich, Phys. Zts. Sovjetunion, 4, 843 (1933).
59. G. Nemethy and H. A. Scheraga, J. Chem. Phys., 36, 3382, 3401 (1962).
60. V. Vand and W. A. Senior, J. Chem. Phys., 43, 1869 (1965).
61. E. Wicke, Angew. Chem., 78, 1 (1966).
62. R. L. Kay, Adv. Chem. Ser. N73, Trace Inorganic in Water, Copyright, 1968, by Amer. Chem. Soc.
63. R. L. Kay, Chem. Abs., 67, 62 491t (1967).
64. G. C. Kresheck and L. Benjamin, J. Phys. Chem., 68, 2476 (1964).
65. S. Subramanian and J. C. Ahluwalia, J. Phys. Chem., 72, 2525 (1968).
66. T. S. Sarma, R. K. Mohanty, and J. C. Ahluwalia, Trans. Faraday Soc., 65, 2333 (1969).
67. R. K. Mohanty, T. S. Sarma, S. Subramanian, and J. C. Ahluwalia, Trans. Faraday Soc., 67, 305 (1971).
68. G. E. Boyd, Q. V. Larson, and S. Lindenbaum, J. Phys. Chem., 72, 2651 (1968).
69. H. Rueterjans, F. Schreiner, U. Sage, and T. Ackermann, J. Phys. Chem., 73, 986 (1969).
70. K. Buijs and G. Choppin, J. Chem. Phys., 39, 2035 (1963).
71. A. Eucken, Gött. Nach., (Math.-Phys. Kl.), 1 (1949).
72. M. Eigen and E. Wicke, Z. Elektrochem., B55, 354 (1951).
73. T. Ackermann and F. Schreiner, Z. Elektrochem. Ber. Bunsenges. Phys. Chem., 62, 1143 (1958).
74. H. S. Frank and A. S. Quist, J. Chem. Phys., 34, 604 (1961).
75. R. B. Hermann, J. Phys. Chem., 75, 363 (1971).
76. A. Ben-Naim, Trans. Faraday Soc., 66, 2749 (1970).
77. R. A. Lovett and A. Ben-Naim, J. Chem. Phys., 51, 3108 (1969).
78. G. A. Krestov, Izv. Vys. Ucheb. Zaved. SSSR, Khim. i Khim. Tekhnol., 6, 228 (1963).
79. G. A. Krestov and V. I. Klopov, Zhur. Strukt. Khim., 4, 507 (1963).
80. O. Ya. Samoilov, "Struktura Vodnykh Rastvorov Elektrolitov i Gidratatsiya Ionov" (The Structure of Aqueous Solutions of Electrolytes and the Hydration of Ions), Izd. Akad. Nauk SSSR, Moscow, 1957.
81. V. A. Latysheva, in collected papers, "Khimiya i Termodinamika Rastvorov" (Collected Papers on the Chemistry and Thermodynamics of Solutions), No. 2, Izd. Leningrad. Gos. Univ., Leningrad, 1966, p. 119.
82. T. J. Morrison and N. B. Johnstone, J. Chem. Soc., 3441 (1954).
83. G. I. Mikulin, Summary of Doctoral Thesis, Khar'kov State University, 1967.
84. S. I. Drakin, L. V. Lantukhova, and M. Kh. Karapet'yants, Zhur. Fiz. Khim., 41, 98 (1967) [Russ. J. Phys. Chem., No. 1 (1967)].
85. V. F. Myasnikova, S. I. Drakin, and M. Kh. Karapet'yants, Zhur. Fiz. Khim., 43, 2141 (1969) [Russ. J. Phys. Chem., No. 8 (1969)].
86. V. F. Myasnikova, S. I. Drakin, M. Kh. Karapet'yants, and L. V. Lantukhova, Zhur. Fiz. Khim., 42, 2055 (1968) [Russ. J. Phys. Chem., No. 8 (1968)].
87. R. I. Sergeeva, Summary of Candidate's Thesis, Mendeleev Moscow Institute of Chemical Technology, Moscow, 1970.
88. F. T. Gucker and K. H. Schminke, J. Amer. Chem. Soc., 54, 1358 (1932).
89. V. A. Vasilev, Summary of Candidate's Thesis, Mendeleev Moscow Institute of Chemical Technology, Moscow, 1963.
90. M. Kh. Karapet'yants, V. A. Vasilev, and N. V. Fedyainov, Trudy Moskov. Khim.-Tekhn. Inst. im. D. I. Mendeleeva, No. 62, 67 (1969).
91. M. Kh. Karapet'yants, V. A. Vasilev, and N. V. Fedyainov, Trudy Moskov. Khim.-Tekhn. Inst. im. D. I. Mendeleeva, No. 62, 70, (1969).
92. N. V. Fedyainov, V. A. Vasilev, and M. Kh. Karapet'yants, Zhur. Fiz. Khim., 44, 1817 (1970) [Russ. J. Phys. Chem., No. 7 (1970)].
93. M. Kh. Karapet'yants, V. A. Vasilev, and N. V. Fedyainov, Zhur. Fiz. Khim., 44, 1822 (1970) [Russ. J. Phys. Chem., No. 7 (1970)].
94. N. V. Fedyainov, Summary of Candidate's Thesis, Mendeleev Moscow Institute of Chemical Technology, Moscow, 1971.
95. J. C. Ahluwalia and J. W. Cobble, J. Amer. Chem. Soc., 86, 5377 (1964).
96. J. C. Ahluwalia and J. W. Cobble, J. Amer. Chem. Soc., 86, 5381 (1964).
97. E. C. Jekel, C. M. Criss, and J. W. Cobble, J. Amer. Chem. Soc., 86, 5404 (1964).
98. R. E. Mitchell and J. W. Cobble, J. Amer. Chem. Soc., 86, 5401 (1964).
99. E. C. Jekel, Diss. Abstr., 26 (4), 1907 (1965).
100. W. L. Gardiner, R. E. Mitchell, and J. W. Cobble, J. Phys. Chem., 73, 2025 (1969).
101. W. L. Gardner, E. C. Jekel, and J. W. Cobble, J. Phys. Chem., 73, 2017 (1969).
102. W. L. Gardner, Diss. Abstr., B29 (8), 2827 (1969).
103. J. M. Readnour and J. W. Cobble, Inorg. Chem., 8, 2174 (1969).
104. W. L. Gardner, R. E. Mitchell, and J. W. Cobble, J. Phys. Chem., 73, 2021 (1969).

105. F. T. Gucker, Nuclear Sci. Abstr., 21, (22), 40814 (1967).
106. V. P. Kolesov, S. M. Skuratov, and V. Ya. Uvarov, Zhur. Neorg. Khim., 5, 1934 (1960) [Russ. J. Inorg. Chem., No. 9 (1960)].
107. N. P. Novoselov and K. P. Mishchenko, Zhur. Obshch. Khim., 41, 255 (1971).
108. N. P. Novoselov and K. P. Mishchenko, Zhur. Obshch. Khim., 38, 2129 (1968).
109. N. P. Novoselov, Summary of Candidate's Thesis, Leningrad Technical Institute for the Cellulose and Paper Industry, 1969.
110. K. P. Mishchenko and E. A. Podgornaya, Zhur. Obshch. Khim., 31, 1743 (1961).
111. E. A. Podgornaya, Trudy Leningrad. Tekhnol. Inst. im. Lensoveta, No. 61, 43 (1960).
112. G. I. Mikulin, N. P. Novoselov, and K. P. Mishchenko, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., 13, 1433 (1970).
113. N. P. Novoselov and K. P. Mishchenko, Zhur. Fiz. Khim., 45, 1254 (1971) [Russ. J. Phys. Chem., No. 5 (1971)].
114. G. V. Karpenko, K. P. Mischenko, N. P. Novoselov, G. M. Poltoratskii, E. P. Prosviryakova, V. P. Tungusov, and S. V. Shadskii, "Tezisy Dokladov 3-i Vsesoyuznoi Konferentsii po Kalorimetrii" (Summaries of Papers Presented at the Third All-Union Conference on Calorimetry), Izd. Moskov. Gos. Univ., Moscow, 1966, p. 41.
115. N. V. Novoselov and K. P. Mishchenko, "Tezisy Dokladov 3-i Vsesoyuznoi Konferentsii po Kalorimetrii" (Summaries of Papers Presented at the Third All-Union Conference on Calorimetry), Izd. Moskov. Gos. Univ., Moscow, 1966, p. 76.
116. K. P. Mishchenko, Trudy Leningrad. Tekhnol. Inst. Tsell.-Bum. Prom., No. 20, 94 (1967).
117. N. P. Novoselov and K. P. Mishchenko, in Ref. 26, p. 43.
118. N. P. Novoselov and K. P. Mishchenko, in Ref. 52, p. 44.
119. N. P. Novoselov and K. P. Mishchenko, "Tezisy Dokladov 2-i Vsesoyuznoi Konferentsii po Teorii Rastvorov" (Summaries of Papers Presented at the Second All-Union Conference on the Theory of Solutions), Izd. Nauka Kaz. SSR, Alma-Ata, 1968, p. 78.
120. N. P. Novoselov and K. P. Mishchenko, Zhur. Obshch. Khim., 41, 489 (1971).
121. R. I. Sergeeva, S. I. Drakin, and M. Kh. Karapet'yants, Zhur. Fiz. Khim., 44, 2611 (1970) [Russ. J. Phys. Chem., No. 10 (1970)].
122. R. I. Sergeeva, S. I. Drakin, and M. Kh. Karapet'yants, Zhur. Fiz. Khim., 44, 2922 (1970) [Russ. J. Phys. Chem., No. 11 (1970)].
123. S. I. Drakin, V. F. Myasnikova, and M. Kh. Karapet'yants, in Ref. 26, p. 46.
124. M. Kh. Karapet'yants, V. A. Vasilev, K. K. Vlasenko, N. V. Fedyainov, and A. P. Lebedeva, "Tezisy Dokladov 5-i Vsesoyuznoi Konferentsii po Kalorimetrii" (Summaries of Papers Presented at the Fifth All-Union Conference on Calorimetry), Izd. Moskov. Gos. Univ., Moscow, 1971, p. 193.
125. S. I. Drakin and M. Kh. Karapet'yants, in Ref. 52, p. 18.
126. S. I. Drakin, M. Kh. Karapet'yants, and V. F. Myasnikova, in Ref. 119, p. 33.
127. E. R. Gardner, Trans. Faraday Soc., 65, 91 (1969).
128. L. Benjamin, Canad. J. Chem., 41, 2210 (1963).
129. V. A. Latyshev, in "Materialy Vsesoyuznogo Simpoziuma po Termokhimii Rastvorov Elektrolitov i Neelektrolitov, Ivanovo, 1971" (Proceedings of the All-Union Symposium on the Thermochemistry of Solutions of Electrolytes and Non-electrolytes, Ivanovo, 1971), p. 41.
130. V. B. Parker, Thermal Properties of Aqueous Uni-univalent Electrolytes, US NBS Refer. Data, No. 2 (1965).
131. C. M. Criss and J. W. Cobble, J. Amer. Chem. Soc., 83, 3223 (1961).
132. G. N. Lewis and M. Randall, "Thermodynamics", New York, 1961.
133. G. A. Krestov and V. K. Abrosimov, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., 10, 1005 (1967).
134. V. A. Kobenin, G. A. Krestov, and V. K. Abrosimov, in Ref. 26, p. 47.
135. V. A. Kobenin, Summary of Candidate's Thesis, Ivanovo Institute of Chemical Technology, 1970.
136. L. P. Masal'skaya, E. I. Akhumov, K. P. Mishchenko, and G. M. Poltoratskii, "Tezisy Dokladov 5-i Vsesoyuznoi Konferentsii po Kalorimetrii" (Summaries of Papers Presented at the Fifth All-Union Conference on Calorimetry), Izd. Moskov. Gos. Univ., Moscow, 1971, p. 158.
137. I. I. Lonkevich, K. P. Mishchenko, and S. V. Shadskii, Zhur. Obshch. Khim., 39, 1210 (1969).
138. H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", 3rd Edition, Reinhold Publ. Corp., New York, 1958, p. 354.
139. "Selected Values of Chemical Thermodynamic Properties", N. B. S., 1965, p. 1.
140. M. Randall and F. D. Rossini, J. Amer. Chem. Soc., 51, 323 (1929).
141. A. F. Kapustinskii, B. M. Yakushevskii, and S. I. Drakin, Zhur. Fiz. Khim., 27, 588 (1953).
142. T. W. Richards and M. Dole, J. Amer. Chem. Soc., 51, 794 (1929).
143. C. L. De Ligny, M. Alfenaar, and N. G. Van der Veen, Rec. trav. chim. Pays-Bas, 87, 585 (1968).
144. T. Ackermann, Z. Phys. Chem., N. F., 27, 253 (1961).
145. G. A. Krestov and V. A. Kobenin, in Ref. 129, p. 165.
146. C. M. Criss and J. W. Cobble, J. Amer. Chem. Soc., 86, 5390 (1964).
147. C. M. Criss and J. W. Cobble, J. Amer. Chem. Soc., 86, 5385 (1964).
148. G. B. Naumov, B. N. Ryzhenko, and I. L. Khodakovskii, "Spravochnik Termodinamicheskikh Velichin" (Reference Book of Thermodynamic Quantities), Atomizdat, 1971.
149. G. B. Naumov, B. N. Ryzhenko, and I. L. Khodakovskii, Geokhimiya, 795 (1968).
150. I. L. Khodakovskii, B. N. Ryzhenko, and G. B. Naumov, Geokhimiya, 1486 (1968).
151. I. L. Khodakovskii, Geokhimiya, 57 (1969).
152. G. B. Naumov and I. L. Khodakovskii, Dokl. Akad. Nauk SSSR, 170, 886 (1966).
153. G. A. Krestov and V. A. Kobenin, Izv. Vys. Ucheb. Zaved., 13, 1722 (1970).
154. M. Kh. Karapet'yants, "Metody Sravnitel'nogo Rascheta Fiziko-khimicheskikh Svoistv" (Methods for the Comparative Calculation of Physicochemical Properties), Izd. Nauka, Moscow, 1965.
155. G. A. Krestov and V. K. Abrosimov, Zhur. Strukt. Khim., 8, 822 (1967).
156. G. A. Krestov and V. K. Abrosimov, Zhur. Strukt. Khim., 5, 510 (1964).

157. G. A. Krestov, Zhur. Strukt. Khim., 3, 137 (1962).
158. G. A. Krestov, Izv. Vys. Ucheb. Zaved. SSSR, Khim. i Khim. Tekhnol., 6, 408 (1963).
159. Atomic Energy Levels, Vol. II, by C. E. Moore, Circular N. B. of Std., 467 (1952).
160. A. G. Turnbull, "Second Australian Conference on Electrochemistry, Melbourne, 1968 (abstr.)", p. 7.
161. J. L. Kurz, J. Amer. Chem. Soc., 89, 3524 (1967).
162. S. I. Drakin, R. Kh. Kurmalieva, and M. Kh. Karapet'yants, Zhur. Teor. i Eksper. Khim., 2, 52 (1966).
163. S. I. Drakin, Zhur. Strukt. Khim., 4, 514 (1963).
164. G. M. Mrevlishvili and P. L. Privalov, Zhur. Strukt. Khim., 9, 8 (1968).
165. P. L. Privalov and G. M. Mrevlishvili, Biofizika, 11, 951 (1966).
166. S. I. Drakin, L. V. Lantukhova, and M. Kh. Karapet'yants, Zhur. Fiz. Khim., 40, 451 (1966) [Russ. J. Phys. Chem., No. 2 (1966)].
167. A. Ya. Stagis, Summary of Candidate's Thesis, Leningrad Technological Institute for the Cellulose and Paper Industry, Leningrad, 1970.
168. K. P. Mishchenko and A. Ya. Stagis, Zhur. Obshch. Khim., 40, 2537 (1970).
169. G. C. Kresheck, J. Chem. Phys., 52, 5966 (1970).
170. K. P. Mishchenko, in Ref. 52, p. 3.
171. V. A. Latysheva, S. V. Karavan, and O. A. Kozhevnikov, in collected papers, "Problemy Sovremennoi Khimii Koordinatsionnykh Soedinenii" (Collected Papers on Problems of the Present-day Chemistry of Coordination Compounds), Izd. Leningrad. Gos. Univ., Leningrad, 1970, No. 3, p. 95.
172. S. V. Karavan, Summary of Candidate's Thesis, Leningrad State University, 1969.
173. S. V. Karavan and V. A. Latysheva, "Tezisy Dokladov Soveshchaniya po Probleme Sovremennoi Khimii Koordinatsionnykh Soedinenii" (Summaries of Papers Presented at the Conference on Problems in the Present-day Chemistry of Coordination Compounds), Izd. Khimiya, Leningrad, 1966, p. 21.
174. V. A. Latysheva, in Ref. 52, p. 27.
175. S. V. Karavan and V. A. Latysheva, in Ref. 52, p. 28.
176. L. S. Lilich, in collected papers, "Problemy Sovremennoi Khimii Koordinatsionnykh Soedinenii" (Collected Papers on Problems in the Present-day Chemistry of Coordination Compounds), Izd. Leningrad. Gos. Univ., 1966, No. 1, p. 97.
177. G. A. Krestov, in Ref. 129, p. 52.
178. I. Grenthe, H. Ots, and O. Ginstrup, Acta Chem. Scand., 24, 1067 (1970).
179. J. F. Coetzee and C. D. Ritchie (Editors), "Solute-solvent Interaction", New York, London, 1969, p. 1.
180. C. S. Leung and E. Grunwald, J. Chem. Phys., 74, 687 (1970).
181. E. J. King, "Acid-base Equilibria", Pergamon Press, New York, 1965.
182. P. Lumme, P. Lahermo, and J. Tummavuori, Acta Chem. Scand., 19, 2175 (1965).
183. J. Tummavuori and P. Lumme, Acta Chem. Scand., 32, 2003 (1968).
184. D. J. G. Ives and P. D. Marsden, J. Chem. Soc., 649 (1965).
185. E. C. W. Clarke and D. N. Glew, Trans. Faraday Soc., 62, 539 (1966).
186. J. J. Christensen, H. D. Johnston, and R. M. Izatt, J. Chem. Soc. (A), 454 (1970).
187. J. J. Christensen, J. L. Oscarson, and R. M. Izatt, J. Amer. Chem. Soc., 90, 5949 (1968).
188. V. P. Vasil'ev and L. A. Korchagina, Zhur. Fiz. Khim., 40, 3024 (1966) [Russ. J. Phys. Chem., No. 12 (1966)].
189. R. P. Bell, "The Proton in Chemistry", Cornell Univ. Press, Ithaca, New York, 1959.
190. A. N. Pant, R. N. Soni, and S. L. Gupta, Indian J. Chem., 9, 270 (1971).
191. R. N. Roy and B. Sen, J. Chem. Eng. Data, 13, 79 (1968).
192. N. M. Nikolaeva, "Kratkie Soobshcheniya Nauchno-tekhnicheskoi Konferentsii Termodinamika i Struktura Gidroksokompleksov v Rastvorakh" (Brief Reports from the Scientific and Technical Conference on the Thermodynamics and Structure of Hydroxo-complexes in Solution), Izd. Leningrad. Tekhnol. Inst. im. Lensoveta, Leningrad, 1971, p. 10.
193. G. R. Kolonin, T. P. Aksenova, and S. K. Ryakhovskaya, "Kratkie Soobshcheniya Nauchno-tekhnicheskoi Konferentsii Termodinamika i Struktura Gidroksokompleksov v Rastvorakh" (Brief Reports from the Scientific and Technical Conference on the Thermodynamics and Structure of Hydroxo-complexes in Solution), Izd. Leningrad. Tekhnol. Inst. im. Lensoveta, Leningrad, 1971, p. 12.
194. K. A. Burkov, N. I. Zinevich, and L. S. Lilich, "Kratkie Soobshcheniya Nauchno-tekhnicheskoi Konferentsii Termodinamika i Struktura Gidroksokompleksov v Rastvorakh" (Brief Reports from the Scientific and Technical Conference on the Thermodynamics and Structure of Hydroxo-complexes in Solution), Izd. Leningrad. Tekhnol. Inst. im. Lensoveta, Leningrad, 1971, p. 16.
195. T. E. Rogers and G. M. Waind, Trans. Faraday Soc., 57, 1360 (1961).
196. D. D. Perrin, J. Chem. Soc., 2197 (1962).
197. D. D. Perrin, J. Chem. Soc., 4500 (1962).
198. J. A. Bolzan and A. J. Arvia, Eleketrochim. Acta, 7, 589 (1962).
199. R. L. Pecsok and A. N. Fletcher, Inorg. Chem., 1, 155 (1962).
200. J. A. Bolzan and A. J. Arvia, Electrochim. Acta, 8, 375 (1963).
201. Yu. A. Volokhov, L. N. Pavlov, N. I. Eremin, and V. E. Mironov, Zhur. Prikl. Khim., 44, 246 (1971).
202. R. Arnek, Ark. Kemi, 32, 55 (1970).
203. A. McAuley and G. H. Nancollas, J. Chem. Soc., 2215 (1961).
204. S. Boyd, J. R. Brannan, H. S. Dunsmore, and G. H. Nancollas, J. Chem. Eng. Data, 12, 601 (1967).
205. J. R. Brannan, H. S. Dunsmore, and G. H. Nancollas, J. Chem. Soc., 304 (1964).
206. V. S. K. Nair and G. H. Nancollas, J. Chem. Soc., 4367 (1961).
207. V. P. Vasil'ev and G. A. Lobanov, Zhur. Fiz. Khim., 41, 1969 (1967) [Russ. J. Phys. Chem., No. 8 (1967)].
208. V. P. Vasil'ev and G. A. Lobanov, Zhur. Neorg. Khim., 12, 878 (1967) [Russ. J. Inorg. Chem., No. 4 (1967)].
209. V. A. Latysheva and I. N. Andreeva, Zhur. Fiz. Khim., 43, 483 (1969) [Russ. J. Phys. Chem., No. 2 (1969)].
210. L. A. Kochergina and V. P. Vasil'ev, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., 13, 1448 (1970).
211. O. D. Bonner, H. Dolyniuk, C. F. Jordan, and G. B. Hanson, J. Inorg. Nuclear Chem., 24, 689 (1962).
212. T. I. Kunin, A. A. Shutov, and L. I. Pankratova, Zhur. Prikl. Khim., 34, 451 (1961).

213. R. A. Aleksandrova, O. A. Kozhevnikov, V. A. Latysheva, I. N. Sarafanova, and N. A. Shcherbakova, in "Tezisy Dokladov 2-i Vsesoyuznoi Konferentsii po Kalorimetrii" (Summaries of Papers Presented at the Second All-Union Conference on Calorimetry), Leningrad, 1963, p. 30.
214. V. A. Latysheva and I. N. Andreeva, in Ref. 26, p. 45.
215. I. N. Andreeva, V. A. Latysheva, and A. N. Goldenberg, in "Tezisy Dokladov na X Vsesoyuznogo Soveshchaniya po Khimii Kompleksnykh Soedinenii" (Summaries of Papers Presented at the Tenth All-Union Conference on the Chemistry of Complex Compounds), Izd. Naukova Dumka, Kiev, 1969, p. 68.
216. V. A. Latysheva and I. N. Andreeva, Zhur. Obshch. Khim., 41, 1649 (1971).
217. V. P. Vasil'ev, Zhur. Fiz. Khim., 42, 1830 (1968) [Russ. J. Phys. Chem., No. 7 (1968)].
218. V. P. Vasil'ev and V. N. Vasil'eva, Zhur. Fiz. Khim., 41, 1675 (1967) [Russ. J. Phys. Chem., No. 7 (1967)].
219. V. P. Vasil'ev, in Ref. 26, p. 48.
220. V. P. Vasil'ev, in Ref. 129, p. 88.
221. V. P. Vasil'ev, G. A. Lobanov, and L. A. Kochergina, in Ref. 52, p. 28.
222. V. P. Vasil'ev and V. N. Vasil'eva, Zhur. Fiz. Khim., 45, 564 (1971) [Russ. J. Phys. Chem., No. 3 (1971)].
223. V. A. Latysheva and I. N. Andreeva, in collected papers, "Khimiya i Termodinamika Rastvorov" (Collected Papers on the Chemistry and Thermodynamics of Solutions), No. 3, Izd. Leningrad. Gos. Univ., Leningrad, 1972.
224. N. N. Baranova, Zhur. Neorg. Khim., 14, 3257 (1969) [Russ. J. Inorg. Chem., No. 12 (1969)].
225. G. H. Nancollas, Croat. Chem. Acta, 42, 311 (1970).
226. I. N. Andreeva, Summary of Candidate's Thesis, Leningrad State University, Leningrad, 1971.
227. J. H. Dee, Diss. Abstr., 29B, 4128 (1969).
228. A. McAuley and G. H. Nancollas, J. Chem. Soc., 4458 (1961).
229. A. F. Kapustinskii, M. S. Stakhanova, and V. A. Vasilev, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 12, 2089 (1960).
230. Yu. A. Epikhin, M. S. Stakhanova, and M. Kh. Karapet'yants, Zhur. Fiz. Khim., 40, 377 (1966) [Russ. J. Phys. Chem., No. 2 (1966)].
231. M. S. Stakhanova, M. Kh. Karapet'yants, V. A. Vasilev, I. V. Bazolova, and K. K. Vlasenko, in collected papers, "Redkie Shchelochnye Elementy" (Collected Papers on the Rare Alkali Metals), Izd. Perm. Politekhn. Inst., Perm', 1969, p. 185.
232. M. Kh. Karapet'yants and K. K. Vlasenko, Zhur. Fiz. Khim., 44, 1920 (1970) [Russ. J. Phys. Chem., No. 8 (1970)].
233. V. A. Vasilev, N. V. Fedyainov, and M. Kh. Karapet'yants, Trudy Moskov. Khim.-tekhnol. Inst. im. D. I. Mendeleeva, Fiz. Khim. i Elektrokhim., No. 57, 31 (1970).
234. M. Kh. Karapet'yants and K. K. Vlasenko, Zhur. Fiz. Khim., 44, 2333 (1970) [Russ. J. Phys. Chem., No. 9 (1970)].
235. K. K. Vlasenko, Summary of Candidate's Thesis, Mendeleev Moscow Institute of Chemical Technology, Moscow, 1970.
236. V. A. Vasilev, N. V. Fedyainov, M. Kh. Karapet'yants, and T. F. Fedotova, Trudy Moskov. Khim. -tekhnol. Inst. im. D. I. Mendeleeva, No. 67, 31 (1970).
237. V. A. Vasilev, N. F. Fedyainov, M. Kh. Karapet'yants, and T. I. Serefimova, Zhur. Fiz. Khim., 45, 1867 (1971) [Russ. J. Phys. Chem., No. 7 (1971)].
238. H. L. Anderson and L. A. Petree, J. Phys. Chem., 74, 1455 (1970).
239. H. L. Anderson, R. D. Wilson, and D. E. Smith, J. Phys. Chem., 75, 1125 (1971).
240. E. P. Smirnova, N. L. Matveichuk, A. D. Mikhailin, and V. V. Illarionov, Dokl. Akad. Nauk SSSR, 189, 344 (1969).
241. V. A. Latysheva and A. S. Bondarev, in Ref. 53, p. 47.
242. V. A. Latysheva, A. S. Bondarev, and S. V. Shishkina, in Ref. 14, p. 56.
243. L. C. Labowitz and E. F. Westrum, J. Phys. Chem., 65, 408 (1961).
244. F. Franks and D. J. G. Ives, J. Chem. Soc., 741 (1960).
245. F. Franks, M. Gent, and H. H. Johnson, J. Chem. Soc., 2716 (1963).
246. T. Ackermann, in Proc. Ist. Intern. Conf. Calorimetry and Thermodynamics, Warsaw, 1969.
247. Arthur Cole (Editor), "Theoretical and Experimental Biophysics", Vol. I, New York, 1967.
248. J. W. Cobble, Science, 152, 1479 (1966).
249. J. W. Cobble, Proc. 8th, Int. Conf. Coord. Chem., Vienna, 1964, p. 439.
250. J. W. Cobble, J. Amer. Chem. Soc., 86, 5394 (1964).
251. E. M. Arnett, W. B. Kover, and J. V. Carter, J. Amer. Chem. Soc., 91, 4028 (1969).
252. O. A. Kozhevnikov, L. P. Makarenkova, and V. A. Latysheva, Izv. VUZov, Khim. i Khim. Tekhn., 14, 694 (1971).
253. F. T. Gucker, U. S. At. Energy Comm., COO-504-11 (1967).
254. I. M. Rodnyanskii, V. I. Korobkov, and I. S. Galinker, Zhur. Fiz. Khim., 36, 2216 (1962) [Russ. J. Phys. Chem., No. 10 (1962)].
255. I. S. Galinker, I. M. Rodnyanskii, V. I. Korobkov, and N. B. Lekakh, Ukr. Fiz. Zhur., 9, 401 (1964).
256. S. V. Karavan and V. A. Latysheva, Zhur. Neorg. Khim., 16, 2020 (1971) [Russ. J. Inorg. Chem., No. 7 (1971)].
257. V. A. Latysheva, Zhur. Org. Khim., 41, 1889 (1971).
258. M. S. Stakhanova, M. Kh. Karapet'yants, V. A. Vasilev, and Yu. A. Epikhin, Zhur. Fiz. Khim., 38, 2420 (1964) [Russ. J. Phys. Chem., No. 10 (1964)].
259. V. A. Vasilev and E. Ya. Shevchenko, Izv. VUZov, Khim. i Khim. Tekhn., 13, 789 (1970).
260. A. P. Rutskov, Zhur. Fiz. Khim., 34, 734 (1960) [Russ. J. Phys. Chem., No. 4 (1960)].
261. H. J. V. Tyrrell and M. Zamon, J. Chem. Soc., 6126 (1964).
262. M. Kennerley, H. J. V. Tyrrell, and M. Zamon, J. Chem. Soc., 1041 (1966).
263. M. Kennerley and H. J. V. Tyrrell, J. Chem. Soc. (A), 607 (1968).
264. A. J. De-Bethune and H. D. Dalay, J. Electrochem. Soc., 116, 1395 (1969).

Leningrad State University,
Department of Inorganic
Chemistry