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ABSTRACT

Reported are the findings of the Uspekhi experiment in creating a labeled machine file, as well as sample products of this system - an article from a scientific journal and an index page. Production cost tables are presented for the machine file, primary journals, and journal indexes. Comparisons were made between the 1965 predicted costs and the actual 1969 costs. Despite the greater 1969 production cost, the authors anticipated cost reductions with the implementation of advanced equipment; such as Cathode-ray tube (CRT) equipment, on-line PDP-8 editing equipment, adequate Photon disc and translation bridge from Scientific Keyboard Input Language (SKIL) to Scientific Information Processing Language (SIPL), and suitable character set for CRT typesetting equipment. (RR)

CREATION OF A MACHINE FILE AND SUBSEQUENT COMPUTER-ASSISTED PRODUCTION OF PUBLISHING OUTPUTS, INCLUDING A TRANSLATION JOURNAL AND AN INDEX

Status of *Uspekhi* Experiment, July 1969;
Report to the American Institute of Physics

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Status of *Uspekhi* Experiment
July 1969

Summary

The main points of the June 1965 Buckland-Weaver proposal to AIP for an experiment in creating a labeled machine file together with some of the assorted by-product publishing outputs, have now been successfully carried out.

Eighteen pages of journal photocomposition appended hereto were generated from a labeled machine file of *Uspekhi* data by computer programs, as planned. A sample of an index page, similarly generated, but from a different journal,* is also included.

These programs are tested and ready to be used in the production of further journals and indexes.

Costs and procedure breakdowns are shown in Table II-VI. Production details will be seen to have varied in some cases from the 1965 concepts, but not the concepts themselves.

Comparisons between 1965 predicted costs and actual costs in 1969 are shown in Tables VII-IX.

Briefly:

- The machine file right now costs about 18% more than predicted; it will cost slightly less (6%) within the year.
- The journal page output costs at this point 24% more than predicted, mainly due to poorly adapted character generating equipment. CRT character generation promises a lowering of these costs significantly—to 27% below 1965 predictions.
- Index output presently costs 14% more than predicted, with the promise of substantial savings dependent upon the use of CRT equipment.
- The systems developed can be applied without changes to immediate *Uspekhi* production at a cost of $37.91 per (English) page. With the installation of on-line PDP-8 editing equipment (planned for Fall), the page cost drops to $34.00. Further im-

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**The Physical Review.*

provements (provision of an adequate Photon disc and a translation bridge from SKIL to SIPL*) would reduce the page cost to $31.00. With an investment in a translation program and a suitable character set for CRT typesetting equipment, the page price falls to $24.00.

- Assuming the addition to TPS of display-equation programs, SKIL access, and the CRT character generator bridge, one can try to predict per-page costs for a primary journal on the *Uspekhi* model:

Operation	*Per page costs (6700 cc)*
Copymark	$ 1.00
Keyboard text (4,200 cc)	6.60*
Keyboard equations (equiv. 2,500 cc)	6.00*
Proofread (1) all data	4.00
Proofread (2) storage data only	.40
Edit and correct	2.80
Edit-display monitor	1.30
Generate master file	1.10
TPS, including equations	4.20
CRT proof run (for author)	3.30
Keyboard additional corrections	2.00
CRT final run	3.30
Page makeup, manual	3.00
Proofs, miscellany	1.00
TOTAL	$40.00

*For simplicity, it is assumed that illustration, tabular material, etc. can be handled within the cost limits for a 60-40 text-equation mix.

Procedures: Creating the Machine File

Copymarking

It will be seen from Table II that only $.70 per page has been allocated to copymarking. This is a low figure compared to the line for this item in AIP's normal production budget. One of the major reasons for this is that the data for *Uspekhi* has already been typeset once in Russia, and a style established during this process.

It has been found in other experiments, however, that even for primary manuscript the amount of copymarking necessary to guide keyboard operators through material of this complexity is minimal; certainly far less than in conventional direct-setting systems. To a large extent the reason for this is that the need for repetition

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*See *SKIL: Science Keyboard Input Language*, V. Weaver, October 1968, a report to AIP. SIPL is an acronym for *Scientific Information Processing Language*, used in Inforonics' Master File.

of complex strings of typographical commands is avoided. The entire command for choosing a typeface, leading, measure, and format for a footnote. for example, is **fn**. More than 250 separate information items exist in the *Uspekhi* program, but the identification vocabulary is considerably smaller. **Eq**, meaning **equation**, has different control meanings depending on whether it occurs in a **text** or **footnote**.

Another reason is that identifier language is chosen for mnemonic value. If □**m** transfers the keyboarder to the **mathematics** character set, then a calls out an **arrow**, g calls out **greater than**, and i calls out **infinity**. These are standard for all typefaces and jobs, and are quickly learned. Since only the general identification is required (the specific choice of typeface and point size being made by the computer), there would be no point in copymarking such occurrences.

In practice, about 20 labels (**fn**, **tx**, **eq**, etc.), each with easy mnemonic associations, keep recurring, and these can be written in the manuscript margins by people withhlittle or no typographical background.

Codes

Creation of the machine file requires that all data be labeled as to its nature so that future uses, including typographical ones, can be designed to take advantage of the labeling. (Author names, for example, can be searched and/or typeset distinctively, provided they are flagged.)

In addition, certain purely typographical functions (such as the use of boldface for vector expressions, for example) are embedded in the data, since they do not follow simple deductive rules.

It is interesting that in the present case the number of tape codes required to label the data on input is almost the same as the number of control codes required on the Photon tape (see Table I). They are, of course, quite different. The recognition that β belongs to the **Greek** character set and the assignment of a prefix □g to the b code, does not require the same degree of mathematical or typographical sophistication needed to recognize that the β must be italic because it is embedded in a mathematical expression and that a certain Photon matrix position and lens must be synchronized to produce the proper point size on output.

It is surprising that the number of codes needed in the two cases is so nearly equal. One objective of input system design should be to make fewer input codes do the job.

The SKIL system (described in reports of March and October 1968 to AIP) moves in this direction, cutting the number of keyboard labeling codes by 40%, actually somewhat below the number needed to tag the data in machine storage.

Since the program to translate SKIL input into master-file codes is still missing, no consideration of the effect of this potentially powerful tool is given in the cost analysis section of this report.

Keyboarding

Input languages used in these experiments have been largely independent of the kind of equipment employed. Custom built keyboards have been avoided, and input systems have been designed to work within the standard 44-keybutton range. Costs shown in the tables are based on work with paper-tape perforating keyboards. Experiments for other purposes have convinced us that magnetic tape keyboards are faster and more reliable. Table IV, showing costs for a Fall 1969 production system, is built around the use of an IBM Selectric keyboard (#735 I/O), linked to a time-shared computer and writing a magnetic tape whose records (typewriter lines) are immediately numbered and made accessible to a keyboard-operated editing program.

This system, known as Astrocomp, is being marketed by Information Control Systems, Inc., of Ann Arbor, Michigan. It is scheduled to be installed at VWC in August, and we hope it will be operating shortly thereafter.

Using this system, control language is identified by a key-controlled shift to **control mode** which is accompanied by a ribbon color shift. Otherwise, the keyboard is the standard IBM Graphics configuration, on 44 buttons.

Astrocomp is discussed further under *Editing.*

Listback and Proofreading

For all input systems in which hardcopy is to be proofread, we have employed a listing of the keyboarded tapes to provide an accurate record of codes and to identify, via a parity check, as many machine errors as possible.

The actual method of production for the Martynov article (Table II) included a listback of DURA tapes before proofreading.

The recommended method (Table III) substitutes for this an immediate conversion to magnetic tape and a line-printer dump to obtain proofreading copy. This step provides a better check of codes, and also a larger character set (and therefore fewer characters to be proofread in coded form).

From a proofreader's standpoint, an ideal initial printout would involve the full character set, and enough formatting to verify that item labels had been correctly recorded (including, of course, the assembly of displayed equations when that becomes part of the system). Such a system—involving a preliminary Photon output in a typographical form designed exclusively for efficient proofreading, and not intended for any publishing output—is being used to produce *The Physical Review Index,* but has not yet been designed for *Uspekhi.*

Considering that the computer processing and character-generation time and expense for such an ideal step would probably be only very slightly less than that for actually producing journal pages, it is doubtful whether this is a practical feature of any system designed to handle translation journals. Where a proof of his data must be submitted to an author for approval, the costs of such a procedure may seem less formidable.

It will be noted that Table I reflects two complete and independent proofreadings of the input data file. If the entire file is to be stored in machine form, this is the recommended procedure. If, however, the file be thought of as having two parts: one, those items to be stored for later search and processing, and two, those items that will be used only once—for typographical production of the primary journal; the proofreading technique can be altered. A single proofreading can be given the "journal only" portions (which is the present practice under conventional production methods), with a double reading reserved for the "storage" portions of the file. This is the procedure shown in Tables III and IV. The assumption is that the "journal-only" part of the file will be discarded after output of the journal pages.

Editing and Master-File Generation

Tables II and III include the use of Inforonics' CRT-monitored Edit-Display programs for correction of the data. Changes are made as the tapes are fed into the Master File. A human editor works from marks previously made on a listback hard-copy, and checks his work immediately on a scope display.

Table IV recommends use of the Astrocomp editing and correction programs. These are not unlike the IBM Datatext package (also called the Administrative Terminal System). Checking is not via CRT, but via computer-controlled printout on the Selectric I/O; a slower, but cheaper method. Since the system is not yet installed, reliable predictions as to price cannot be made. A small allowance is left in the budget for continued monitoring of the read-in operation, with the hope that this step will prove unnecessary.

The Master File format is a standardized coding scheme used within the Inforonics Text Processing Service. It forms the basis for all future file manipulation and storage functions.

Cost Tables

TABLE I. Comparative output character and code counts for the Martynov article.

	Total	*Per English page*	*Percent of nondata codes*
Input keyboard codes, Inforonics keyboard language	87,800	5,100	18
Input keyboard codes, SKIL	81,400	4,750	12
Master file (storage) codes	84,756*	4,930	15
Typesetting tape codes, Photon (for journal pages)	87,552*	5,100	18
Output (printing) characters and spaces (journal pages)	71,800	4,200	–

*These two totals are computer-counted. Other totals are human estimates.

TABLE II. Step-by-step costs for production of the machine file for the Martynov article, actual method.

	Hours	*Rate*	*Total*	*Per thousand output characters*	*Per page*[1]
Copymark	1.5	$ 8.	$ 12.00	$ .17	$ .70
Keyboard[2]	12.3	11.	136.00	1.90	7.90
Listback	2.4	4.	7.60	.14	.56
Proofread (1st)	6.0	8.	48.00	.67	2.81
Proofread (2nd)	6.0	8.	48.00	.67	2.81
Consolidate marks	2.0	8.	16.00	.23	.94
Edit display			102.00	1.42	5.93
Generate master file	.25	45.	11.25	.16	.66
TOTALS				$5.36	$22.31

[1] A convenient unit for comparison; there is no such thing in the machine file, of course.

[2] DURA Mach 10. Paper tape. Inforonics keyboard language.

TABLE III. Step-by-step costs for production of machine file, recommended and immediately applicable method.

	Hours	*Rate*	*Total*	*Per thousand output characters*	*Per page*
Copymark	1.5	$ 8.	$ 12.00	$ .17	$ .70
Keyboard[1]	12.3	11.	136.00	1.90	7.90
Convert to mag tape, dump on line printer[2]	.67	45.	30.00	.42	1.75
Proofread (1st)[3]	4.2	8.	33.60	.47	1.97
Proofread (2nd)[4]	.5	8.	4.00	.06	.24
Edit display			102.00	1.42	5.93
Generate master file[5]	.25	45.	11.25	.16	.66
TOTALS				$4.60	$19.15

[1] DURA. Inforonics language.

[2] 120-character chain. Partial typographic conversion.

[3] Read full record.

[4] Read storage data only. Storage data consists of information items to be retrieved for other purposes than primary journal production.

[5] Full record.

TABLE IV. Step-by-step costs for production of machine file, recommended and applicable in the Fall of 1969.

	Hours	*Rate*	*Total*	*Per thousand output characters*	*Per page*
Copymark	1.5	$ 8.	$ 12.00	$ .17	$ .70
Keyboard[1]	11.3	12.	136.00	1.90	7.90
Listback[2]	2.6	5.	13.00	.18	.76
Proofread (1st)[3]	5.0	8.	40.00	.56	2.34
Proofread (2nd)[4]	.6	8.	4.80	.07	.28
Edit and correct[5]	2.0	15.	30.00	.42	1.76
Edit display[6]			14.50	.20	.84
Generate master file	.25	45.	11.25	.16	.66
TOTALS				$3.66	$15.24

1. Inforonics language. Selectric #73 735 I/O.
2. #735 I/O.
3. Complete record.
4. Storage data only.
5. Astrocomp editing programs via keyboard.
6. Monitored read-in via Edit-Display and scope.

NOTE: Use of the SKIL system for input was tested earlier on this same data. No computer programs are available to read SKIL coding into Inforonics' Master File. It can nevertheless be reliably stated that use of SKIL in the production system outlined above would result in savings of $1.26 per page for keyboarding and $.67 per page for proofreading, resulting in a page cost of $13.31.

TABLE V. Costs for primary journal output from the machine file, (Martynov article), actual method.

	Hours	*Rate*	*Total*	*Per thousand output characters*	*Per page*
Inforonics typesetter program run	1.0	$45.	$ 45.00	$ .63	$ 2.63[1]
Photon 560 run	5.5	30.	165.00	2.30	9.65[2]
IBM Composer, patches[3]	.65	11.	7.15	.10	.42
Check, set or steal missing characters, insert[4]	5.0	11.	55.00	.77	3.22
Makeup pages[5]	7.0	9.50	66.50	.93	3.89
Proofs, miscellaneous			20.00	.28	1.17
TOTALS				$5.01	$20.98

1. The Inforonics typesetter program now produces paper tape to drive the Photon 560. Running speed is punch-limited (about 110 cps). Conversion to CRT typesetting implies magnetic tape, which can be written faster, with consequent reduction in computer time. This would be reflected in a lower price. Since the exact amount is not known, the effect is ignored.
2. No interface program has yet been written to drive a CRT character-generator from the Inforonics typesetter program. Such a program would create access to service-bureau composition facilities currently quoting rates per thousand characters less than one-fourth those for the Photon. It should be borne in mind that none of these service bureau operations yet offers a character-set adequate for *Uspekhi*. The potential saving is $7.15 to $7.55 per page.
3. To translate patches for figure labels and table heads.
4. The Martynov article was originally chosen to present a difficult character set. The average *Uspekhi* article contains approximately one-fifth as many off-disc symbols. A price for inserting these characters for the average article would be $1.00 rather than $3.22. An investment in a suitable disc would entirely eliminate this item.
5. This item includes stealing, re-breaking (in some cases), and inserting displayed equations from the Russian typeset version.

TABLE VI. Costs for subject and author index output from the machine file, (Martynov article), actual method.[1]

	Present cost per title	*Mag-tape CRT cost per title*
Author and subject sort	$ .19	$ .19
Inforonics typesetter	.42	.42[2]
Photocomposition	.78	.30
Check, dummy, and makeup	.81[3]	.55[4]
Update master file[5]	.10	.10
TOTALS	$2.30	$1.56

[1] Taken from experience with *The Physical Review Index*, now in production. Photon 560 character generation.

[2] See note 1 to Table V.

[3] This figure subject to reduction with greater work volume; the present load is 16-20 pages per month, too small for efficiency.

[4] No consideration is given to the economics inherent in computer-controlled page makeup, although (for indexes) this capability is already a part of some systems.

[5] This item allows an editor to apply hindsight to subject category loadings prior to cumulations.

TABLE VII. Predicted *vs.* actual costs for creation of machine file, per page.

	Predicted 1965	*Actual 1969*	*Percent variation*
Actual Martynov method (Table II)	$16.25[1]	$22.31	+7
Recommended method, immediate (Table III)		19.15	+8
Recommended, Fall 1969 (Table IV)		15.24	–6

[1] See June 1965 proposal, pp. 3 and 4. This figure is the total of items 1-4, 14, and 15 ($7.72), multiplied by the Russian-English page ratio (1.7:1) and adjusted for the Consumer Price Index increase (109.9 to 130.0). Seventy cents per page has been added for copymarking, which was considered an editorial function in 1965.

TABLE VIII. Predicted *vs.* actual costs for paged journal-form output from machine file, per page.

	Predicted 1965	*Actual 1969*	*Percent variation*
Actual Martynov method (Table V)	\$15.10[1]	\$20.98	+39
Average *Uspekhi* article (Table V, see Note 1)		18.76	+24
Average *Uspekhi* article, adequate Photon disc		17.76	+18
With CRT character-generation (Table V, note 2)	approx.	11.00	–27

[1] See June 1965 proposal, pp. 3 and 4 and footnote to Table VII. This figure covers items 5-11 and 13. Note that in 1965 the Linofilm was (a) assumed to have an adequate character set, (b) quoted at \$20 an hour, versus the \$30 an hour now being billed for the Photon, and (c) predicted to have a throughput rate of 7 cps, versus an actual Photon throughput rate discovered to be 3.5-4 cps.

TABLE IX. Predicted *vs.* actual costs for paged index-form output from machine file, per article.

	Predicted 1965	*Actual 1969*	*Percent variation*
Actual *Physical Review* method (Table VI)	\$2.02[1]	\$2.30	+14
With CRT character-generation		1.56[2]	–23

[1] See June 1965 proposal, p. 4 and footnote to Table VII.

[2] This is a maximum, with no consideration given to computer-controlled page make-up capabilities. See Note 4 to Table VI.

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Statistical Theory of Electrolyte Solutions of Intermediate Concentrations

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INTRODUCTION

I. In his preface to the Russian translation of Robinson and Stokes' monograph *Electrolyte Solutions*, published in 1963, Academician A. N. Frumkin writes, "Although the number of experimental and theoretical studies on electrolyte solutions at present considerably exceeds ten thousand, interest in this field is not waning. On the one hand, this is explained by its great practical significance both in technology and in laboratory practice, and on the other hand, by the difficulties that the theory encounters in trying to interpret and generalize the experimental facts." The latter statement is of especial interest here, and it can be formulated more sharply: the theory of electrolyte solutions is now undergoing a definite crisis. As we see it, the reason for this is that people try automatically to extend to more concentrated solutions the methods that have brilliantly proved themselves for dilute systems, while neglecting a certain qualitative difference existing between them.

In fact, as the Debye-Hückel theory[1] implies, in dilute solutions the radius of correlation R_c between the positions of individual ions (which equals the Debye radius $r_{\mathscr{D}} = \{\epsilon\Theta/8\pi\nu k^2e^2\}$*) is considerably greater than the mean distance $\bar{R}$ between particles. Hence, the Debye sphere contains a large number of particles at one time, and the mean electrostatic-interaction energy per particle is small in comparison with Θ. In consequence of the latter, the spatial distribution of the particles hardly differs from that in an ideal gas. Finally, since $R_c \gg r_0$, where r_0 is the diameter of the ions, the contribution of the Born repulsive forces to all the macroscopic characteristics of the system is negligibly small in comparison with that of the electrostatic forces.

The volume of the Debye sphere $v_{\mathscr{D}} = 4\pi r_{\mathscr{D}}^3$ declines with increasing concentration as ν^{-32}, while the mean volume per particle v declines as ν^{-1}. Consequently, e.g., in aqueous solutions having

$$\nu \simeq \frac{0.05-0.10}{k^6} \text{ moles/liter} \qquad \text{(I)}$$

the quantity $v_{\mathscr{D}}$ becomes equal to v. At the same time, a substantial rearrangement takes place in the system: when $v > v_{\mathscr{D}}$, each ion is now shielded by only one counterion. Hence, a pairing of oppositely-charged particles seems to occur in solutions of intermediate concentrations. In this process, the mean distance $\bar{R}_{+-} = \bar{R}_{-+}$ between ions of opposite type becomes considerably less than the mean distance $\bar{R}$ calculated without account of the interaction between the particles.* And although $\bar{R}$ is rather large, as before, in solutions of intermediate concentrations, Born repulsion forces begin to play an important role because $\bar{R}_{+-} \approx r_0$. Evidently, $\bar{R}_{+-}$ can differ appreciably from $\bar{R}$ only when the energy of pair interaction of the ions $> \Theta$.

In going to very concentrated solutions or to molten ionic salts, the radius of correlation R_c increases again, and in the limit it becomes several times r_0. The structure of the melt thus proves to be similar to that of determined by Born repulsion forces.

Thus, the type of distribution of the ions in the system undergoes substantial changes with increasing concentration. Correspondingly, the approach in constructing a theory of electrolytes of different concentrations must also differ.

II. In 1946, Bogolyubov[2] was the first to find the second (Debye) term of the virial series of a system of charged particles by expanding the configuration integral of the system in a power series in the small parameter $v/v_{\mathscr{D}} = 3\chi\kappa$, where

$$\chi^2 = \frac{8\pi\nu k^2e^2r_0^2}{\varepsilon\Theta}, \quad \chi \cdot \frac{k^2e^2}{\varepsilon\Theta r_0}, \quad \varkappa^2 \quad 4\chi\rho, \quad \rho - 2\pi\nu r_0^3. \qquad \text{(II)}$$

Subsequently Mayer[3] and Haga[4] have considerably refined Bogolyubov's result by calculating several more terms of the series

$$p = 1 - \frac{\chi\varkappa}{6} - \frac{1}{2}(\chi\varkappa)^2 \sum_{j=0}^{\infty} \frac{\chi^{2j-3}}{(2j)!\,(2j-3)} \quad \frac{1}{8}(\chi\varkappa)^3 \ln(\chi\varkappa)$$

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*The following notation is adopted here: ϵ is the dielectric constant of the solvent, $\Theta = kT$ is the temperature $e_a = k_a e$ is the charge of an ion of type a, and k_a is its valence,

$$\nu^* = \sum_{1 \leqslant a \leqslant M} \nu_a$$

is the total number of particles per unit volume, and M is the number of different types of particles in the system. Hereinafter we shall restrict ourselves to treating only binary symmetric electrolytes. for which $M = 2$, $k_+ = -k_- = k$, and $\nu_+ = \nu_- = \nu$.

*This effect is manifested more strongly as the maximum value of the electrostatic energy $e^2k^2/\epsilon r_0$ increases in comparison with the energy Θ of thermal motion.

$$-\frac{1}{8}(\chi\varkappa)^3\left\{\frac{3}{2\chi^2}+C-\frac{2}{3}+\ln\frac{4}{\chi}\right.$$

$$\left.-6\sideset{}{'}\sum_{j=2}^{\infty}\frac{\chi^{2j-2}}{(2j+1)!\,(2j-2)}\right\}+O[(\chi\varkappa)^4], \qquad \text{(III)}$$

where $p = P/P_{id}$, $P_{id} = 2\nu\Theta$ is the ideal-gas pressure, and $C = 0.577...$ is Euler's constant. One can easily convince one's self by direct substitution that when $\chi > 1$* and $\nu > \nu_{\mathcal{D}}$ (i.e., when $\chi\varkappa > 1/3$), the virial series (III) converges very slowly, or perhaps may diverge completely. Hence, condition (I) practically defines the boundary between systems for which one can construct a theory by expanding the initial quantities in power series in the small parameter $\nu/\nu_{\mathcal{D}}$ (or equivalently, in the concentration ν), and systems not admitting such an approach.

At present there are only two groups of methods in statistical physics for calculating the configuration integral of gaseous and liquid systems: the methods based on virial expansions and the so-called methods of liquid-state theory.[5] However, as was shown above, the former are unsuitable for constructing a theory of electrolyte solutions of intermediate concentrations. Hence there remains only one way out: to use for this purpose the integral-equations method of liquid-state theory.† As will be shown below, one can make some progress in this way, mainly because the absolute values of the density of the ionic subsystem, which are characterized by the dimensionless parameter $\rho = 2\pi\nu r_0^3$, are sufficiently small, as before. On the one hand, the latter situation permits us to neglect the nonlinear terms in the integral equations, which considerably simplifies the entire calculation. On the other hand, it permits us to limit the treatment to a very simple model of the electrolyte solution in which the solvent is described by its dielectric constant ϵ alone, and the ions are treated as hard spheres of diameter r_0. Within the framework of this model, the energy of pair interaction of particles of types a and b is evidently equal to

$$\Phi_{ab}(r) = \phi^{(s)}(r) + \phi^{(el)}_{ab}(r),$$

$$\phi^{(s)} = \begin{cases} +\infty, & 0 \leqslant r \leqslant r_0, \\ 0, & r_0 \leqslant r \leqslant \infty, \end{cases} \qquad \phi^{(el)}_{ab} = \frac{e_a e_b}{\varepsilon r}. \qquad \text{(IV)}$$

Both these simplifications lose force in going to concentrated solutions or to fused ionic salts. Hence, the calculation of the configuration integral for concentrated systems is entirely a special problem, which we shall not take up in this review.

CHAPTER I: THE BINARY DISTRIBUTION FUNCTION OF THE IONIC SUBSYSTEM OF THE SOLUTION

In essence, any integral equation of liquid-state theory (and there are a great many of them at present*) can be used to describe systems of charged particles. (This is because, as a rule, no special restrictions on the nature of the decline with distance of the binary-interaction energy are introduced in deriving these equations.) Nevertheless, all of the progress in the theory of electrolytes has involved only several very simple equations,[2, 6-9] to which we shall limit the treatment here. Here we shall begin with presenting the theory of Debye and Hückel,[1] an analysis of which will permit us to reveal the physical meaning of the later theories more pictorially.

1.1 The Debye-Hückel Theory[1]

I. Let us put the coordinate origin at the center of an ion of type a bearing the charge e_a. Since this ion interacts with the other ions in the solution, the mean concentration of particles near it will be altered. This will produce a spherically-symmetric charge ("Debye atmosphere") about the central particle, of density

$$q_a(r) = \sum_{1\leqslant b\leqslant M} e_b \nu_b \mathcal{G}_{ab}(r), \qquad (1.1)$$

where $\mathcal{G}_{ab}(r)$ is the binary distribution function determining the probability of finding an ion of type b at the distance r from ion a. If the two particles are so far apart that they no longer interact, then all correlations between them vanish, and $\mathcal{G}_{ab}$ becomes unity, while $q_a(r)$ becomes the constant

$$q_a(\infty) = \sum_{1\leqslant b\leqslant M} e_b \nu_b.$$

Obviously the latter quantity must equal zero, since otherwise an electric field of non-zero intensity would exist at great distances from our selected particle. This would give rise to an electric current. Hence, the condition of neutrality

$$\sum_{1\leqslant b\leqslant M} \nu_b e_b = 0 \qquad (1.2)$$

must be fulfilled in order that the system of charged particles be at equilibrium.

We can derive another, very important formulation of the condition of neutrality from the well-known formula of electrostatics[10]

$$\varphi_a(r) = \frac{e_a}{\varepsilon r} + \int_V q_a(r') \frac{d^3r'}{\varepsilon\,|\mathbf{r}-\mathbf{r}'|}, \qquad (1.3)$$

which describes in this case the potential distribution $\varphi_a(r)$

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*We recall that $\chi \cong 2$-3 for aqueous solutions of univalent electrolytes, and for bivalent ones, $\chi \cong 8$-12.

†Another variant of liquid-state theory, the "free-volume" method, which is based on a certain analogy between a liquid and a crystal is also unsuitable in this case, since the structure of the ionic subsystem of electrolyte solutions of intermediate concentrations is very far from crystalline.

*The most complete review of the results obtained in the theory of ordinary liquids is given in [13].

near the central spherical particle. By using Green's formula to transform the integral appearing in this expression, and taking into account the fact that $q_a(\infty) = 0$, we obtain

$$\varphi_a = -\frac{4\pi}{\varepsilon} \int_r^\infty \frac{d\tau}{\tau^2} \int_\tau^\infty q_a(t)\, t^2\, dt$$

$$+ \frac{1}{\varepsilon r} \left\{ e_a + 4\pi \int_{r_0}^\infty q_a(r)\, r^2\, dr \right\}. \qquad (1.4)$$

Now we note that any macroscopic system can have finite values of its thermodynamic parameters only when

$$\lim_{r \to \infty} r^3 [\mathcal{G}_{ab} - 1] = 0.^*$$

Correspondingly, as is known, q_a must approach zero faster than r^{-3}, and φ_a faster than r^{-1}. However, the latter is possible only when the expression enclosed in curly brackets in (1.4) is zero. That is

$$e_a + 4\pi \int_{r_0}^\infty \sum_{1 \leq b \leq M}{}' e_b \nu_b \mathcal{G}_{ab}(r)\, r^2\, dr = 0. \qquad (1.5)$$

In other words, in order that the binary distribution function decline rapidly enough toward infinity, the sum of charges of the central ion and its atmosphere must be zero. Fulfillment of condition (1.5) provides for shielding of the field of the central ion, since only in this case does the integral term in (1.3), which represents the potential producing the Debye atmosphere, "throw out" a term "cancelling" the potential $e_a/\epsilon r$ of the central ion. As will be shown below, such a situation is typical of the integral equations describing systems of charged particles.

II. The Debye-Hückel theory is based on the idea of using formula (1.3)† to calculate $\mathcal{G}_{ab}(r)$. Evidently, to do this we must assume that $\mathcal{G}_{ab} = \mathcal{G}_{ab}(\varphi_a(r))$, since otherwise (1.3) does not form a closed equation. The concrete form of the sought relation can be found as follows.

First we note that the definition of the binary distribution function implies that it can always be represented in the form[2,5] $\mathcal{G}_{ab}(r) = \gamma(r) G_{ab}(r)$, where the coefficient $\gamma(r) = \exp[-\varphi^{(a)}(r)/\Theta]$ does not depend on the charges of the ions. Hence, $\mathcal{G}_{ab}$ and φ_a can be related only by way of the function G_{ab}. Second, $\mathcal{G}_{ab}$ must by definition be a symmetric function of the charges e_a and e_b of the particles.[2] On the other hand, we can easily derive from (1.3) and the neutrality condition (1.5) the fact that $\varphi_a \sim e_a$. This implies that G_{ab} can depend only on the product $e_b \varphi_a$. Third, since G_{ab} is dimensionless, it can be a function only of the dimensionless potential $e_b \varphi_a / \Theta = (e_a e_b / \epsilon \Theta r_0) \psi(r) = (e_a e_b / k^2 e^2) \chi \psi(r)$.

Thus, if $\mathcal{G}_{ab}$ is determined by the value of φ_a, then this relation must have the form $\mathcal{G}_{ab} = \gamma G_{ab}[(e_a e_b / k^2 e^2) \chi \psi]$. Let us expand the unknown function G_{ab} in a series, and limit it to the first two terms. In this approximation,

$$\mathcal{G}_{ab}(r) = \gamma(r) \left[1 - \frac{e_a e_b}{k^2 e^2} \chi B^2 \psi(r) \right]. \qquad (1.6)$$

The unknown expansion coefficient B^2 appearing here is in general a function of the dimensionless parameters χ and κ of the problem. Debye and Hückel assumed it to be unity. As will be shown below, the more exact theories confirm this assumption.

III. Taking $B^2 = 1$, let us substitute (1.6) into (1.3), taking (1.1) and (1.2) into account. Consequently, (1.3) acquires the form

$$\psi(t) - \frac{1}{t} + \frac{\kappa^2}{4\pi} \int_V \gamma(t') \psi(t') \frac{d^3 t'}{|\mathbf{t} - \mathbf{t}'|} = 0, \qquad (1.7)$$

where $\mathbf{t} = \mathbf{r}/r_0$ and $\gamma(t) = 0$ when $0 \leqq t < 1$;* or 1 when $1 \leqq t \leqq \infty$. Let us calculate the integral appearing in (1.7) using Green's formula, using the condition of neutrality (1.5). Thereupon, (1.7) is reduced to

$$\psi(t) + \kappa^2 \int_t^\infty \frac{d\xi}{\xi^2} \int_\xi^\infty \psi(\zeta) \zeta^2\, d\zeta = 0. \qquad (1.8)$$

Now assuming that $\psi = m''(t)/t$, we transform the integral equation (1.8) into a differential equation:

$$m''(t) - \kappa^2 m(t) = 0. \qquad (1.9)$$

It directly follows that $m = Ae^{-\kappa t}$. Finally, we determine the constant A from the condition of neutrality (1.5), and we obtain

$$\mathcal{G}_{ab}(t) = \gamma(t) \left\{ 1 - \frac{e_a e_b}{k^2 e^2} \frac{\chi}{1 + \kappa} \frac{e^{-\kappa(t-1)}}{t} \right\}, \qquad (1.10)$$

Upon substitution into the expression[11]

$$U(V, \Theta) = U_0(\Theta)$$

$$+ \frac{1}{2} \int_0^\infty \sum_{1 \leq a,\, b \leq M}{}' \frac{N_a N_b}{V} \Phi_{ab}(r) \mathcal{G}_{ab}(r)\, 4\pi r^2\, dr, \qquad (1.11)$$

which relates the internal energy U of the system to $\mathcal{G}_{ab}$, it gives (Φ_{ab} being defined by formula (IV))

$$U(V, \Theta) = U_0(\Theta) - \frac{N\Theta}{2} \frac{\chi\kappa}{1 + \kappa} \qquad (1.12)$$

This is the final result of the Debye-Hückel theory.

IV. We shall make some remarks on the formulas derived above.

First, the Debye-Hückel theory is based on the hypothesis that, in the region $r > r_0$, the distribution function arises only from the Coulombic interaction among the particles (since it is assumed that $G_{ab} = G_{ab}(e_b \varphi_a / \Theta)$. Evidently, the latter implies complete neglect

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*For example, the density fluctuations, which are proportional to $\int_0^\infty [\mathcal{G}_{ab}(r) - 1] r^2 dr$, go to infinity when this condition is violated.

†Or, equivalently, Poisson's equation, of which (1.3) is the solution.

*Of course, the latter is true only of systems of hard spheres.

of short-range forces at distances exceeding the diameter r_0 of the ions. However, as is known, $\mathcal{G}_{ab} \neq 1$ for $r > r_0$, even in a system of uncharged hard spheres. Here the thickness of the spherical shell $r_0 \leqq r \leqq R_c^{(s)}$ in which the positions of the individual particles are correlated increases rapidly with increasing concentration.[5,11] Conversely, the thickness of the spherical shell $R_c^{(el)} - r_0$ manifesting electrostatic correlation declines with increasing concentration. The decline approximately follows the law $R_c^{(el)} - r_0 \cong r_0/\kappa \sim 1/\sqrt{\nu}$, as (1.10) implies. Hence, the condition $R_c^{(s)} - r_0 \ll R_c^{(el)} - r_0$, which has to be fulfilled in order that we can take G_{ab} to depend only on the electrostatic potential φ_a, holds only over the limited concentration range $\rho \lesssim \rho_{max}$. If we use the more precise values of the radii of correlation $R_c^{(s)}$ and $R_c^{(el)}$ given in [9,12], we find that for aqueous solutions of univalent electrolytes for which $2.0 \leqq \chi \leqq 3.0$ (see below), the value of $\rho_{max} \approx 0.2$. This corresponds to concentrations of the order of 2–3 moles/liter.*

Second, the Debye-Hückel theory is based on expanding the function $G_{ab} = G_{ab}[(e_a e_b/k^2e^2)\chi\psi]$ in a power series in $\chi\psi(r)$, and dropping terms of the order of $(\chi\psi)^2$ and higher. Evidently, the latter is possible only when $\chi\psi(r) \ll 1$ throughout the region $r \geqq r_0$. Hence, the results obtained become more accurate for smaller χ, other conditions remaining the same. And since χ is proportional to k^2, it follows that the Debye-Hückel theory is inapplicable to solutions of intermediate concentrations for bivalent electrolytes, for which $\chi \cong$ 8–12, as is known.* At the same time, the Debye-Hückel theory should give quite satisfactory results for univalent electrolytes, for which the product $\chi\psi$ is less than unity for almost all $r > r_0$.†

Third, the Debye-Hückel theory has the fundamental defect that it doesn't permit one to obtain full information on the distribution function. Indeed, we note that, since the charges of the particles enter into the configurational energy U_N of the system only in the form of pair products, therefore $G_{ab} = G_{ab}(e_a e_b)$. Hence, let us represent G_{ab} in the form

$$G_{ab} = 1 + g_{ab}(e_a e_b) = 1 + \frac{1}{2}[g_{ab}(e_a e_b) - g_{ab}(-e_a e_b)] + \frac{1}{2}[g_{ab}(e_a e_b) + g_{ab}(-e_a e_b)], \quad (1.13)$$

where we have written the term unity separately in order to emphasize the fact that $G_{ab} \to 1$ when $r \to \infty$. Evidently, for a symmetrical binary electrolyte, for which $e_+ = -e_- = ke$, the expression within the left-hand square brackets changes sign as we go from $G_{++} = G_{--}$ to $G_{+-} = G_{-+}$, while the second square bracket remains unchanged. This implies that the binary distribution function can always be written as

$$\mathcal{G}_{ab} = \Upsilon(t)\left\{1 - \frac{e_a e_b}{k^2 e^2}\chi M(t) + R(t)\right\}, \quad (1.14)$$

where we have written the coefficient $(-\chi)$ separately only for convenience. Evidently, since

$$\lim_{t\to\infty} t^3(\mathcal{G}_{ab} - 1) = 0,$$

$$\lim_{t\to\infty} t^3 M(t) = \lim_{t\to\infty} t^3 R(t) = 0. \quad (1.15)$$

Substituting (1.14) into (1.3) and (1.5), we obtain

$$\psi(t) - \frac{1}{t} + \frac{\varkappa^2}{4\pi}\int \Upsilon(t')M(t')\frac{d^3t'}{|\mathbf{t}-\mathbf{t}'|} = 0, \quad (1.16)$$

$$1 - \varkappa^2\int_1^\infty M(t)\,t^2\,dt = 0. \quad (1.17)$$

Thus we see that the function $R(t)$ completely vanishes from all the electrostatic equations, owing to the condition of neutrality (1.2). Nevertheless, if we could find from (1.15)-(1.17) the exact value of the function $M(t)$, then this would suffice for correct calculation of the internal energy U of the system in the case in which the pair potential $\Phi_{ab}(r)$ is given by relation (IV). In fact, by substituting (IV) and (1.14) into (1.11) we obtain

$$U(V,\Theta) = U_0(\Theta) - \frac{N\Theta}{2}\chi\varkappa^2\int_1^\infty M(t)\,t\,dt, \quad (1.18)$$

That is, $U(V,\Theta)$ does not depend on $R(t)$ at all. At the same time, the pressure of the system

$$P(V,\Theta) = P_{id}(V,\Theta) - \frac{1}{6}\int_0^\infty \sum_{1\leq a,b\leq M}\frac{N_a N_b}{V^2}\, r\,\frac{d\Phi_{ab}(r)}{dr} \times \mathcal{G}_{ab}(r)\,4\pi r^2\,dr \quad (1.19)$$

cannot be found by using only one function M, since after substituting (IV) and (1.14) into (1.19), we get the expression

$$p = \frac{P}{P_{id}} = 1 - \frac{\chi\varkappa^2}{6}\int_1^\infty M(t)\,t\,dt + \frac{2}{3}\rho[1 + R(1)], \quad (1.20)$$

from which $R(t)$ does not drop out. Hence, (1.10) gives $U(V,\Theta)$ correctly, but $P(V,\Theta)$ incorrectly.

1.2. The Kirkwood-Poirier Theory[6]

I. Following Debye and Hückel, we set $\psi(t) = M(t)$ in (1.16). Here the physical meaning of Eq. (1.16) is changed considerably. Indeed, it formerly gave the electrostatic potential $\psi(t)$ at some arbitrary point t not directly associated with any particle of the system. However, after ψ has been identified with M, it now gives the probability

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*It is usually assumed that the Debye-Hückel theory is applicable only for $\nu \leqslant 0.01$ moles/liter. This statement is based on a misunderstanding, since it results from comparing formula (1.12) with virial series such as (III). However, such a comparison cannot serve as a satisfactory criterion, since when $\nu > \nu_{\mathcal{D}}$, the virial series generally diverge, while (1.12) continues to hold true. Insofar as we know, no one has yet made any special estimates of the limits of applicability of formulas (1.10) and (1.12).

†One can easily convince one's self of this by considering Eq. (1.1).

of finding the particle b at the distance t from the "central" particle a (since the correlation function M is part of the binary distribution function $\mathcal{G}_{ab}$). Hence, while the integral found in (1.16) formerly described the field created by the $N - 1$ particles at the point $\mathbf{t}$ (i.e., all the particles of the system but the central one), now it must describe the influence of $N - 2$ particles on the pair of particles a and b that we have chosen, whose positions are fixed. Correspondingly, we must perform the integration in (1.16) over the entire space V, excepting the volume occupied by these particles. However, the factor $\gamma(t')$ within the integral already takes into account the excluded volume occupied by the particle a. Hence, we have yet only to take into account the volume of the particle b. We can do this by introducing the factor $\gamma(t - t')$ into the integral. Consequently, (1.16) is converted into the equation

$$M(t)-\frac{1}{t}+\frac{\varkappa^2}{4\pi}\int_V M(t')\,\gamma(t')\,\gamma(|\mathbf{t}-\mathbf{t}'|)\,\frac{d^3t'}{|\mathbf{t}-\mathbf{t}'|}=0, \tag{1.21}$$

which is the basis of the Kirkwood-Poirier theory. We see from the arguments given above that it is a natural refinement of the initial equation (1.7) of the Debye-Hückel theory.

II. The integral over the volume occurring in (1.21) can be transformed by Green's formula into integrals over the surface of spheres having centers at $\mathbf{t} = 0$ and at $\mathbf{t}$. Upon substituting $M = m''t$, the latter are easily calculated. Consequently, when $t > 2$, Eq. (1.21) becomes

$$\underline{2<t<\infty,}\quad \frac{m''(t)}{t}-\frac{1}{t}\left\{1-\varkappa^2\int_1^\infty M(t)\,t^2\,dt\right\}$$
$$-\frac{\varkappa^2}{2t}[m(t+1)+m(t-1)]=0. \tag{1.22}$$

If we let $t \to \infty$ here, and take (1.15) into account, we come again to the condition of neutrality (1.17), which must be satisfied to remove the $1/y$ xxt term from Eq. (1.21). After simplifying (1.22) in t, we finally obtain (cf. (1.9)):

$$\underline{2<t<\infty,}\quad m''(t)-\frac{\varkappa^2}{2}[m(t+1)+m(t-1)]=0. \tag{1.23}$$

If the distance between the particles $t < 2$, then the spheres intersect (Fig. 1). Correspondingly, the integral must be taken only over the outer surface of the figure formed. The end result of this is the expression

$$\underline{1<t<2,}\quad m''(t)-\frac{1}{2}\varkappa^2 m(t+1)=\frac{1}{2}\varkappa^2 m(1)$$
$$-\varkappa^2\left(1-\frac{1}{2}t\right)m'(1). \tag{1.24}$$

The region $1 \leqq t \leqq 2$ is marked out physically because there is always a "forbidden" zone between two particles of diameter r_0 when $r_0 \leqq r \leqq 2r_0$. The third particle over whose coordinate the integration in (1.21) is performed cannot enter this zone (see Fig. 1).

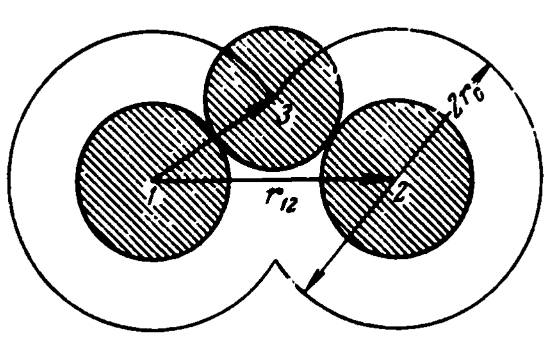

FIG. 1. Diagram of the collision of three particles with $r_0 \leqq r_{12} \leqq 2r_0$.

We can easily convince ourselves by direct substitution that a special solution of Eq. (1.23) is e^{-at}, where a is the root of the transcendental equation

$$a^2=\varkappa^2\operatorname{ch}a. \tag{1.25}$$

Since (1.25) has an infinite number of roots, the general solution of (1.23) can be written as

$$m(t)=\sum_{i=1}^{\infty}A_ie^{-a_it}=A_1\sum_{i=1}^{\infty}\left(\frac{A_i}{A_1}\right)e^{-a_it}=A_1\tilde{m}(t). \tag{1.26}$$

The unknown constants A_i occurring here must be determined from Eq. (1.24). Upon substituting (1.26) into the latter, it gives

$$\underline{1<t<2,}\quad \sum_{i=1}^{\infty}A_i^*e^{-a_it}=\frac{1}{2}\varkappa^2\{\tilde{m}(1)-(t-2)\,m'(1)\}. \tag{1.27}$$

where $A_i^* = (A_i/A_1)[a_i^2 - \frac{1}{2}\kappa^2e^{-a_i}]$. In essence, Eq. (1.27) is an expansion of the known function (within the accuracy of the constants $\tilde{m}(1)$ and $\tilde{m}'(1)$) on the right-hand side in a series of the characteristic functions e^{-a_it} of Eq. (1.23). In principle we can find from (1.27) all the A_i but A_1, which actually drops out of (1.27), owing to homogeneity. The constant A_1 can be determined from the condition of neutrality (1.17), which gives the following when (1.26) has been substituted into it:

$$A_1=[\varkappa^2(\tilde{m}(1)-\tilde{m}'(1))]^{-1}. \tag{1.28}$$

The study of the transcendental equation (1.25) made in [14] showed that it has only two real roots $a_{1,2} = \alpha_{1,2}$; the remaining roots are complex conjugates: $a_k = \alpha_k \pm i\omega_k$. When $\kappa \lesssim 0.5$, $\alpha_1 \approx \kappa$, $\alpha_2 \geqq 5.5$, and the values of the other α_k are even greater. Hence, when $\kappa \lesssim 0.5$, we can drop all the terms of the series in (1.26) but the first, to a sufficient degree of accuracy. As a result we obtain the Debye formulas (1.10) and (1.12) for $\mathcal{G}_{ab}$ and U.

III. We shall now make some remarks on the Kirkwood-Poirier theory.

First, we stress the fact that its starting equation (1.21) was initially derived directly from the Gibbs canonical distribution, rather than from the electrostatic equation (1.3) with the substitution of (1.6), as was done above. Hence, the problem of the value of the expansion constant B^2 in (1.6) does not arise at all in this case. We see from the derivation given in [6] that $B^2 \equiv 1$.

Second, in Eq. (1.10), which is also a consequence of the Kirkwood-Poirier theory, let us transform to the limit of uncharged hard spheres having $e_a = e_b = 0$. Then $\mathcal{G}_{ab}$ proves to equal $\gamma(r)$. Upon substitution into (1.19), this gives the expression $p = 1 + \frac{2}{3}\rho$, which amounts to the first two terms of the virial series.[11] We can easily convince ourselves by comparing $p = 1 + \frac{2}{3}\rho$ with the more precise equations of state that this expression gives satisfactory accuracy only when $\rho \lesssim 0.2$. For $r_0 \cong 3$–4 Å, this corresponds to a concentration $\nu \cong 2$–3 moles/liter. As we should expect, this value coincides with the limit of applicability of the Debye-Hückel theory (see above).

Third, Kirkwood and Poirier derived Eq. (1.21) by expanding the initial quantities in a power series in χ, and then dropping the terms proportional to χ^n, where $n \geqq 2$.* This is the very reason why (1.10) gives correctly only the first two terms of the virial series of the system of charged spheres (III) depending linearly on χ: the remaining terms of the series (III) depending on the higher powers of χ cannot be found by using (1.21).

Fourth, Eq. (1.21), just like (1.7), determines only the "electrostatic" component $M(t)$ of the binary distribution function; its "short-range" component $R(t)$ cannot be found within the framework of the Kirkwood-Poirier theory.

1.3. A Theory Based on Bogolyubov's Equations[8,9]

I. Let us apply the operator ∇ to (1.16), and assume that $\psi = M$, following Debye and Hückel. Then by following the same argument as in deriving the Kirkwood-Poirier equation (1.21), we obtain

$$\nabla M(t) - \nabla\left(\frac{1}{t}\right)$$

$$+\frac{\varkappa^2}{4\pi}\int_V M(t')\gamma(t')\gamma(|\mathbf{t}-\mathbf{t}'|)\nabla\left(\frac{1}{|\mathbf{t}-\mathbf{t}'|}\right)d^3t = 0. \qquad (1.29)$$

This expression is the equation of balance of electrostatic forces acting on the particle b.† We can easily convince ourselves of this by noting that in (1.29) the term $\nabla\frac{1}{t}$ is proportional to the electric field intensity produced by the central ion a at the point t, while the integral is the mean electric field intensity produced by the remaining $N - 2$ particles of the system at the same point. Evidently, the force balance written in this way cannot under any conditions be considered complete. This is because it does not take into account the non-Coulombic forces causing the impenetrability of the particles. Hence, a natural generalization of the theories developed above is to go over to Bogolyubov's equation[2]

$$\Theta\nabla_1\mathcal{G}_{ab} + \mathcal{G}_{ab}\nabla_1\Phi_{ab} + \int_V \sum_{1\leqslant c\leqslant M} \nu_c\mathcal{G}_{abc}\nabla_1\Phi_{ac}d^3r_3 = 0, \qquad (1.30)$$

which is the equation of balance of all forces. In fact, let us divide each term in (1.30) by $\mathcal{G}_{ab}$. In the expression that we get thus, the term $-\nabla_1\Phi_{ab}$ will represent the total force exerted on the particle a by the particle b, whose position is fixed, while

$$-\int\sum_c \nu_c(\mathcal{G}_{abc}/\mathcal{G}_{ab})\nabla_1\Phi_{ac}d^3r_3$$

is the total average force exerted on a by the remaining $N - 2$ particles of the system (here $\mathcal{G}_{abc}$ is the ternary distribution function). Correspondingly, the term $-\nabla_1\{\Theta \ln \mathcal{G}_{ab}\}$ will represent the "force" of the thermal movement of the particle a balancing the potential forces acting on it. We see from the derivation of Eq. (1.30) given in [2] that it follows strictly from Gibbs' canonical distribution. This is the very reason why we can write it in the form of a condition of constancy of chemical potential of the particle a in the system in which the position of particle b is fixed.

II. Among the infinite multitude of solutions of Bogolyubov's equation (1.30), the only ones that fit the canonical distribution (and hence have physical meaning) are those that satisfy the conditions of normalization, symmetry, etc.[2,5,11] In essence, the latter play the role here of ordinary boundary conditions as used in solving differential equations (since both have as their purpose the selection of a given solution from the entire class of possible solutions). Hence, it is natural from the outset to try to put (1.30) into such a form that the imposition of additional conditions (or at least part of them) would be superfluous.

The definition of the distribution function implies[11] that $\mathcal{G}_{ab}$ and $\mathcal{G}_{abc}$ can always be represented in the form $\mathcal{G}_{ab}(r_{12}) = \gamma(r_{12})[1 + g_{ab}]$, $\mathcal{G}_{abc}(r_{12}, r_{13}, r_{23}) = \gamma(r_{12})\gamma(r_{13})\gamma(r_{23}) \times [1 + G_{abc}]$.* Here the unity terms are written separately to emphasize the fact that

$$\lim_{r_{12}\to\infty} \mathcal{G}_{ab} = 1,$$

and

$$\lim_{r_{12}, r_{13}, r_{23}\to\infty} \mathcal{G}_{abc} = 1.$$

The condition that the correlation should decline also implies that if, in the group of three particles a_1, b_2, and c_3, one of them (e.g., c_3) moves infinitely far away, then $\mathcal{G}_{abc}$ becomes equal to $\mathcal{G}_{ab}$. Hence, when $r_{13}, r_{23} \to \infty$, the function $G_{abc} \to g_{ab}$. Taking into account the symmetry of G_{abc} with respect to permutation of particles, we obtain

$$\mathcal{G}_{ab} = \gamma_{12}[1 + g_{ab}],$$

$$\mathcal{G}_{abc} = \gamma_{12}\gamma_{13}\gamma_{23}[1 + g_{ab} + g_{ac} + g_{bc} + g_{abc}], \qquad (1.31)$$

Evidently, the correlation function g_{abc} describes here the

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*See also the original derivation of (1.21) given by Falkenhagen and Kelbg.[15]

†Or, equivalently, the forces acting on the particle a, since the latter are equal except for sign to those acting on the particle b.

*Here as before, $\gamma = \exp[-\varphi^{(s)}/\Theta]$.

non-linear effects that arise in the simultaneous interaction of all three particles. Substituting (1.31) into (1.30), we get a system of two equations for the functions $g_{++} = g_{--}$ and $g_{+-} = g_{-+}$:

$$\Theta\nabla_1 g_{ab} + (1 + g_{ab})\,\nabla_1\Phi_{ab}^{(el)} + \int\limits_V \sum_{1\leqslant c\leqslant M}{}' \nu_c\,[1 + g_{ab} + g_{ac} + g_{bc} + g_{abc}] \times \gamma_{13}\gamma_{23}\nabla_1\Phi_{ac}\,d^3r_3 = 0. \qquad (1.32)$$

This way of writing Bogolyubov's equation (1.30) has the advantages that it ensures satisfaction of the conditions of normalization and symmetry, the condition of declining correlation, and the condition that the distribution function be bounded at the zero-point,* for any approximation of the unknown function g_{abc}.

III. Now we recall that each ion is shielded by only one counterion in electrolyte solutions of intermediate concentrations. Here the mean distances between the thus-formed particle pairs are rather large, as before. This means that in these systems the simultaneous collision of three or more particles is a rather rare event. And if this is so, then we can completely drop the term g_{abc} in (1.32) describing the non-linear effects in ternary collisions. Using (1.14) to transform from g_{ab} to the functions $M(t)$ and $R(t)$, we obtain instead of (1.32) the system of two equations:

$$\nabla M(t) - \nabla\left(\frac{1}{t}\right) + \frac{\varkappa^2}{4\pi}\int\limits_V M(t')\,\gamma(t')\,\gamma(|\mathbf{t}-\mathbf{t}'|)\,\nabla\frac{1}{|\mathbf{t}-\mathbf{t}'|}\,d^3t' - \frac{\rho}{\pi}M(t)\int\limits_V \gamma(t')\,\nabla\gamma(|\mathbf{t}-\mathbf{t}'|)\,d^3t' = R(t)\,\nabla\left(\frac{1}{t}\right), \qquad (1.33)$$

$$\nabla R(t) - \frac{\rho}{\pi}\int\limits_V [1 + R(t) + R(t')]\,R(|\mathbf{t}-\mathbf{t}'|)\,\gamma(t')\,\nabla\gamma(|\mathbf{t}-\mathbf{t}'|)\,d^3t' = \chi^2\Big\{M(t)\,\nabla\left(\frac{1}{t}\right) + \frac{\rho}{\pi}\int\limits_V M(|\mathbf{t}-\mathbf{t}'|)\,\gamma(|\mathbf{t}-\mathbf{t}'|)\,\gamma(t')\,\nabla\frac{1}{|\mathbf{t}-\mathbf{t}'|}\,d^3t'. \qquad (1.34)$$

The left-hand sides of (1.33) and (1.34) are the equations of balance of the electrostatic (cf. (1.29)) and short-range forces, respectively. The right-hand sides describe the interaction effects.

IV. We shall restrict ourselves in solving the system (1.33) and (1.34) to the case of not very great concentrations, for which $\rho \ll 1$. Dropping all the terms proportional to ρ in (1.33) and (1.34), we obtain

$$\nabla M(t) - \nabla\left(\frac{1}{t}\right) + \frac{\varkappa^2}{4\pi}\int\limits_V M(t')\,\gamma(t')\,\gamma(|t-t'|)\,\nabla\frac{1}{|\mathbf{t}-\mathbf{t}'|}\,d^3t' = R(t)\,\nabla\frac{1}{t}, \qquad (1.35)$$

$$\nabla R(t) = \chi^2 M(t)\,\nabla\frac{1}{t}, \quad R(t) = \chi^2\int\limits_t^\infty \frac{M(\tau)}{\tau^2}\,d\tau. \qquad (1.36)$$

By assuming in (1.35) that $M = m''(t)/t$, and transforming the integral contained in it by Green's formula, we can reduce the system (1.35) and (1.36) to a single equation:

$$\underline{2 \leqslant t \leqslant \infty}, \quad m^{IV}(t) - \chi^2\frac{m''(t)}{t^4} - \frac{\varkappa^2}{2}[m'(t+1) - m'(t-1)] = 0. \qquad (1.37)$$

In going from (1.35) and (1.36) to (1.37), we have taken into account the condition of neutrality (1.17). As before, the latter must be fulfilled to remove from (1.35) the term $\nabla\frac{1}{t}$, which declines too slowly toward infinity. When $t^2 > \kappa\chi$, we can drop the term containing χ^2 in (1.37).* As a result, we obtain the following equation (cf. (1.9) and (1.23)):

$$\underline{t^* = \sqrt{\varkappa\chi} < t \leqslant \infty}, \quad m^{IV}(t) - \frac{\varkappa^2}{2}[m'(t+1) - m'(t-1)] = 0, \qquad (1.38)$$

Evidently, the general solution of the latter has the form

$$m(t) = \sum_{i=1}^{\infty} A_i e^{-a_i t} \approx A_1\tilde{m}(t), \quad a_i^2 = \varkappa^2\frac{\operatorname{sh} a_i}{a_i}. \qquad (1.39)$$

The constants A_i, $i \geqq 2$ appearing here must be determined from the condition that Eq. (1.37) should vanish identically in the region $2 \lesssim t \lesssim t^*$, and the equation obtained from (1.35) and (1.36) should vanish in the region $1 \leqq t \leqq 2$, which is considered separately, as before. Just as in the Kirkwood-Poriier irier theory, the constant A_1 is found from the condition of neutrality (1.17), which leads to the expression (1.28).

The study of the transcendental equation (1.39) made in [9] shows that when $\kappa \lesssim 1$,† the first root of this equation $\alpha_1 \cong \kappa$, while the real part of the remaining roots $\alpha_i \gtrsim 6$, $i \geqq 2$. Hence, when $\kappa \lesssim 1$, we can drop all the terms of the series (1.39) but the first. Consequently, the expression for the binary distribution function takes on the form

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*The latter condition is ensured by writing the factors γ separately in $\mathcal{G}_{ab}$ and $\mathcal{G}_{abc}$.

*This estimate can be obtained by substituting the special solution $e^{-\alpha_1 t}$ of Eq. (1.38) into (1.37), and matching the terms in χ^2 and κ^2.

†Rather than $\kappa < 0.5$, as in the Kirkwood-Poirier theory.

$$\mathcal{G}_{ab}(t) = \gamma(t)\left\{1 - \frac{e_a e_b}{h^2 e^2}\frac{\chi}{1+\varkappa}\frac{e^{-\varkappa(t-1)}}{t} + \frac{\chi^2 e^{\varkappa}}{1+\varkappa}\int_t^{\infty}\frac{e^{-\varkappa\tau}}{\tau^3}\,d\tau\right\}. \qquad (1.40)$$

In distinction from the Debye formula (1.10), it is positive for all values of t and χ. However, upon substituting (1.40) into the formula (1.11) for the internal energy, we get the Debye expression (1.12) as before.

V. We shall now make some remarks on the theory developed here.

First, if we go to the limit $e_a = e_b = 0$ in the initial system (1.34), (1.35), then we obtain

$$\nabla F(t) - \frac{\rho}{\pi}\int_V [1 + R(t) + R(t') + R(|\mathbf{t}-\mathbf{t}'|)]\,\gamma(t')\,\nabla\gamma(|\mathbf{t}-\mathbf{t}'|)\,d^3t' = 0. \qquad (1.41)$$

It was shown in [16] that (1.41) gives correctly the first three virial coefficients, but gives the fourth one with a small error, which amounts to only 3.5 percent for a system of hard spheres.* The more precise solution obtained in [12] showed that (1.41) gives quite satisfactory results up to $\rho \approx 0.6$–1.0. For $r_0 = 4$ Å, this corresponds to a concentration of 20 moles/liter or more 1. The latter overlaps the entire region of electrolyte solutions of intermediate concentrations with room to spare. However, we cannot say the same for the system (1.35) and (1.36), since it was derived from (1.33) and (1.34) by dropping all the terms of the order of ρ. In this approximation, (1.41) correctly describes only the first two virial coefficients. Correspondingly, the region of applicability of the solutions obtained cannot exceed 2–3 moles/liter.

Second, as the derivation given above implies, the fundamental system of equations (1.33) and (1.34) involves no expansions whatever in the parameter χ. This is the very reason why it gives correctly the first three virial coefficients of the system of charged hard spheres. We can convince ourselves of this as follows. In the case of dilute enough solutions at small distances, we can neglect in (1.32) not only the non-linear effects in the collective interactions (i.e., the term g_{abc}), but also generally all the collective effects described in (1.33) by the integral term (since the latter are small in comparison with the pair interaction described by the term $\nabla\varphi_{ab}^{(el)}$). Thus we directly find that at small distances $1 + g_{ab} = \exp\,[(-e_ae_b/\epsilon\Theta)(1/r)]$. Correspondingly, for great distances with $\kappa \ll 1$, we find from (1.40) that $1 + g_{ab} = 1 - (e_ae_b/\epsilon\Theta)\cdot\{[\exp\,(-r/r_{\mathcal{D}})]/r\}$. Combining the two results together into a single interpolation formula, we arrive at the well-known Tyablikov-Tolmachev[17,18] expression

$$\mathcal{G}_{ab}(r) = \gamma(r)\exp\left[-\frac{e_ae_b}{\varepsilon\Theta}\frac{e^{-r/r_{\mathcal{D}}}}{r}\right]. \qquad (1.42)$$

Upon substituting (1.42) into (1.19) and calculating the integral by expanding the exponential in a power series in $(e_ae_b/\epsilon\Theta)\cdot[\exp\,(-r/r_{\mathcal{D}})/r]$, we obtain $p = 1 - (\chi\kappa/6) - \frac{1}{2}(\chi\kappa)^2 \times \Sigma[\chi^{2j-3}/(2j)(2j-3)] + O(\kappa^3)$. This exactly corresponds with the first three terms of the series (III). Since here the κ^2 term contains all the powers of χ, evidently dropping the g_{abc} term in (1.32) imposes no limitations on the value of the parameter χ.

Since the formula (1.42) can also be derived from the "abbreviated" system (1.35), (1.36), the latter remark fully pertains to it as well. However, this does not mean that the expression (1.40) for the binary distribution function found by solving the "abbreviated" system is valid for all values of χ. As was shown in [9], the result of dropping all the terms of the series of (1.39) but the first is that (1.40) describes only aqueous solutions of univalent electrolytes, for which χ does not exceed 2–3; it is not valid for multivalent electrolytes.

Third, as we see from (1.40), the equation of balance of all forces (1.32) completely determines the binary distribution function. This permits us directly to calculate not only the internal energy U of the system, but also the equation of state $P(V, \Theta)$. When Φ_{ab} and $\mathcal{G}_{ab}$ are given by the formulas (IV) and (1.40), the latter has the form

$$p = 1 - \frac{1}{6}\frac{\chi\varkappa}{1+\varkappa} + \frac{2}{3}\rho\left[1 + \frac{\chi^2 e^{\varkappa}}{1+\varkappa}\int_1^{\infty}\frac{e^{-\varkappa\tau}}{\tau^3}\,d\tau\right]. \qquad (1.43)$$

If we know P and U, we can test the theory for self-consistency. In fact, we know from thermodynamics that P and U are connected by the relation[19]

$$(\partial U/\partial V)_\Theta = \Theta^2(\partial/\partial\Theta)(P/\Theta)_V.$$

Hence,

$$P = \Theta\left\{\int_\infty^\Theta(\partial U/\partial V)(d\Theta/\Theta^2) + \text{const}\right\}.^*$$

If we substitute into this U from (1.11), we obtain

$$p = 1 - \frac{\chi}{2\varkappa^2}[(1+\varkappa) - (1+\varkappa)^{-1} - 2\ln(1+\varkappa)] + \frac{2}{3}\rho. \qquad (1.44)$$

This expression differs greatly from (1.43) in external form. However, as we see from the data of Table I, which gives the values of $\Delta = p^{(1.44)} - p^{(1.43)}$ calculated for $\chi = 2$, the quantitative difference between the two formulas practically nowhere exceeds the experimental error $\delta = \pm 1 \times 10^{-3}$. The fact that Δ nevertheless is not strictly

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*We recall that (1.7) and (1.21) give correctly only the first two virial coefficients.

*The constant appearing here must be assumed equal to $\frac{2}{3}\rho$ for the case of hard spheres in order to take into account the excluded volume of the particles within an accuracy of terms of the order of ρ, inclusive.

Table I

$\varkappa$	0.1	0.2	0.4	0.6	0.8	1.0
$[1-p^{(1.44)}]\cdot 10^3$	28.1	46.8	66.1	67.0	54.1	30.5
$\Lambda\cdot 10^3$	0.0	0.3	1.2	1.8	2.3	3.2
$\frac{\Lambda\cdot 100}{1-p^{(1.44)}}$ %	0.0	0.6	1.8	2.7	4.3	10.0

zero is most probably to be explained by the fact that (1.40) is an approximate solution of the system (1.35), (1.36). Thus, the initial equation unambiguously determines the thermodynamic parameters of the system of charged spheres.* This is quite natural, since the conditions of normalization, correlation, etc., in turn determine unambiguously the linear terms of Eq. (1.32).

We see by comparing the equations for the distribution functions (1.7), (1.21) with (1.33), (1.34) that each of the latter is a natural refinement of the former. Without vitiating the fundamental corollary of Eq. (1.7) (the Debye-Hückel formula (1.12) for the internal energy), these refinements nevertheless show that the latter is valid only for $\kappa \lesssim 1$ and $\chi \lesssim 3$. A direct calculation of the value of $U(V, \Theta)$ by the Monte Carlo method confirms this conclusion.[35]

CHAPTER II: THERMODYNAMIC FUNCTIONS OF SOLUTIONS AND COMPARISON WITH EXPERIMENT

The formula (1.12) for the internal energy of the ionic subsystem of the solution was first derived by Debye and Hückel as early as 1923.[1] In the 40 years that have passed, all its consequences have been subjected to thorough experimental testing. It has turned out that the theory does not satisfactorily agree with experiment at any appreciable concentrations unless one introduces empirical corrections.[20,21] Up to now, the observed disagreement has usually been explained by saying that the theory itself is crudely approximate and semiempirical. Although this viewpoint has become widespread now, it is wrong, since as was shown above, Eq. (1.12) is a direct consequence of the Gibbs canonical distribution. But then the question arises anew: what then is responsible for the stated discrepancy?

To answer it, we recall that the theory involves the dielectric constant ϵ of the solvent, which arises from averaging the configuration integral of the system over all possible states of the solvent molecules.[19,22,23] Evidently, the result of this averaging cannot fail to depend on the temperature Θ of the system and the concentration ν of the solute (and of course, on the other parameters of the electrolyte and the solvent, such as the valence of the ions, the diameter of the particles, etc.). Hence we can state a priori that always $\epsilon = \epsilon(\Theta, \nu)$.

It was noted long ago that one must take into account the temperature-dependence $\epsilon = \epsilon(\Theta)$ to explain certain properties of extremely dilute aqueous solutions of electrolytes.* On the other hand, the concentration-dependence $\epsilon(\nu)$ was said to play no role. However, such a disparity between Θ and ν only stems from the fact that the concentration parameter $\epsilon_\nu = (\nu/\epsilon)(\partial\epsilon/\partial\nu)$ is always small in dilute solutions, while the temperature parameter $\epsilon_\Theta = (\Theta/\epsilon)(\partial\epsilon/\partial\Theta)$ for water proved fortuitously to be of the order of unity (more exactly, $\epsilon_\Theta = -1.4$.[24]). The situation alters with increasing concentration, since then the value of ϵ_ν also rises. For aqueous solutions it attains a value of $\cong 0.2$ at $\nu = 1$ mole/liter.[25] If in addition we take into consideration the fact that ϵ_ν occurs in the final expressions in the form of the product $\chi\epsilon_\nu$,† and that always $\chi \gtrsim 2$–3, then it becomes obvious that we must in no way neglect the concentration-dependence $\epsilon = \epsilon(\nu)$, even at $\nu \gtrsim 0.1$–0.2 moles/liter. Unfortunately, this feature hasn't received due attention in calculating the thermodynamic characteristics of electrolyte solutions of intermediate concentrations. On the one hand, this has given rise to some inner contradictions in the thermodynamics itself (see below). On the other hand, it has made it impossible to attain good agreement of theory with experiment.

2.1. Thermodynamics of Electrolyte Solutions

I. Averaging the configuration integral of an electrolyte solution over all possible positions of the solvent molecules is equivalent to going from the real solution to a model system consisting of N charged particles, each of which moves freely (i.e., frictionlessly) in a continuous medium of dielectric constant ϵ. However, the previous chapter essentially treated not this model, but a gas of particles bearing the effective charge $e/\sqrt{\epsilon}$, and moving in a vacuum. Hence we must first of all analyze to what extent the results obtained above can be used to construct a thermodynamics of electrolyte solutions.

All calculations of the binary distribution function of an ion gas are based on the assumption that its configurational energy U_N equals the sum of the pair potentials $\Phi_{ab}(r)$ given by relation (IV). In order that U_N should have the same form for the model system as well, we must assume: a) that the charge within the ion-spheres is distributed with spherical symmetry, and b) that the dielectric constant $\epsilon^{(i)}$ of the medium within the ions

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*One can show that Eq. (1.41), which is a special case of (1.33), (1.34), also unambiguously determines the thermodynamic parameters in the case of a system of uncharged particles.

*Without this, for example, one fails to explain not only the concentration-dependence of the heats of dilution, but even the sign of the effect itself.[24]

†See, e.g., the expression (2.7) for the free energy, which contains the term $\frac{1}{2}(\chi - \chi_0) \cong \frac{1}{2}\chi_0\epsilon_\nu$.

equals the dielectric constant ϵ of the solvent.* If both these conditions are satisfied, then we can assume that the above-derived formulas for $\mathscr{G}_{ab}$ are equally valid both for the ion gas and for the model. However, the expressions for the thermodynamic functions of the ion gas derived by using (1.11) and (1.19) cannot be extended to electrolyte solutions. This is because, generally speaking, these formulas do not define the relation between the binary distribution and the macroscopic characteristics of the model that we are studying. The latter can be seen especially well from the example of the formula (1.19) for the pressure, which implies that the solvent influences the equation of state of the solution only by way of the ionic subsystem. However, as is physically evident, the contribution of the ionic subsystem to P is generally very small, and fundamentally P depends precisely on the properties of the solvent.

In order to establish the relation between the binary distribution function and the macroscopic parameters of electrolyte solutions, we shall start with the well-known expression for the internal energy of the system[26,27]†

$$U_N^{(el)}(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \int_V \left(1+\frac{\Theta}{\varepsilon}\frac{\partial\varepsilon}{\partial\Theta}\right)\frac{\varepsilon E^2}{8\pi}\,d^3r$$

$$= \left(1+\frac{\Theta}{\varepsilon}\frac{\partial\varepsilon}{\partial\Theta}\right)\int_V \frac{\varepsilon E^2}{8\pi}\,d^3r. \tag{2.1}$$

Since in our case

$$\mathbf{E} = \sum_i \mathbf{E}_i,$$

where $\mathbf{E}_i = \mathbf{E}_i(|\mathbf{r} - \mathbf{r}_i|)$ is the field of the ith ion, then

$$E^2 = \sum_i \mathbf{E}_i^2 + \sum_{i \neq j} \mathbf{E}_i\mathbf{E}_j.$$

Substituting this expression into (2.1), we obtain the following for the electrostatic component of the configurational energy of the solution:

$$U_N^{(el)} = \frac{1}{2}\left(1+\frac{\Theta}{\varepsilon}\frac{\partial\varepsilon}{\partial\Theta}\right)\left\{\sum_{1\leq i\leq N}' \frac{e_i^2}{\varepsilon r_0} + \sum_{1\leq i,\, j\leq N}' \frac{e_ie_j}{\varepsilon r_{ij}}\right\}, \tag{2.2}$$

where $r_{ij} = \mathbf{r}_i - \mathbf{r}_j$. Here, in calculating integrals such as

$$\int_V E_i^2 d^3r,$$

we have omitted the portion of them that is localized i a sphere of radius r_0 centered at $\mathbf{r}_i$, since the latter depends only on the nature of the charge distribution within the ion. Hence, it is of no interest.

Averaging (2.2) over the ensemble at constant volume V of the system, we obtain

$$U^{(el)} = \left(1+\frac{\Theta}{\varepsilon}\frac{\partial\varepsilon}{\partial\Theta}\right)\left\{\frac{1}{2}\sum_{1\leq a\leq M} \frac{N_a^2e_a^2}{\varepsilon r_0}\right.$$

$$+\frac{1}{2}\int_0^\infty \sum_{1\leq a,b\leq M}' \frac{N_aN_b}{V}\Phi_{ab}^{(el)}(r)$$

$$\left.\times\, \mathscr{G}_{ab}(r)\,4\pi r^2\,dr\right\} = \left(1+\frac{\Theta}{\varepsilon}\frac{\partial\varepsilon}{\partial\Theta}\right)\int_V \frac{\varepsilon \overline{E^2}}{8\pi}\,d^3r. \tag{2.3}$$

This expression represents the electrostatic component of the internal energy of the solution.* It differs from the usual formula (1.11) for U, first, by containing the factor $1 + (\Theta/\epsilon)(\partial\epsilon/\partial\Theta)$, which describes the change in the entropy of the folvent in the field of the ions, and second, in having the additional term

$$\sum_a (N_a^2e_a^2/\epsilon r_0)$$

characterizing the intrinsic energy of the ions. Both these corrections make an appreciable contribution to the increment of the internal energy of a solution of finite concentration with respect to an infinitely-dilute solution, for which $\epsilon = \epsilon_0$, and $\mathscr{G}_{ab} \equiv 1$,

$$\Delta_v U^{(el)} = U^{(el)}(v) - U^{(el)}(v=0)$$

$$= \frac{1}{2}\left(1+\frac{\Theta}{\varepsilon}\frac{\partial\varepsilon}{\partial\Theta}\right)\left\{\sum_{1\leq a\leq M}' \frac{N_ae_a^2}{\varepsilon r_0}\right.$$

$$\left.\times \int_0^\infty \sum_{1\leq a,b\leq M}' \frac{N_aN_b}{V}\Phi_{ab}^{(el)}(r)\,G_{ab}(r)\,4\pi r^2\,dr\right\}$$

$$-\frac{1}{2}\left(1+\frac{\Theta}{\varepsilon_0}\frac{\partial\varepsilon_0}{\partial\Theta}\right)\sum_{1\leq a\leq M}' \frac{N_ae_a^2}{\varepsilon_0 r_0}. \tag{2.4}$$

In the special case in which $\mathscr{G}_{ab}$ is given by Eq. (1.40), $\Delta_v U^{(el)}$ has the form

$$\Delta_v U^{(el)} = \frac{N}{2}\left\{\left(1+\frac{\Theta}{\varepsilon}\frac{\partial\varepsilon}{\partial\Theta}\right)\left[\frac{k^2e^2}{\varepsilon r_0} - \frac{k^2e^2}{\varepsilon(r_0+r_D)}\right]\right.$$

$$\left. - \left(1+\frac{\Theta}{\varepsilon_0}\frac{\partial\varepsilon_0}{\partial\Theta}\right)\frac{k^2e^2}{\varepsilon_0 r_0}\right\}. \tag{2.5}$$

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*If $\epsilon^{(0)} \neq \epsilon$, then the solution of Poisson's equation $\Delta\varphi = -(4\pi/\epsilon)\rho(\mathbf{r}_1, \ldots \mathbf{r}_N)$ for the system of charged spheres, where the $\mathbf{r}_i$ are the coordinates of the ith ion, cannot be represented in the form

$$\varphi = \sum_i e_i/\epsilon|\mathbf{r} - \mathbf{r}_i|.$$

The introduction of the quantity $\epsilon^{(0)}$, which has no clear physical meaning, is necessary only because otherwise we cannot formulate the initial electrostatic problem.

†Since the macroscopic volume average of any quantity in a homogeneous system is a constant, then ϵ also cannot depend on the value of the coordinate $\mathbf{r}$. The latter is highly essential, since in the literature attempts have repeatedly been undertaken to treat ϵ as a function of the distance between ions. This, of course, is false.

*The initial formula (2.1) for $U_N^{(el)}$ can represent either the internal energy, or the enthalpy, depending on whether the expression $(1/4\pi)\epsilon E\,dE$ was integrated at constant volume or at constant pressure. In distinction, the formula (2.3) always represents the internal energy, since the condition V = const was made explicitly in the averaging.

If the dielectric constant $\epsilon(\Theta, \nu) =$ const, then (2.5) coincides with the Debye formula (1.12). However, in the general case in which $\epsilon = \epsilon(\Theta, \nu)$, they differ quite substantially.

II. When the quantity $\Delta_\nu U$ has been found, it is not hard to calculate the increment in the free energy of the system $\Delta_\nu F = F(\nu) - F(\nu = 0)$ by the Gibbs-Helmholtz formula $U = -\Theta^2(\partial/\partial\Theta)(F/\Theta)$. Indeed, upon substituting into it the $\Delta_\nu U$ from (2.5) and integrating the expression obtained between the limits $\Theta = \Theta_1$ and $\Theta = \Theta_2$, we find that

$$-\int_{\Theta_1}^{\Theta_2} \frac{\Delta_\nu U(\Theta)}{\Theta^2}\, d\Theta = \Delta_\Theta \left\{\frac{\Delta_\nu F}{\Theta}\right\}$$

$$= \Delta_\Theta N \left\{\frac{1}{2}(\chi - \chi_0) - \frac{\chi}{\varkappa^2}\left[\ln(1+\varkappa) - \varkappa + \frac{1}{2}\varkappa^2\right]\right\}, \tag{2.6}$$

where $\Delta_\Theta\{\ \} = \{\ \}_{\Theta=\Theta_2} - \{\ \}_{\Theta=\Theta_1}$. The subscript 0 applied to χ implies that in $\chi = k^2e^2/\epsilon\Theta r_0$ the quantity $\epsilon = \epsilon(\nu)$ is taken at $\nu = 0$, and is equal to $\epsilon_0 = \epsilon(0)$. We note now that the free energy F of the system is a single-valued state function. Hence, the value of $\Delta_\nu F(\Theta)$ at $\Theta = \Theta_1$ cannot depend on the arbitrary temperature $\Theta = \Theta_2$. The latter condition is compatible with (2.6) only if

$$\Delta_\nu F = N\Theta\left\{\frac{1}{2}(\chi - \chi_0) - \frac{\chi}{\varkappa^2}\left[\ln(1+\varkappa) - \varkappa + \frac{1}{2}\varkappa^2\right] + f(n) - f(0)\right\} = \Delta_\nu F^{(el)} + \Delta_\nu F^{(s)}. \tag{2.7}$$

Here $\Delta_\nu F^{(s)} = N\Theta[f(n) - f(0)]$ and the function $f(n)$, which is an arbitrary integration constant (since $\Delta f(n) = 0$), can depend only on the relative concentration $n = N/N_s$, where N_s is the total number of solvent molecules and N is the total number of particles of the solute. Since the expression enclosed within curly brackets in (2.6) is valid only at concentrations not exceeding one mole/liter (since always $\varkappa \lesssim 1$), then we can assume to a higher degree of accuracy that $f(n) - f(0) \cong Bn$.

If we assume in (2.7) that $\chi = \chi_0$, then the term $\frac{1}{2}(\chi - \chi_0)$ first introduced by Hückel[24] vanishes, and we arrive anew at the ordinary Debye expression for the free energy increment. We emphasize that this applies particularly to the free energy $\Delta_\nu F$, but not at all to the thermodynamic potential $\Delta_\nu\mathcal{F} = \Delta_\nu F + P\Delta_\nu V$, as has often been stated.[20,24] And although the numerical difference between $\Delta_\nu\mathcal{F}$ and $\Delta_\nu F$ is small (because liquids are practically incompressible and $\Delta_\nu V \cong 0$), it is very important, since it means that the chemical potential of the solvent has been calculated incorrectly heretofore (see below).

III. Using the ordinary formulas of thermodynamics, we can find from (2.7) the rest of the thermodynamic functions of the solution: its entropy, enthalpy, etc. However, we shall not do this, but shall restrict ourselves to treating only the chemical potentials of the solute μ and the solvent μ_s. We must bear in mind in calculating them the fact that $\Delta F^{(el)} = f(\Theta, V, N, \epsilon, \epsilon_0)$, and in turn, that $\epsilon = \epsilon(\Theta, V, N, N_s)$, and $\epsilon_0 = \lim_{N\to 0} \epsilon(\Theta, V, N, N_s)$. Since by definition $\mu = (\partial F/\partial N)_{\Theta,V,N_s}$, and $\mu_s = (\partial F/\partial N_s)_{\Theta,V,N}$, we can neglect the dependence of ΔF, ϵ, and ϵ_0 on Θ and V in the differentiation. Hence,

$$\Delta\mu = \mu - \mu_{id} = \left(\frac{\partial\Delta F}{\partial N}\right)_{\Theta,V,N_s}$$

$$= \frac{\partial\Delta F}{\partial N} + \frac{\partial\Delta F}{\partial\epsilon}\frac{\partial\epsilon}{\partial N} + \frac{\partial\Delta F}{\partial\epsilon_0}\frac{\partial\epsilon_0}{\partial N}, \tag{2.8}$$

$$\Delta\mu_s = \mu_s - \mu^{(s)}_{id} = \left(\frac{\partial\Delta F}{\partial N_s}\right)_{\Theta,V,N}$$

$$= \frac{\partial\Delta F}{\partial N_s} + \frac{\partial\Delta F}{\partial\epsilon}\frac{\partial\epsilon}{\partial N_s} + \frac{\partial\Delta F}{\partial\epsilon_0}\frac{\partial\epsilon_0}{\partial N_s}, \tag{2.9}$$

where $\mu_{id} = \mu^{(0)} + \Theta \ln n$ and $\mu_s^{(0)} + \Theta \ln(1 - n) \cong \mu_s^{(0)} - \Theta_n$ are the chemical potentials of the solute and the solvent for the case of an ideal solution, $\partial\epsilon_0/\partial N = \lim_{N\to 0}(\partial\epsilon/\partial N)$, and $\partial\epsilon_0/\partial N_s = \lim_{N\to 0}(\partial\epsilon/\partial N_s)$. In taking the derivative in (2.9), we must bear in mind the fact that only $\Delta_\nu F^{(s)} = \Theta B(N^2/N_s)$ depends directly on N_s in (2.7); on the other hand, the electrostatic component $\Delta_\nu F^{(s)} = B(N^2/N_s)$ depends directly on the electrostatic component $\Delta_\nu F^{(el)}$ of the free energy depends only indirectly on N_s via ϵ and ϵ_0.* Substituting (2.7) into (2.8) and (2.9), we obtain

$$\Delta\mu = \Theta \ln f = \Theta\left\{2Bn - \frac{1}{2}\left[\chi - \frac{\chi\varkappa}{1+\varkappa}\right]\left(1 - \frac{N}{\epsilon}\frac{\partial\epsilon}{\partial N}\right) + \frac{1}{2}\chi_0\left(1 - \frac{N}{\epsilon_0}\frac{\partial\epsilon_0}{\partial N}\right)\right\}, \tag{2.10}$$

$$\Delta\mu_s = \Theta n(1 - g) = -\Theta n\left\{Bn + \frac{1}{2}\left[\chi - \frac{\chi\varkappa}{1+\varkappa}\right]\frac{N_s}{\epsilon}\frac{\partial\epsilon}{\partial N_s} - \frac{1}{2}\chi_0\frac{N_s}{\epsilon_0}\frac{\partial\epsilon_0}{\partial N_s}\right\}, \tag{2.11}$$

where $\mu = \mu_{id} + \Theta \ln f$, and f is the activity coefficient; $\mu_s = \mu_{id}^{(s)} - \Theta_{gn}$, and g is the osmotic coefficient.

By using (2.3), the electrostatic component of the chemical potentials can be written in the form

$$\Delta\mu^{(el)} = \frac{1}{N}\Delta_\nu\left\{\int_{V_0}\frac{\epsilon\overline{E^2}}{8\pi}\,dV - \int_{V_0}\frac{\overline{E^2}}{8\pi}N\frac{\partial\epsilon}{\partial N}\,dV\right\}. \tag{2.12}$$

$$\Delta\mu_s^{(el)} = -\frac{1}{N_s}\Delta_\nu\left\{\int_{V_0}\frac{\overline{E^2}}{8\pi}\tau\frac{\partial\epsilon}{\partial\tau}\,dV_0\right\}. \tag{2.13}$$

where $\tau = N_s/V_0$ is the density of the solvent. Thus we see that $\Delta\mu^{(el)}$ is determined (as calculated per ion) by the increment in the total electrostatic energy (the integral $\int_{V_0}(\epsilon E^2/8\pi)\,dV$, minus the portion due to the change in the dielectric constant of the solvent (the integral $\int_{V_0}$

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*And of course, via $V = N\nu + N_s\nu_s$, where ν and ν_s are the partial molar volumes of the solute and solvent, respectively. However, we need not take into account the dependence of $\Delta_\nu F^{(el)}$ on N_s via $\varkappa \sim V^{-1/2}$, since V is held constant in the differentiation

$(E^2/8\pi)N(\partial\epsilon/\partial N)\,dV$), while $\mu_s^{(el)}$ is the electrostatic work done in changing the density of the solvent. As we should expect, the expression for $\mu_s^{(el)}$ exactly coincides with the usual definition of the chemical potential of a dielectric in an external field.[26]

IV. If we assume in (2.10) that $\epsilon = \epsilon_0 = \text{const}$, then we get the well-known Debye expression for the activity coefficient with Onsager's correction*

$$\ln f = -\frac{1}{2}\frac{\chi\kappa}{1+\kappa} + 2Bn, \tag{2.14}$$

whereas the expression (2.11) for the osmotic coefficient g does not transform under any conditions into the formula used in the theory of electrolyte solutions.[20,21,24] In order to understand what the trouble is here, let us examine the course of the arguments usually used in deriving the expression for g. First, one assumes at the outset that (2.7) gives the increment in the thermodynamic potential $\Delta_\nu\mathcal{F}$, which is wrong, as we have seen. Then one finds $\Delta\mu_s$ by the formula

$$\Delta\mu_s = \left(\frac{d\Delta\mathcal{F}}{dN_s}\right)_{\Theta,P,N}$$

$$= \frac{\partial\Delta\mathcal{F}}{\partial N_s} + \frac{\partial\Delta\mathcal{F}}{\partial V}\frac{\partial V}{\partial N_s} + \frac{\partial\Delta\mathcal{F}}{\partial\epsilon}\frac{\partial\epsilon}{\partial N_s} + \frac{\partial\Delta\mathcal{F}}{\partial\epsilon_0}\frac{\partial\epsilon_0}{\partial N_s},$$

Here one drops the terms containing $\partial\epsilon/\partial N_s$ and $\partial\epsilon_0/\partial N_s$ for unknown reasons, although, as we know, $(\tau/\epsilon)(\partial\epsilon/\partial\tau) \cong 1$.[10] The error in this derivation is evident. Even if we define μ_s as $(\partial\mathcal{F}8\partial N_s)_{\Theta,P,N}$, then by virtue of the identity $\mathcal{F} = F + PV$, $P = -\partial F/\partial V$, the term in μ_s containing $\partial\ \ /\partial V$ nevertheless vanishes, and we again arrive at Eq. (2.9). This is natural, since $\mu = (\partial F/\partial N)_{\Theta,V} = (\partial\mathcal{F}/\partial N)_{\Theta,P}$.[19]

V. Now we shall show that neglecting the concentration-dependence $\epsilon = \epsilon(N)$ leads to inner contradictions in the case of electrolyte solutions of intermediate concentrations for which $\kappa \gtrsim 0.1$. To do this, we recall that when $P, \Theta = \text{const}$, the chemical potentials μ_s of the solvent and μ of the solute satisfy the Gibbs-Duhem relation $n^*(\partial\mu/\partial n^*) + (1 - n^*)(\partial\mu_s/\partial n^*) = 0$, where $n^* = N/(N + N_s)$ is the so-called mole fraction. Upon transforming from μ and μ_s to $\ln f$ and g, we obtain $1 - g + (1 - n^*)\ln(1 - n^*)(dg/dn) + (d\ln f/dn^*) = 0$. When $N \ll N_s$, so that $n^* \cong n$, this leads to the well-known Bjerrum relation[21]:

$$1-g = -n\frac{d}{dn}[1-g+\ln f]. \tag{2.15}$$

To start with, we shall assume that $\epsilon = \epsilon(N_s)$ is independent of the concentration $n = N/N_s$.* In this case, substituting (2.10) and (2.11) into (2.15) gives

$$\frac{\tau}{\epsilon}\left(\frac{\partial\epsilon}{\partial\tau}\right)_{\Theta,P} = \frac{1}{3+2\kappa}. \tag{2.16}$$

Such an equality is impossible, since the left-hand side of (2.16) is a constant, while the right-hand side substantially depends on ν by way of $\kappa \sim \sqrt{\nu}$. This contradiction can be removed only by assuming that $\epsilon(\nu) \neq \text{const}$. In fact, if $\epsilon = \epsilon(\tau, \nu)$, then substitution of (2.10) and (2.11) into Bjerrum's relation (2.15) transforms the latter into a partial differential equation in the unknown function ϵ. By solving it, we can find $\epsilon(\tau, \nu)$, apart from an arbitrary function $\epsilon^{(0)} = \epsilon^{(0)}(\tau_0, \nu)$.

Equation (2.16) implies that $(\tau/\epsilon)(\partial\epsilon/\partial\tau) = 1/3$ for extremely dilute solutions, for which $\kappa \to 0$. Upon substitution into (2.11), this gives $1 - g = {}^1\!/_6\,\chi\kappa$. Since this expression, which coincides with the well-known Debye-Hückel formula, agrees well with the results of measurements,[20,21,24] we can consider that in this case Eq. (2.11) admits of experimental verification. However, this becomes impossible at higher concentrations, since (2.11) contains the unknown derivatives $\partial\epsilon(\tau, \nu)/\partial\tau$. In order to remove this difficulty, we can determine the osmotic coefficient g by integrating (2.15):

$$1-g = -\frac{1}{n}\int_0^n n\frac{d\ln f}{dn}\,dn, \tag{2.17}$$

where $\ln f$ is given by (2.10). The expression thus obtained, which contains only ϵ and $\partial\epsilon/\partial N$, will evidently be exact, since it is transformed into an identity upon substitution of (2.10) and (2.17) into (2.15).

2.2. Comparison with Experiment[28]

I. Before going on to comparing directly the formulas derived above with the experimental data, we shall make some preliminary remarks.

First, the final formula (1.40) for the binary distribution formula satisfies the system of equations (1.35), (1.36) better as χ and κ becomes smaller. If we assume that the system (1.35), (1.36) ensures the necessary accuracy, then the discrepancy between the thermodynamic and experimental curves must systematically increase with increase of these parameters. Here it should become very large for $\kappa \gtrsim 1$ and $\chi \gtrsim 3$ (since $\kappa \cong 1$ and $\chi \cong 3$ determine the limits of applicability of the derived solution). In essence, only this sort of agreement can serve to prove the correctness of the initial system (1.35), (1.36). However, if the error of the theory proves to be independent of the values of χ and κ, this might mean only that it is due to some causes other than a systematic error in the derived solution.

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*Onsager suggested that in (2.14 the term Bn coincides with the second virial coefficient $2\rho/3$ of a system of hard spheres. Hence $B = \frac{1}{2}(\pi r^3 N/V)(N_s/N) = 4(\pi r_0^3/6)(N_s/V) = V_0/4V_s$, where $V_0 = \pi r_0^3/6$ and $V_s = V/N_s$.

*Since the constant ϵ results from averaging over the N_s solvent molecules, it cannot fail to depend on N_s (or more exactly 1, on the density $\tau = N_s/V_0$).

Second, in the Debye model of an electrolyte solution, all the forces of non-Coulombic origin are subsumed under an intrinsic volume $v_0 = \pi r_0^3/6$ occupied by the particles of the solute. However, real systems can manifest also other forces of a similar sort,* not explicitly considered in this model. In part, the effect of these additional (with respect to the chosen model) forces can always be compensated by varying the value r_0 with respect to the crystallographic diameter r_c of the ions. Hence, in experimentally testing the theoretical formulas, r_0 must be treated as a certain adjustable parameter effectively characterizing all forces of non-Coulombic origin acting in the system.

Third, any theory taking the solvent in to account only i terms of its dielectric constant involves the arbitrary function $\epsilon = \epsilon(\nu, \Theta)$. Generally speaking, the form of the latter can be determined by independent measurements and appropriate calculation. However, such measurements are practically lacking at present, rendering impossible an all-sided test of the theory. The concentration dependence $\epsilon = \epsilon(\nu)$ has been determined only at 25°C with more or less accuracy for aqueous solutions of certain alkali halides. Here it turned out that[25]

$$\epsilon = \epsilon_0(1 - \epsilon_1\nu). \qquad (2.18)$$

where ν is measured in moles/liter, $\epsilon_0 = 78.5$ is the dielectric constant of pure water, and the mean value of ϵ_1 for solutions of LiCl, NaCl, KCl, RbCl, NaBr, and NaI is 0.20 ± 0.03 (there are no data for the other alkali halides). Using (2.18), we can calculate only the activity coefficient (2.10)*

$$\ln f = -\frac{\chi_0^*\varkappa_0^*\sqrt{\nu}}{(1-\epsilon_1\nu)^2(\sqrt{1-\epsilon_1\nu}+\varkappa_0^* r_0\sqrt{\nu})}$$

$$+\frac{\chi_0^*}{2r_0}\epsilon_1\nu\frac{1+\epsilon_1\nu+\epsilon_1^2\nu^2}{(1-\epsilon_1\nu)^2} + 50.46\cdot10^{-4}r_0^3\nu. \qquad (2.19)$$

where at 25°C, $\chi_0^* = 7.134$, $\kappa_0^* = 0.3289$, r_0 is measured in A, and

$$\chi = \frac{\chi_0}{1-\epsilon_1\nu} = \frac{\chi_0^*}{r_0(1-\epsilon_1\nu)};$$

$$\varkappa = \frac{\varkappa_0}{\sqrt{1-\epsilon_1\nu}} = \varkappa_0^* r_0\frac{\sqrt{\nu}}{\sqrt{1-\epsilon_1\nu}}. \qquad (2.20)$$

The remaining formulas of the previous section contain the unknown derivatives $\partial\epsilon/\partial\tau$ or $\partial\epsilon/\partial\Theta$, preventing any comparison of them with the experimental data.

II. In order to show the nature of the influence of the concentration-dependence of the dielectric constant, we shall begin by discussing the very simple case $\epsilon = \epsilon(\nu) =$ const (i.e., $\epsilon_1 = 0$). Here, using (2.14) and (2.17), we get the ordinary Debye expression for the osmotic coefficient g:

$$1 - g = \frac{\chi}{2\varkappa^2}[1+\varkappa-(1+\varkappa)^{-1}-2\ln(1+\varkappa)] - \frac{2}{3}\rho. \qquad (2.21)$$

As was shown above, this gives qualitative results hardly differing from Eq. (1.43), which was found firectly from the expression (1.40) for the binary distribution function by using (1.19).

Equation (2.21) (or equivalently, Eq. (1.43)) was compared with experiment as follows: the theoretical curve $g = g(r_0, \nu)$ was fitted to the experimental curve at $\nu = 0.1$ moles/liter by proper choice of r_0. Then, assuming $r_0 =$ const, the difference $\Delta g = g_{theor} - g_{exp}$ was found at $\nu = 0.5$ and 1.0 moles/liter. The values of g_{exp} were taken from the tables in [34]. The results of the corresponding calculations for aqueous solutions of 15 alkali halides are given in Table II.* We see from these data that (2.21) gives an error that on the average is fourteen times the experimental error $\delta = 0.001$, even at $\nu = 0.5$ moles/liter. At $\nu = 1.0$ moles/liter, the discrepancy increases to a factor of thirty. Furthermore, there is no correlation whatsoever between Δg and the parameter $\chi = e^2/\epsilon\Theta r_0$. Thus, the experimental test of Eq. (2.21) has shown it unsuitable for describing electrolyte solutions of intermediate concentrations. However, we should have expected this (we recall that in deriving (2.21) the assumption was made that $\epsilon(\nu) =$ const, which is inadmissible).

III. It is of definite interest to compare Eq. (2.21) with other currently known expressions for the osmotic coefficient. As was shown above, the most rigorous of these is the Mayer-Haga formula (III). However, the series in (III) converges rapidly enough only when $\nu \lesssim 0.05$ moles/liter, i.e., in the concentration range in which the correction to the limiting Debye-Hückel law is so small that it can't be determined experimentally to a sufficient degree of accuracy. Hence there is no point in comparing (2.21) with the Mayer-Haga formula.

The next in order of reliability is the Tyablikov-Tolmachev formula (1.42) for the distribution function. At low concentrations it gives results agreeing with the Mayer-Haga formula. Of course, (1.42) is approximate at higher concentrations, since it does not include all terms of the same order of smallness. However, as was shown in [30], it can be derived quite rigorously by selective summation of a definite class of diagrams. If we assume that the rest of the diagrams contribute only little to the final expression, then we can consider the Tyablikov-

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*E.g., repulsive forces due to overlap of the hydration shells of the ions, or ion-dipole attractive forces (see below).

*Here, according to Onsager,[29] the product Bn in (2.10) has been assumed equal to $\frac{2}{3}\rho$; the more general case in which $Bn \neq \frac{2}{3}\rho$ has also been discussed in [28].

*All the calculations were performed by Yu. M. Kessler, for which the author is highly grateful.

Table II

Name of electrolyte	ν = 0.1 moles/liter			ν = 0.5 moles/liter			ν = 1.0 moles/liter		
	Δ	r_0 (Å)		Δ	$\Delta g = g_{theor} - g_{exp}$		Δ	$\Delta g = g_{theor} - g_{exp}$	
		Eq. (2.23)	Eq. (2.21)		Eq. (2.23)	Eq. (2.21)		Eq. (2.23)	Eq. (2.21)
LiI	0.04	4.43	4.54	0.23	0.009	0.009	0.41	0.035	0.037
LiBr	0.04	4.04	4.16	0.26	0.014	0.011	0.45	0.025	0.019
LiCl	0.04	3.86	3.94	0,27	0.007	0.000	0.47	0.016	0.004
NaI	0.04	3.81	3.89	0.27	0.014	0.007	0.48	0.032	0.020
NaBr	0.04	3.60	3.65	0.28	0.018	0.012	0.50	0.044	0.027
NaCl	0.04	3.53	3.57	0.28	0.024	0.018	0.51	0.058	0.039
KI	0.04	3.53	3.56	0.28	0.028	0.022	0.51	0.067	0.048
KBr	0.04	3.32	3.32	0.30	0.027	0.020	0.54	0.062	0.042
KCl	0.04	3.27	3.27	0.30	0.028	0.019	0.55	0.067	0.044
RbCl	0.03	3.07	3.07	0.31	0.025	0.016	0.58	0.056	0.033
RbBr	0.03	2.99	2.98	0.32	0.020	0.011	0.60	0.051	0.028
RbI	0.03	2.94	2.93	0.32	0.020	0.010	0.61	0.048	0.025
CsCl	0.02	2.76	2.73	0.34	0.026	0.016	0.63	0.050	0.027
CsBr	0.02	2.74	2.70	0.34	0.027	0.018	0.64	0.056	0.032
CsI	0.02	2.70	2.64	0.34	0.027	0.017	0.65	0.056	0.031
$\overline{\Delta r_0} = r_0^{(2.23)} - r_0^{(2.21)} = 0.025$ Å				$\overline{\Delta g} = 0.021;\ 0.014$			$\overline{\Delta g} = 0.048;\ 0.030$		

Tolmachev formula to be a sort of extrapolation valid for any concentration. We cannot determine directly the size of the error that we make in such an extrapolation, since this would require that we find an exact expression for the binary distribution function. However, we can estimate it indirectly to the same degree of accuracy to which, e.g., the condition of neutrality (1.5) is obeyed. By substituting (1.42) into it and transforming to dimensionless variables, we obtain

$$\Delta = \chi - \varkappa^2 \int_1^\infty \operatorname{sh}\left[\chi \frac{e^{-\varkappa t}}{t}\right] t^2\, dt. \qquad (2.22)$$

Table II gives values of Δ calculated by this formula for $\varkappa = 0.3$, 0.7, and 1.0 (this corresponds approximately to $\nu = 0.1$, 0.5, and 1.0 moles/liter).* Since when the Tyabilikov-Tolmachev formula is accurate enough: however, on going to more concentrated solutions, the value of $\nu = 0.1$ moles/liter, Δ is very small,† we can assume that at this concentration the Tyablikov-Tolmachev formula is accurate enough: however, on going to more concentrated solutions, the value of Δ increases sharply, and hence the accuracy of (2.22) must decline.

Table II gives the values of r_0 and Δg calculated by the formula‡

$$1 - g = \frac{\varkappa^2}{6} \int_1^\infty \operatorname{sh}\left[\chi \frac{e^{-\varkappa t}}{t}\right] t\, dt - \frac{\varkappa^2}{6\chi} \operatorname{ch}\left[\chi e^{-\varkappa}\right], \qquad (2.23)$$

obtained upon substituting (1.42) into the expression (1.19) for the pressure. The value of r_0 was determined by fitting the experimental and theoretical curves at $\nu = 0.1$ moles/liter. As we see from the data given in the table, practically coincide (the arithmetic-mean value of the difference $\overline{\Delta r_0}$ is only 0.025 Å). However, Eq. (2.21) proves to be more accurate at high concentrations than the Tyablikov-Tolmachev formula (2.23), since at $\nu = 0.5$ and 1.0 moles/liter the value of Δg calculated by Eq. (2.23) is about 1.5 times as great as the value found by Eq. (2.21).

IV. We shall now proceed to test Eq. (2.21), which was derived under the assumption that $\epsilon = \epsilon(\nu) = \text{var}$. Table III gives the values of r_0 calculated for aqueous solutions of 15 alkali halides by fitting the theoretical and experimental values of log *f* at $\nu = 0.1$ moles/liter.* The effective diameters r_{ef} of the ions are given in the same table for comparison, as found from electrical-conductivity data.[32] If we consider that in the former case the ionic diameters are found by studying the equilibrium properties of the solutions, but in the latter case, by their kinetic properties, we must acknowledge the agreement of the two quantities to be strikingly good.

A general graph of the relation of log *f* to the concentration ν of the electrolyte is given in Fig. 2. We see that it shows good qualitative agreement between the theoretical and experimental curves; however, the quantitative agreement, which is very good for LiCl,

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*These data are taken from [31].

†We recall that Δ must be identically zero in an exact theory.

‡The values of Δg are taken from [31].

*The values of *f* are taken from [34].

Table III

No.	Name of salt	r_0 (Å)	r_{eff} (Å)	$\chi_0 = \frac{7.134}{r_0}$	r_K (Å)	$\Delta r_0 = r_0 - r_K$ (Å)
1	LiI	4.48	–	1.59	2.88	1.60
2	LiBr	4.00	—	1.78	2.64	1.36
3	LiCl	3.89	3.27±0.13	1.84	2.49	1.40
4	NaI	3.69	3.81±0.26	1.94	3.18	0.51
5	NaBr	3.45	3.45	2.07	2,94	0.51
6	NaCl	3.30	3.28±0.22	2.16	2.79	0.51
7	KI	3.23	3.67±0.19	2.21	3.53	—0.30
8	KBr	3.00	3.30±0.08	2,37	3.29	−0,29
9	KCl	2.90	3.06±0.16	2.46	3.14	—0.24
10	RbCl	2.59	2.90	2.76	3.30	—0.71
11	RbBr	2.54	—	2.81	3.45	−0.94
12	RbI	2.45	—	2.91	3.69	−1.24
13	CsCl	2.04	2.61	3.49	3.46	− 1.42
14	CsBr	2.04	—	3.49	3.61	—1.57
15	CsI	2.04	—	3.49	3.85	−1.81

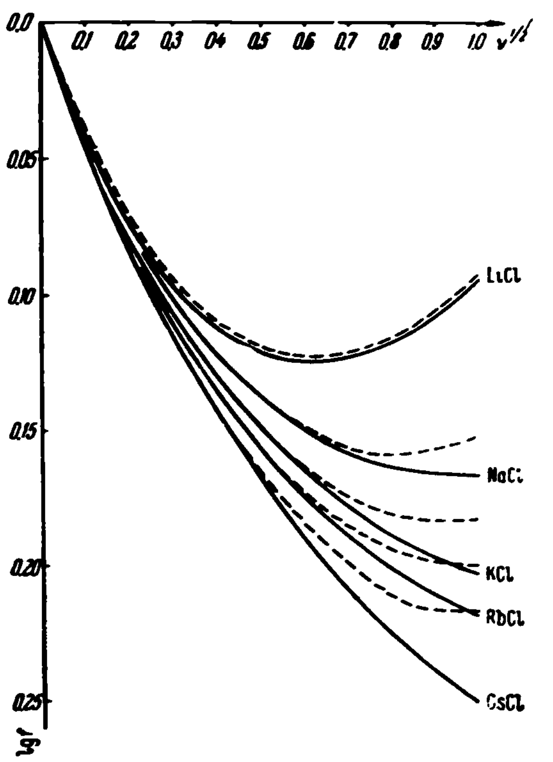

FIG. 2. Concentration-dependence of the activity coefficients of the alkali chlorides. ——— experiment, – – – theory.

gradually deteriorates in the series Li > Na > K > Rb > Cs. Here we observe a distinct correlation between the error of the theory $\Delta \log f = \log f_{theor} - \log f_{exp}$ and the values of the parameters κ and χ (Fig. 3). The latter is a convincing proof of the idea that the disagreement between theory and experiment in this case is due to a systematic inaccuracy of the obtained solution. However, this inaccuracy is not so great, since the relative error $\Delta \log f$ of the theory nowhere exceeds 13 percent, even at $\nu = 1$ mole/liter.*

V. As was noted above, the parameter r_0 effectively characterizes the value of all the forces acting in the real solution. At the same time, the mean crystallographic diameter $r_c = \frac{1}{2}(r_c^{(-)} + r_c^{(+)})$, where the $r_c^{(\mp)}$ are the crystallographic diameters of the anion and cation, respectively, defines the value of only those forces involving the excluded volume occupied by the ions themselves. Hence it is natural to assume that the difference $\Delta r_0 = r_0 - r_c$ is proportional to the additional forces acting in the real solution, and not taken into account explicitly in the charged-sphere model. And if this is so, then some correlative dependence should exist between Δr_0 and the parameters determining the strength of the additional forces.

One of the sources of the additional forces in a real solution could be the hydration of the ions.[33,34] Two particles of the solute can approach closely only after their hydration shells have been disrupted, which takes a certain expenditure of energy. Then evidently, hydration must give rise to additional repulsive forces that can be compensated only by an increase in r_0 with respect to r_c. Hence, correlation between the value of Δr_0 and the hydration energy $U^{(hydr)}$ of ions must be observed most clearly for those salts for which $\Delta r_0 \geqq 0$.

Now we recall that hydration is due to the influence of the electric field of the ions on the solvent molecules, which have a permanent dipole moment. Other conditions being equal, the energy of this interaction is proportional to the electric field intensity at the center of the water molecules. The latter in turn is inversely proportional to the square of the distance $r_{i-m}^{(\pm)} = [\frac{1}{2}(r_c^{(\pm)} + r_{H_2O})]$ between the centers of the ion and of the solvent

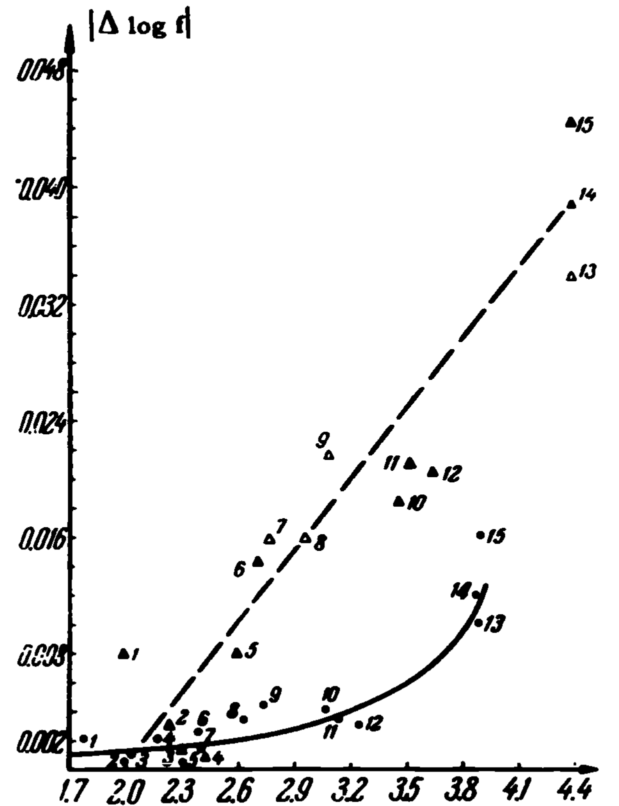

FIG. 3. Relation of the absolute error $\Delta \log f = \log f_{theor} - \log f_{exp}$ to the parameter χ.

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*The relative error is 13 percent only for CsCl. It drops to ≅10 percent for RbCl, KCl, and NaCl, and is still less for LiCl.

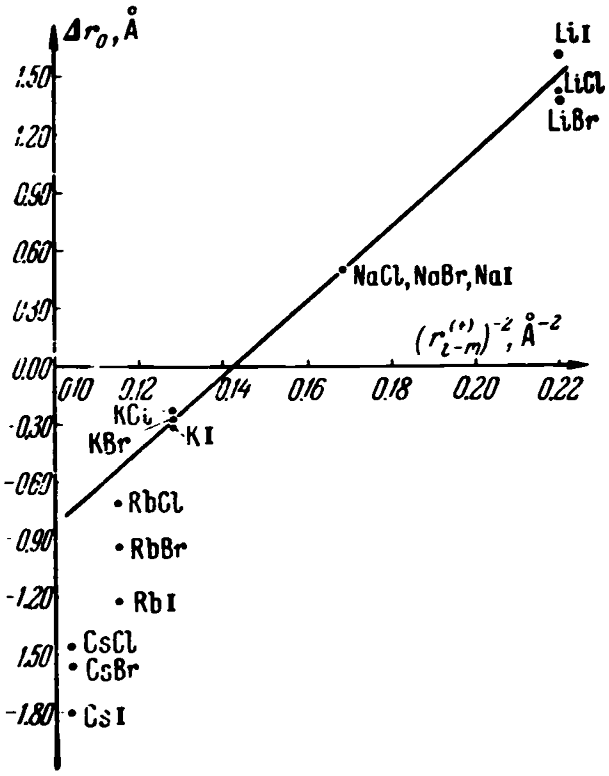

FIG. 4. Relation of $\Delta r_0 = r_0 - r_c$ to the hydration energy of the cations $U^{(\mathrm{hydr})} \sim (r_{i-m}^{(+)})^{-2}$.

molecule ($r_{H_2O} = 2.90$ Å is the diameter of a water molecule). Hence we see that the anions, which have a large diameter $r_c^{(-)}$, are almost unhydrated, since their hydration energy $U^{(\mathrm{hydr})} \sim (r_{i-m}^{(-)})^{-2}$ is very small.* However, it is considerably larger for the cations, and furthermore, $U^{(\mathrm{hydr})}$ for them varies over the rather large range ($0.10 \leqq (r_{i-m}^{(+)})^{-2} \leqq 0.20$). Hence Δr_0 should be distinctly correlated only with the hydration energy of the cations, as is well confirmed by the factual data. Indeed, Fig. 4 shows that the value of Δr_0 increases practically linearly with increasing $U^{(\mathrm{hydr})}$ for salts of Li^+, Na^+, and K^+. On the other hand, the salts of Rb^+ and Cs^+, for which Δr_0 is negative and large, fall off the curve.

We shall now examine what happens to the parameter r_0 in the series MCl, MBr, MI, where M is one of the five metal cations (i.e., Li, Na, K, Rb, or Cs). Since the cations are hydrated but the anions practically not, then when the Cl^- anion in the salt MCl is replaced by Br^- or I^-, the increase in r_0 must be close to the increase in the radius (rather than the diameter) of the anion $\frac{1}{2} r_c^{(-)}$. In other words, the difference $\frac{1}{2}[(r_0)_{MI} - (r_0)_{MCl}]$ must be approximately equal to $\frac{1}{2}[r_c^{(I^-)} - r_c^{(Cl^-)}] = 0.15$ Å. We see from the data given in Table IV that this requirement is satisfied quite well for the Li, Na, and K cations, but not for Rb and Cs. All of this leads to the conclusion that the additional forces in Rb and Cs salts do not arise from the hydration effect, but from some other cause.

Since the value of Δr_0 is negative for Rb and Cs salts, we might naturally assume that for them the additional forces are attractive. For example, the latter might be due to ion-dipole interaction of two solute particles. When neither of the particles possesses a permanent dipole moment, the energy of such an interaction is αE_2^2, where α_1 is the polarizability of the first ion, while E_2 is the electric field intensity caused by the second ion at the center or the first ion. When the Cl^- ion in a salt MCl is replaced by I^- or Br^-, the value of E_M remains practically constant (since $E_M \sim 1/r_c^2$, while r_c varies only from 3.30 to 3.85 Å for the Cs and Rb salts; see Table III). However, the polarizability of the Cl^-, Br^-, and I^- ions, being proportional to their volumes (i.e., to $(r_c^{(-)})^3$. On the other hand, Δr_0 should not depend on $(r_c^{(-)})^3$ at all for the salts of Li, Na, and K, which show practically no polarization interaction. This is precisely what is actually observed (Fig. 5).

Table IV

M	Li	Na	K	Rb	Cs
$\frac{1}{2}[(r_0)_{MI} - (r_0)_{MCl}]$	0.59	0.39	0.33	−0.14	0.00
$\frac{1}{2}[(r_0)_{MBr} - (r_0)_{MCl}]$	0.11	0.15	0.10	−0.04	0.00

CONCLUSION

We shall briefly formulate the results obtained above.

(A) Depending on their structures, all electrolyte solutions can be divided into three groups: dilute solutions, solutions of intermediate concentrations, and concentrated solutions. The distinguishing feature of the first group is the high degree of "collectivity," such that the Debye sphere contains a large number of ions at one time. For the second group, the charge of the "central" ion is screened by only one counterion, leading to formation of neutral quasimolecules in the system. Finally, concentrated electrolyte solutions are characterized

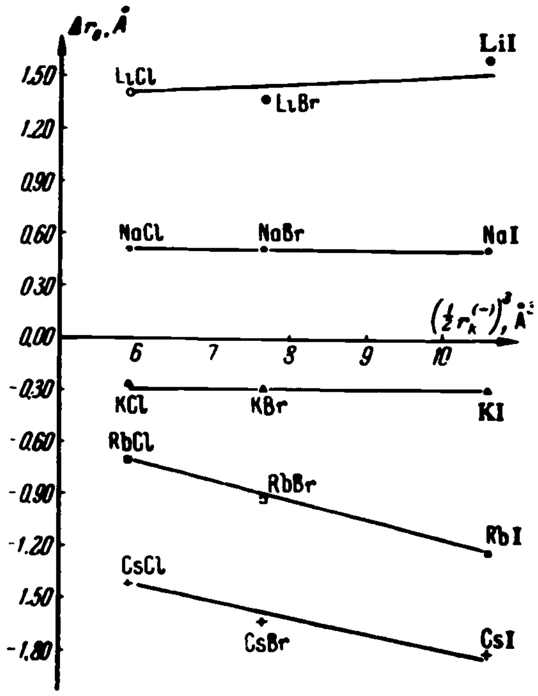

FIG. 5. Relation of $\Delta r_0 = r_0 - r_c$ to the volumes of the anions $v_0^{(-)} \sim (\frac{1}{2} r_c^{(-)})^3$.

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*In the series Cl^-, Br^-, I^-, the value of $(r_{i-m}^{(-)})^{-2}$ ranges only from 0.078 to 0.098.

by a structure of the ionic subsystem greatly reminiscent of the structure of ordinary liquids in its close-range order and coordination spheres.

(B) Since the absolute values of the density of the ionic subsystem in dilute solutions and solutions of intermediate concentrations are small enough, one can describe the solvent in them in terms of the dielectric constant $\epsilon = \epsilon(\Theta, \nu)$ alone. Here one can neglect in dilute solutions the dependence of ϵ on the concentration ν (but not on the temperature Θ!). However, in solutions of intermediate concentrations, one must always take into account the fact that $\epsilon = \epsilon(\nu)$. One can't introduce the dielectric constant at all in concentrated solutions, since the discrete structure of the solvent plays the important role in them.

(C) One can use methods of expansion in series in a small parameter in constructing a theory of dilute solutions, but these methods are not suitable for describing solutions of intermediate concentrations or concentrated systems, since then the corresponding series diverge. Hence, the theory of the latter can be based only on methods analogous to those used in the theory of ordinary liquids. However, since the density of the ionic subsystem is small in solutions of intermediate concentrations, one can use the linear equations of the theory of liquids to describe them. The non-linear effects must be taken into account for concentrated solutions.

(D) One can find a solution of the linear equations of liquid theory in analytic form for solutions of intermediate concentrations. Unfortunately, it is applicable only to aqueous solutions of univalent electrolytes for $\nu \lesssim 1$ mole/liter. This solution unambiguously determines the free energy of the ionic subsystem of the solution, and here it turns out that the derived expression for the internal energy exactly coincides with that previously found by Debye and Hückel.

(E) Heretofore, in constructing the thermodynamics of electrolyte solutions of intermediate concentrations, one has had to take account systematically of the fact that $\epsilon = \epsilon(\nu)$ for them. Introduction of the concentration-dependence into the expression for the characteristic functions of the system permits one to eliminate not only the inner contradictions existing in the thermodynamics of electrolyte solutions, but also to gain satisfactory agreement of theory with experiment.

(F) An analysis of the values of the single adjustable parameter of the theory (the ionic diameter r_0) permits one to establish the fact that in some solutions repulsive forces act between the ions, due to overlap of their hydration shells (hydration-type systems), while attractive forces act in others, due to the mutual polarizability of the ions (polarization-type systems).*

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