rates of Steps (16) and (17) as β/K_1 for the pyrolyses of acetaldehyde and dimethyl ether at several temperatures. If this ratio is sufficiently large, i.e., >10, the reaction order for the disappearance of reactant will be determined by Step (17). For smaller values of β/K_1, the reaction will be a transition region [or determined by Step (16) if the ratio is small enough].

Since β (steady state) is proportional to $A^{1/2}$, the rate equation would have the form

$$\text{rate}=k_{16}A+k_{17}'A^{3/2}, \tag{24}$$

where $k_{17}'=k_{17}(k_{16}/k_{19})^{1/2}$. It can be concluded, from the β/K_1 values in Table II, that a shift in order from three-halves toward one could be expected for the pyrolysis of acetaldehyde and dimethyl ether in the temperature region of about 1100° and 900°K, respectively, although the steady-state assumption may be valid at these conditions. The application of Eq. (24) to rate data in the transition region from which k_{16} could be calculated explicitly would be straightforward.

The Rice–Herzfeld mechanism has been presented in its simplest form; side reactions and shifts in mechanism may also complicate the interpretation of data. In addition, the problems of collision activation for the unimolecular steps in the mechanism for the pyrolysis of smaller molecules and collision deactivation for termination (third body) must be considered, as discussed in the previous section. The effects discussed in this presentation should be considered in addition to these other complications.

ACKNOWLEDGMENT

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Integral Equation Computations for Aqueous 1–1 Electrolytes.* Accuracy of the Method

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The computations described earlier [J. Chem. Phys. **48**, 2742 (1968)] have been carried out for a variety of primitive-model parameters representative of aqueous 1–1 electrolyte solutions at 25°C. A number of tests, some new, have been applied to assess the accuracy of the results. One test involves a square-mound model, for which some results are also given. The hypernetted-chain equation is found to be quite satisfactory for these models up to $1M$ electrolyte concentration.

I. INTRODUCTION

Recently an account was given[1] of integral-equation computations of the correlation functions and excess free-energy functions for the primitive model for electrolyte solutions. This comprises charged hard spheres in a dielectric continuum. The results indicated that the hypernetted-chain (HNC) equation is quite accurate for model parameters corresponding to aqueous 1–1 electrolytes up to $1M$ in concentration. A second important conclusion was that previous treatments have grossly underestimated the excluded volume contribution to the free energy, so much so that the *sign* of the change in the model required to get agreement with data for real systems is reversed.

This paper is concerned with extending these results to a variety of sets of primitive-model parameters representative of aqueous 1–1 electrolytes near 25°. One objective is to make the results available for comparison with experiment as a basis for making refinements in the model. The results may also be useful for estimating the behavior of refined models by perturbation methods.

Another objective is to investigate the application of various quality tests to these results. This aspect is given great attention here for several reasons. First, there are at present no computations of the Monte Carlo or molecular-dynamics sort which are suitable for comparison, so some other control of the errors inherent in the integral-equation computations is required. Furthermore, it is very clear that much more elaborate models than the primitive model must be investigated in order to elucidate some of the central problems of the electrolyte solution field: the effect of ion solvation on activity coefficients, for example. While it is anticipated that MC and MD computations will become available for some primitive-model sys-

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* Grateful acknowledgement is made of the support of this work by the Office of Saline Water.

[1] J. C. Rasaiah and H. L. Friedman, J. Chem. Phys. **48**, 2742 (1968). A few misprints which occurred in Ref. 1 should be corrected as follows. Equations (1.7) and (4.8) should have, in each instance, a minus sign before them. In Eq. (2.16) g_{ij} should be replaced by q_{ij}. The equation referred to in the Appendix as defining G_{ij} is Eq. (4.9) and not Eq. (4.5).

TABLE I. Dielectric properties of water.[a]

T(°K)	ϵ	$d\ln\epsilon/d\ln T$
293.16	80.176	−1.3459
298.16	78.358	−1.3679
303.16	76.581	−1.3900

[a] B. B. Owen, R. C. Miller, C. E. Nilner, and H. L. Cogan, J. Phys. Chem. **65**, 2065 (1961).

tems, there will be a continuing need to apply less expensive methods, such as the integral-equation methods, to the more elaborate models.

As discussed in Sec. III, there is an infinite number of self-consistency tests of the integral kind. Of these a number have been selected which only require integral-equation computations that are of immediate interest for some other purpose as well. This consideration has influenced the selection of computations summarized in Sec. II; these include somewhat more than primitive-model results.

II. COMPUTED THERMODYNAMIC FUNCTIONS

The primitive model is defined by the following equation for the direct potential (potential of average force at infinite dilution) acting between ions i and j at separation r:

$$u_{ij}(r)=e_ie_j/\epsilon r+u^*_{ij}(r), \tag{2.1}$$

$$\begin{aligned} u^*_{ij}(r)&=\infty, \quad \text{if} \quad r<a_{ij} \\ &=0, \quad \text{if} \quad a_{ij}<r. \end{aligned} \tag{2.2}$$

Here ϵ is the dielectric constant of the pure solvent, e_i is the ionic charge, and $a_{ij}=r_i+r_j$ is the sum of the radii of ions i and j. It is also assumed that the potential of interaction of an assembly of ions at specified locations in the solvent is a sum of pair potentials.

The computations are carried out by the method described earlier and lead to thermodynamic functions for systems in which the independent variables are the temperature T, the chemical potential of the solvent μ_w, and the volume concentration of the electrolyte c_2. We refer to this as the McMillan–Mayer set of independent variables.[2] For comparison with experimental data one must have the transformation relating this set to the usual set: total pressure, temperature, and molal concentration of electrolyte.[3] All of the thermodynamic functions in this paper are given in the former system.

In addition to the osmotic coefficient[4] ϕ and the mean ionic activity coefficient $\gamma_\pm$, we report computed values of the excess energy per unit volume E^{ex} which we obtain from the computed correlation functions by means of the equation[3,5]

$$E^{\text{ex}}=\frac{1}{2}\sum_{i=1}^{\sigma}\sum_{j=1}^{\sigma}c_ic_j\int_0^\infty\frac{\partial(\beta u_{ij})}{\partial\beta}g_{ij}(r)4\pi r^2dr, \tag{2.3}$$

where $\beta=1/kT$, c_i is the particle number density of solute species i, σ is the number of solute species, and g_{ij} is the pair-correlation function. In computations involving the primitive model we assume that u_{ij}^* is temperature independent and that the only contribution to the temperature dependence of u_{ij} comes from the temperature dependence of the dielectric constant.

In these computations we have used the dielectric properties of water given in Table I. The thermodynamic functions obtained for the primitive model are given in Tables II and III and Figs. 1–4. The functions $d\ln\gamma_\pm/dc_2$ and $\ln\gamma_\pm$ are obtained from the compressibility equation and the function ϕ from the virial equation, except as otherwise noted. Some computations were also made, by the same computer program, with the ion-charge parameters set to zero for comparison with other results for uncharged hard-sphere systems. These results are given in Table IV.

A few computations have also been made with a charged square-mound model, in which the direct potentials are given by Eq. (2.1) together with

$$\begin{aligned} u_{ij}^*(r)&=\infty, \quad \text{if} \quad r<a_{ij} \\ &=d_{ij}, \quad \text{if} \quad a_{ij}<r<a_{ij}+2w \\ &=0, \quad \text{if} \quad a_{ij}+2w<r. \end{aligned} \tag{2.4}$$

While these results are of rather general interest, they are included in this report mainly because of their use in various tests of the accuracy of the computed correlation functions. They are given in Table V.[6]

III. SELF-CONSISTENCY TESTS

In this section we shall mostly discuss equations for a one-component gas in order to keep the notation as simple as possible. The generalization to many-component solutions in the McMillan–Mayer system is straightforward, so the appropriate generalized forms are used only in the actual self-consistency tests reported here.

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[2] W. G. McMillan and J. E. Mayer, J. Chem. Phys. **13**, 276 (1945).

[3] H. L. Friedman, *Ionic Solution Theory* (Interscience Publishers, Inc., New York, 1962).

[4] In the McMillan–Mayer system $\phi=P_{\text{osm}}/ckT$, where P_{osm} is the osmotic pressure, so it corresponds to the compressibility factor PV/NkT often used in describing the equation of state of a gas. Thus $\phi-1$ is an excess function.[3]

[5] The appearance of $\partial(\beta u)/\partial\beta$ in place of u in the integrand is a consequence of the temperature dependence of u, which in turn arises from the fact that it is an average over solvent coordinates. This problem has been discussed in a general way by G. S. Rushbrooke, Trans. Faraday Soc. **36**, 1055 (1940).

[6] Another aspect of this calculation is described by J. C. Rasaiah and H. L. Friedman, J. Phys. Chem. **72**, 3352 (1968).

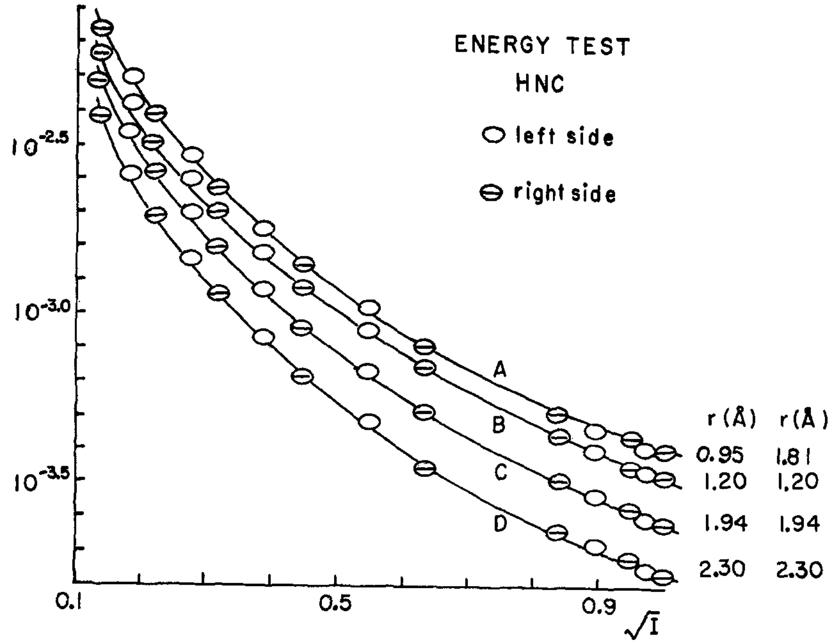

FIG. 1. Energy test of HNC equation for several models. The test compares the left and right sides of Eq. (3.6) which represent alternative ways of calculating the same thermodynamic function from the correlation functions. The ordinate has been increased by a factor of $10^{0.2}$ for Curve A and by $10^{0.1}$ for Curves B and C. I is the ionic strength (moles of electrolyte per liter of solution).

The familiar self-consistency test is the comparison of $P[g(r)]_v$, the pressure from the correlation function by the virial equation, with $P[g(r)]_c$, the pressure calculated from the same correlation function by the compressibility equation. In the previous report[1] the generalization of this test for electrolyte solutions was described and applied to some HNC results with quite satisfactory results. Additional results of this kind are reported in Table VI for a wide range of model parameters. Here ϕ_v and ϕ_c are the osmotic coefficients[4] calculated, respectively, by the virial and compressibility equations. The consistency exhibited in Table VI ought not to be gauged in terms of the absolute magnitude of $\phi_v - \phi_c$, for it is hard to see what this means, nor

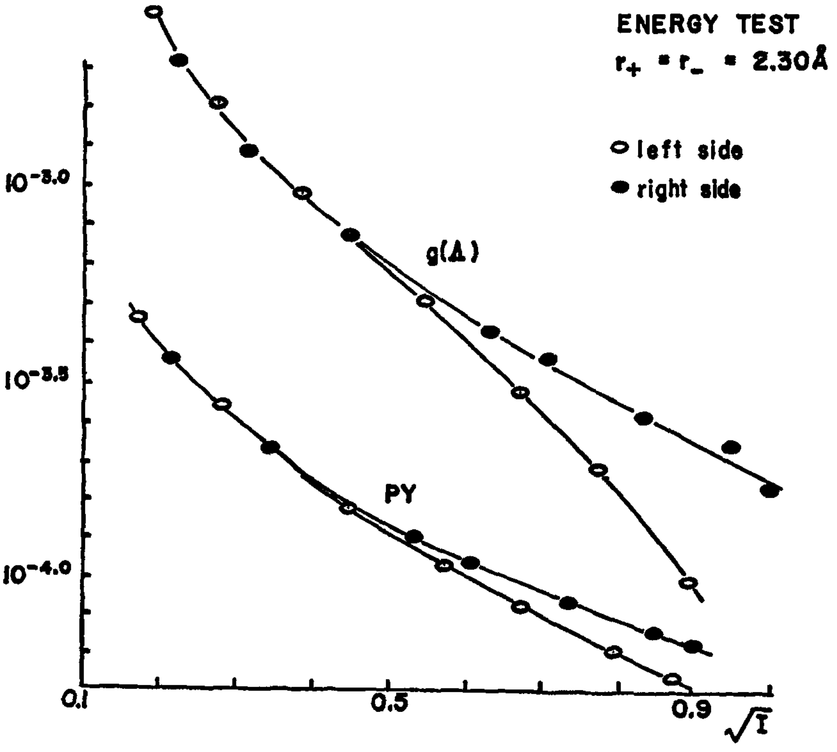

FIG. 2. Energy test for the PY equation and the $g(A)$ approximation for the model in which $r_+ = r_- = 2.3$ Å. Ordinate decreased by a factor of $10^{0.5}$, and abscissa moved to the left by 0.1 for the curve marked PY.

Table II. HNC results for primitive model with ion radii as shown and other parameters corresponding to aqueous solutions of 1–1 electrolytes at 20°, 25°, and 30°C.

c_2 (molar)		$\partial \ln\gamma_\pm/\partial c_2$	ϕ	$E^{ex}/c_2{}^b$		$\partial \ln\gamma_\pm/\partial c_2$	ϕ	$E^{ex}/c_2{}^b$
		$r_+=2.3$Å$=r_-$				$r_+=1.935$Å$=r_-$		
0.002	20°	−11.079	0.98459	19.88	20°	−11.548	0.98410	20.16
	25°	−11.184	0.98444	21.70	25°	−11.653	0.98396	22.01
	30°	−11.291	0.98429	23.60	30°	−11.764	0.98390	23.95
0.02		−2.3790	0.96307	55.88		−2.7395	0.95919	57.85
		−2.4023	0.96272	60.99		−2.7647	0.95882	63.15
		−2.4269	0.96235	66.33		−2.7911	0.95842	68.70
0.05		−1.0309	0.95462	80.65		−1.3446	0.94609	84.45
		−1.0428	0.95415	88.03		−1.3573	0.94558	92.16
		−1.0552	0.95366	95.71		−1.3709	0.94505	100.24
0.1		−0.41394	0.95351	104.11		−0.69787	0.93807	109.98
		−0.42072	0.95295	113.57		−0.70526	0.93747	120.00
		−0.42776	0.95237	123.46		−0.71308	0.93683	130.48
0.2		−0.02218	0.96470	131.57		−0.28621	0.93645	140.25
		−0.02595	0.96406	143.50		−0.29038	0.93575	152.99
		−0.02995	0.96339	155.95		−0.29476	0.93500	166.30
0.4		+0.22934	1.0036	162.88		−0.03036	0.95012	175.08
		0.22722	1.0029	177.62		−0.03271	0.94932	190.94
		0.22496	1.0022	192.98		−0.03510	0.94847	207.49
0.7		0.38023	1.0788	190.81		0.10534	0.98460	206.31
		0.37886	1.0780	208.04		0.10388	0.98373	224.95
		0.37735	1.0772	226.02		0.10235	0.98282	244.39
0.9		0.44438	1.1365	204.08		0.15386	1.0122	221.17
		0.44315	1.1356	222.59		0.15261	1.0112	241.20
		0.44198	1.1348	241.70		0.15137	1.0103	262.02
1.0		0.47196	1.1674	209.84		0.17275	1.0269	227.61
		0.47095	1.1666	228.71		0.17162	1.0260	248.15
		0.46983	1.1657	248.40		0.17050	1.0250	269.54
		$r_+=0.95$Å$, r_-=1.81$Å[a]				$r_+=1.205$Å$=r_-$		
0.002		−12.241	0.98341	20.74		−12.454	0.98316	21.00
		−12.353	0.98325	22.65		−12.570	0.98300	22.94
		−12.472	0.98309	24.65		−12.693	0.98284	24.96
0.02		−3.2299	0.95383	61.94		−3.3923	0.95202	63.76
		−3.2587	0.95341	67.64		−3.4227	0.95157	69.65
		−3.2894	0.95296	73.62		−3.4564	0.95109	75.86
0.05		−1.7455	0.93478	92.41		−1.8771	0.93099	96.01
		−1.7613	0.93417	100.93		−1.8933	0.93037	104.87

TABLE II (*Continued*)

c_2 (molar)	$\partial \ln\gamma_\pm/\partial c_2$	ϕ	E^{ex}/c_2[b]	$\partial \ln\gamma_\pm/\partial c_2$	ϕ	E^{ex}/c_2[b]
0.05	−1.7773	0.93355	109.83	−1.9103	0.92972	114.14
0.1	−1.0381	0.91857	122.48	−1.1461	0.91219	128.09
	−1.0470	0.91785	133.71	−1.1556	0.91142	139.88
	−1.0564	0.91709	145.46	−1.1656	0.91061	152.22
0.2	−0.57720	0.90294	158.97	−0.66539	0.89239	167.24
	−0.58223	0.90208	173.49	−0.67076	0.89146	182.58
	−0.58753	0.90117	188.69	−0.67639	0.89049	198.62
0.4	−0.28680	0.89208	201.71	−0.36107	0.87434	213.36
	−0.28958	0.89109	220.07	−0.36402	0.87327	232.85
	−0.29251	0.89005	239.26	−0.36716	0.87212	253.36
0.7	−0.13756	0.89158	240.71	−0.20450	0.86422	255.47
	−0.13929	0.89049	262.54	−0.20630	0.86304	278.71
	−0.14110	0.88934	285.36	−0.20818	0.86179	303.02
0.9	−0.08799	0.89576	259.37	−0.15293	0.86209	275.71
	−0.08938	0.89463	282.86	−0.15437	0.86087	300.75
	−0.09070	0.89328	307.54	−0.15588	0.85958	326.92
1.0	−0.06975	0.89863	267.41	−0.13410	0.86182	284.440
	−0.07065	0.89731	291.77	−0.13541	0.86057	310.276
	−0.07210	0.89610	317.06	−0.13679	0.85926	337.24

[a] Pauling radii for NaCl.

[b] This ratio has the units calories per mole.

in terms of the relative inconsistency $(\phi_v-\phi_c)/(\phi_v-1)$, for $\phi-1$ results from the balance of a large negative contribution (Coulomb forces) and a large positive contribution (excluded volume) which tend to mutually cancel over much of the given composition range. It is proposed that the appropriate gauge of the consistency by this test is $(\phi_v-\phi_c)/(\phi_v{}^0-1)$, where $\phi_v{}^0$ is the osmotic coefficient of the corresponding uncharged system. Approximate values of $10^4(\phi_v{}^0-1)$ at $c_2=1M$ are given for each system in Table VI.

Another self-consistency test which has been employed[7] exploits two functional relations of the energy

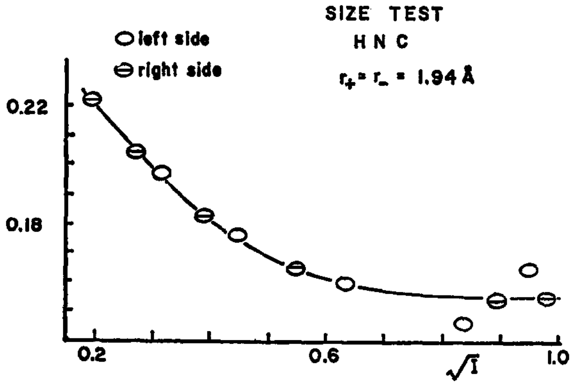

FIG. 3. Test of the HNC equation by Eq. (3.17).

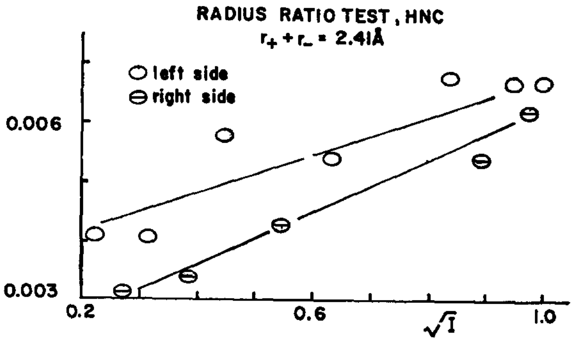

FIG. 4. Test of HNC equation by Eq. (3.19) at $x=1.21$.

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[7] K. Hiroike, J. Phys. Soc. Japan **12**, 326 (1957). See also J. S. Rowlinson, Mol. Phys. **9**, 217 (1965).

Table III. HNC results for primitive model with ion radii as shown and other parameters corresponding to aqueous solutions of 1–1 electrolytes at 25°.

c_2 (molar)	$\partial \ln\gamma_\pm/\partial c_2$	ϕ	E^{ex}/c_2[a]	$\partial \ln\gamma_\pm/\partial c_2$	ϕ	E^{ex}/c_2[a]
	$r_+=1.0$Å, $r_-=3.6$Å			$r_+=1.34$Å, $r_-=3.03$Å		
0.002	−11.094	0.98455	21.74	−11.598	0.98400	22.04
0.02	−2.2608	0.96404	61.34	−2.6922	0.95949	63.36
0.05	−0.87839	0.95790	88.82	−1.2748	0.94782	92.65
0.1	−0.22874	0.96140	115.02	−0.60947	0.94169	120.99
0.2	+0.10886	0.98345	146.21	−0.18088	0.94591	154.58
0.4	0.46887	1.0508	182.19	+0.09787	0.97330	193.81
0.7	0.70069	1.1837	215.61	0.25188	1.0330	230.04
0.9	0.81602	1.2936	231.60	0.32367	1.0820	247.12
1.0	0.88474	1.3557	238.28	0.35008	1.1080	254.93
	$r_+=r_-=1.45$Å			$r_+=0.63$Å, $r_-=2.27$Å		
0.002	−12.246	0.98334	22.55	−12.229	0.98336	22.56
0.02	−3.1993	0.95406	66.92	−3.1804	0.95424	67.01
0.05	−1.7167	0.93549	99.49	−1.6919	0.93606	99.70
0.1	−1.0130	0.91995	131.46	−0.98429	0.92121	131.90
0.2	−0.55649	0.90543	170.05	−0.52247	0.90852	170.80
0.4	−0.27120	0.89603	215.15	−0.23094	0.90339	216.50
0.7	−0.12526	0.89725	256.02	−0.07834	0.91192	258.42
0.9	−0.07704	0.90227	275.58	−0.02552	0.92262	278.58
1.0	−0.05939	0.90548	284.04	−0.01329	0.92863	287.49
	$r_+=0.52$Å, $r_-=1.89$Å					
0.002	−12.560	0.98301	22.94			
0.02	−3.4140	0.95165	69.70			
0.05	−1.8814	0.93063	104.97			
0.1	−1.1419	0.91204	140.62			
0.2	−0.65449	0.89292	182.95			
0.4	−0.34501	0.87668	233.58			
0.7	−0.18457	0.86983	280.08			
0.9	−0.13104	0.87003	302.64			
1.0	−0.11142	0.87125	312.22			

[a] This ratio has the units calories per mole.

to the pair correlation function. One is

$$E[g(r)]_v \equiv \partial\{\beta F^{ex}[g(r)]_v\}/\partial\beta, \tag{3.1}$$

where

$$F^{ex}[g(r)]_v \equiv c\int_0^c \{P[g(r)]_v - c'kT\}c'^{-2}dc' \tag{3.2}$$

and where c is the particle number density in the system of interest and in the integrand $g(r)=g(r,c')$. The other functional is

$$E[g(r)]_e \equiv \tfrac{1}{2}c^2\int e(r)g(r)d\mathbf{r}, \tag{3.3}$$

$$e(r) \equiv \partial[\beta u(r)/\partial\beta]. \tag{3.4}$$

For any $g(r)$ which is exact for some physical model, one necessarily has

$$E[g(r)]_v = E[g(r)]_e, \tag{3.5}$$

TABLE IV. HNC and PY results for uncharged hard spheres.

c_2 Molar	ϕ_v HNC computation	ϕ_v PY computation	ϕ_v PY analytic soln.	$\Delta\phi_v$ Difference PY equation analytical computation
		$r_+=1.8$ Å, $r_-=2.8$ Å.		
0.1	1.0267	1.0267	1.0267	0.0000
0.3	1.0830	1.0829	1.0831	0.0002
0.5	1.1434	1.1429	1.1434	0.0005
0.8	1.2432	1.2412	1.2419	0.0007
1.0	1.3162	1.3122	1.3135	0.0013
		$r_+=r_-=2.3$Å		
0.1	1.0249	1.0249	1.0249	0.0000
0.3	1.0771	1.0770	1.0772	0.0002
0.5	1.1327	1.1323	1.1327	0.0004
0.8	1.2233	1.2219	1.2226	0.0007
1.0	1.2892	1.2862	1.2873	0.0011

which is the basis of a self-consistency test. For a gas, one is accustomed to assuming that $u(r)$ is independent of temperature so $u(r)=e(r)$, but in the generalization of these equations for electrolyte solutions $u(r)$ becomes the potential of the average force between two ions in the pure solvent and can even differ in sign from $e(r)$.

The generalization of this test to electrolyte solutions has been employed in the form

$$-\frac{1}{2RT^2}\left(\frac{\partial(E^{\text{ex}}/c_2)}{\partial c_2}\right)_{T,\mu_w}=\frac{1}{c_2}\left(\frac{\partial\phi_v}{\partial T}\right)_{c_2}, \tag{3.6}$$

where E^{ex}, the appropriate generalization of $E[g(r)]_e$, is given by Eq. (2.3), while ϕ_v is the osmotic coefficient derived from the virial equation. For testing the primitive model E^{ex} has been evaluated with the assumption about the temperature dependence of u_{ij} described following Eq. (2.3). The test was made for several systems by numerical differentiation of the computer results in Sec. II. As shown in Fig. 1 the agreement is completely satisfactory for all of the HNC results which have been examined while (Fig. 2) it is much less satisfactory for some calculations by the PY equation[1] and the $g(\Lambda)$ approximation.[1]

Now returning to the consideration of Eqs. (3.1)–(3.4) for one-component systems, we remark that while the hypersurface $g(r,c,T)$ is a functional of $e(r)$ as

TABLE V. HNC results for square-well model with mound height as shown and other parameters corresponding to aqueous NaCl at 25° ($r_+=0.95$ Å, $r_-=1.81$ Å, $w=1.38$Å,[a] $d_{++}=d_{--}=0$).

c_2	$\partial\ln\gamma_\pm/\partial c_2$	ϕ_v	E^{ex}/c_2[b]	$\partial\ln\gamma_\pm/\partial c_2$	ϕ_v	E^{ex}/c_2[b]
		$d_{+-}=0.25kT$			$d_{+-}=-0.25kT$	
0.002	−12.033	0.98360	22.88	−12.740	0.98276	22.31
0.02	−3.0045	0.95631	69.41	−3.5756	0.94971	63.95
0.05	−1.5518	0.94029	105.27	−2.0182	0.92653	93.01
0.1	−0.87031	0.92832	142.26	−1.2584	0.90504	117.74
0.2	−0.43457	0.91981	190.05	−0.75588	0.88090	146.74
0.4	−0.16313	0.92099	251.60	−0.43402	0.85614	170.70
0.7	−0.02546	0.93666	315.06	−0.26665	0.83761	184.19
0.9	+0.02032	0.95107	348.80	−0.21067	0.83062	186.68
1.0	0.03703	0.95880	364.32	−0.19029	0.82791	186.94

[a] w is the radius of a water molecule.

[b] This ratio has the units calories per mole.

TABLE VI. Virial-equation–compressibility-equation self-consistency: $10^4(\phi_v-\phi_c)$ for the HNC equation.

r_+	2.3 Å	1.0	1.935	0.84	1.205	0.52	1.45	0.63	0.95	0.95[a]
r_-	2.3 Å	3.6	1.935	3.03	1.205	1.89	1.45	2.27	1.81	1.81
c_2 Molar										
0.1	−3	−9	−1	−11	−5	−5	−11	1	3	−2
0.2	−7	−4	0	−4	−13	−9	−8	−5	4	−6
0.4	7	22	0	17	10	−16	−11	−5	−6	−1
0.7	14	95	6	26	1	−31	−10	−8	−15	6
0.9		147	11	62	−7	−37	−8	−7	−14	6
1.0	36		15	79	−11	−36	−7	−10	−15	11
1.0[b]	2900	4900	1600	2600	360	550	640	980	630	
1.0[c]	−9	−46	−1	−9	0	0	0	−1	0	

[a] Square-mound model: $d_{+-}=0.25\ kT$, $d_{++}=d_{--}=0$.

[b] $10^4(\phi_v^0-1)$ at $c_2=1M$ in this row. Approximate values from the HNC equation.

[c] $10^4(\phi_v^0-\phi_c^0)$ for the PY equation at $c_2=1M$. $10^4[\phi_v^0(\text{HNC})-\phi_v^0(\text{PY})]=30$ at $c_2=1M$ for the system $r_+=r_-=2.3$ Å.

well as of $u(r)$, the isothermal surface $g(r, c)$ is a functional only of $u(r)$. Thus a given exact $g(r, c)$ at T' should satisfy an *infinite* set of energy tests in which $u(r)$ at T' is fixed, but $e(r)$ is arbitrary. In our electrolyte-solution computations, for example, the $g_{ij}(r, c)$ at 25° depend on ϵ, the dielectric constant of the solvent, but not on $d\epsilon/dT$. Thus our computations should satisfy an infinite set of consistency tests in which we keep $\epsilon(25°)$ fixed but assume hypothetical forms for $\epsilon(T)$ in the neighborhood of 25°. Each such additional test would, of course, require additional computations of the correlation functions at temperatures near 25° with the assumed $\epsilon(T)$ in order to enable the evaluation of the right side of Eq. (3.6). Since the integral equation computations are expensive and the results for hypothetical $\epsilon(T)$ would not have any known use other than the test, a search has been made for equivalent tests in which the necessary additional computations would have some known intrinsic value.

Before describing such tests it seems helpful to point out that the energy test and the others which follow derive from a single differential form. For example, by functional differentiation of Eq. (3.5) with respect to $e(r)$ we derive (for a one-component system: a, b, i, j specify labeled molecules)

$$r_{ij}\frac{\partial g_{ij}}{\partial r_{ij}}-3c\frac{\partial g_{ij}}{\partial c}=\int d\mathbf{r}_{ab}v_{ab}\frac{\delta g_{ab}}{\delta u_{ij}}, \tag{3.7}$$

$$v_{aj}\equiv r_{ab}(\partial u_{ab}/\partial r_{ab}). \tag{3.8}$$

The last functional derivative may also be eliminated[8,9]; the equation then involves two-, three-, and four-body correlation functions; thus Eq. (3.7) implicitly involves higher-order correlation functions and is not directly useful for testing computations which yield only two-body correlation functions. However, its existence does emphasize the possibility of having a point-by-point test of the self-consistency of computed correlation functions rather than the integral tests employed in this section. Such a point-by-point test would require approximations for the higher-order correlation functions.

Some additional useful consistency conditions of the integral kind may be derived by assuming that there is an arbitrary thermodynamic variable x which may be adjusted independently of T and V, the volume of the system. For the present purpose it may be conceived as a variable on which $u(r)$ depends. It can still be a thermodynamic variable if, for example, one employs the McMillan–Mayer theory and imagines that x is a measure of the effect of changes of solvent composition on the direct potential.

Then we define

$$u_x(r)\equiv\partial u(r)/\partial x, \tag{3.9}$$

$$X[g(r)]_v\equiv-\beta(\partial F^{\text{ex}}/\partial x)_{c,T}, \tag{3.10}$$

where F^{ex} is the excess free energy given by Eq. (3.2). It is easily shown[10] that if we define

$$X[g(r)]_x\equiv-\tfrac{1}{2}\beta c^2\int u_x(r)g(r)d\mathbf{r}, \tag{3.11}$$

then we have, for the exact $g(r)$,

$$X[g(r)]_v=X[g(r)]_x. \tag{3.12}$$

This provides more consistency tests which are quite analogous to those discussed above.

As an example of the new tests we now consider a system in which the direct potential is the sum of hard

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[8] J. K. Percus, in the *Equilibrium Theory of Classical Fluids*, H. L. Frisch and J. L. Lebowitz, Eds. (W. A. Benjamin, Inc., New York, 1964). Also J. L. Lebowitz and J. K. Percus, J. Math. Phys. **4**, 116 (1963).

[9] A somewhat analogous relation has been reported by P. Schofield, Proc. Phys. Soc. (London) **88**, 149 (1966).

[10] H. L. Friedman, J. Chem. Phys. **34**, 73 (1961). The present notation is somewhat different.

core plus soft parts:

$$u(r)=u_{hc}(r)+u_{s}(r), \tag{3.13}$$

$$\begin{aligned} u_{hc}(r)&=\infty, \quad \text{for} \quad r<x \\ &=0, \quad \text{for} \quad x<r. \end{aligned} \tag{3.14}$$

Then $F^{\mathrm{ex}}(x)$ is just what we may compute while investigating the effect of the hard-core diameter on the thermodynamic properties; from it we may obtain $X[g(r)]_v$, perhaps by numerical differentiation. In this example

$$\begin{aligned} -\beta u_x(r)&=\exp(\beta u_{hc})(\partial/\partial x)\exp(-\beta u_{hc}) \\ &=-\exp(\beta u_{hc})\delta(r-x), \end{aligned} \tag{3.15}$$

so Eq. (3.11) becomes

$$X[g(x)]_x=-2\pi x^2c^2g(x+), \tag{3.16}$$

where $g(x+)$ is $g(r)$ evaluated at r infinitesimally larger than x, i.e., just outside the hard core. Thus, when $F^{\mathrm{ex}}(x)$ has been computed over some range of x, no additional integral-equation computations are required to make the test.

This test has been generalized for some electrolyte solution applications. First we consider the restricted primitive-model case in which $r_+=r_-\equiv x/2$. Then the required generalization of Eq. (3.12), in a convenient form for this application, is

$$\begin{aligned} c_2^{-1}(\partial\phi_v/\partial x)_{c_2}&=\pi x^2(1+\partial/\partial\ln c_2) \\ &\quad\times[2g_{+-}(x)+g_{++}(x)+g_{--}(x)]. \end{aligned} \tag{3.17}$$

The differential operator appears on the right side, because on the left we have the osmotic coefficient rather than the total excess free energy. Some tests according to this equation are shown in Fig. 3.

Now we consider primitive-model computations in which r_++r_- is fixed and the variable is

$$x=2(r_--r_+). \tag{3.18}$$

Then the required generalization of Eq. (3.12) in a convenient form for our purpose is

$$\begin{aligned} c_2^{-1}(\partial\phi_v/\partial x)_{c_2,a_{+-}}&=\pi(1+\partial/\partial\ln c_2) \\ &\quad\times[a_{--}^2g_{--}(a_{--})-a_{++}^2g_{++}(a_{++})]. \end{aligned} \tag{3.19}$$

Some tests according to this equation are shown in Fig. 4. The relatively poor behavior of this test seems to be due to the fact that the effect of changing r_+-r_- at fixed r_++r_- is small; in fact, the relevant derivative vanishes at $r_+=r_-$. There is also a particular computational difficulty in this test associated with the difficulty of having each a_{ij} fall on one of the 512 mesh points[1] at every concentration. This is less troublesome at high concentration where the agreement is better, contrary to what one would expect if the failures of the test were due to the intrinsic approximation in the HNC equation.

We remark that the last two tests are complementary in a useful way: Eq. (3.17) depends mostly on g_{+-} at contact while Eq. (3.19) depends only on g_{++} and g_{--} at contact.

For an application of Eq. (3.12) which enables one to test the correlation function away from contact, consider the direct potential which is the sum of a square-mound perturbation and an unperturbed part:

$$u(r)=u_{SQ}(r)+u_0(r), \tag{3.20}$$

$$\begin{aligned} u_{SQ}(r)&\equiv 0, \quad \text{for} \quad r<l \\ &=xkT, \quad \text{for} \quad l<r<L \\ &=0, \quad \text{for} \quad L<r, \end{aligned} \tag{3.21}$$

in which case we have

$$X[g(r)]_x=-\tfrac{1}{2}c^2\int_l^L g(r)4\pi r^2dr. \tag{3.22}$$

The resulting self-consistency test for an electrolyte solution in which u_{+-} is perturbed by a square-mound term as in Eq. (3.20) while u_{++} and u_{--} are unperturbed is

$$c_2^{-1}\left(\frac{\partial\phi_v}{\partial x}\right)_{c_2}=2\pi\int_l^L r^2dr\, 1+\frac{\partial}{\partial\ln c_2}g_{+-}(r). \tag{3.23}$$

Applications of this self-consistency test are shown in Fig. 5. Equally satisfactory results are obtained by this test for the HNC and PY equations.

Finally it may be remarked that the self-consistency tests based on Eq. (3.12) are closely related to Zwanzig's perturbation expression for the equation of state[11] and could be derived from that starting point.

IV. OTHER TESTS

A. Numerical Accuracy

We may test for the accuracy of the numerical methods used, as distinct from the accuracy of any particular integral equation. When the charges are set equal to zero the analogs[1] of the HNC and PY equations which are studied here become identical to the more familiar HNC and PY equations derived for more general intermolecular potentials. For a mixture of uncharged hard spheres the analytic solution to the PY equation is known[12] and may be compared directly with the solutions obtained numerically. This comparison is made in Table IV for the PY and HNC equations; the numerical results have been obtained by setting the charges equal to zero in the very computer program used for ionic systems, but with the same lattice spacings used for a 1:1 electrolyte. The agreement obtained between the analytic and numerical results is excellent.

An important approximation in the numerical procedure for solving the integral equations is the truncation of the integrals.[1] Essentially, in solving the integral

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[11] R. W. Zwanzig, J. Chem. Phys. **22**, 1420 (1954).

[12] J. L. Lebowitz, Phys. Rev. **133**, A295 (1964). J. L. Lebowitz and J. S. Rowlinson, J. Chem. Phys. **41**, 133 (1964).

TABLE VII. HNC results for R_{ij} [Eq. (4.4)] for some typical systems.

System			Molarity			
r_+	r_-	i,j	0.1	0.4	0.7	1.0
1.205	1.205	any	1.0038	1.0065	1.0061	1.0047
1.935	1.935	any	1.0057	1.0032	0.9975	0.9911
		+ +	1.0077	1.0131	1.0173	1.0124
1.0	3.6	+ −	1.0060	1.0038	1.0008	0.9793
		− −	1.0036	0.9970	0.9922	0.9924
		+ +	1.0063	1.0098	1.0108	1.0117
0.84	3.03	+ −	1.0056	1.0050	1.0017	0.9986
		− −	1.0042	1.0004	0.9950	0.9917

equations each Fourier integral is truncated

$$\int_0^\infty f(r)\,\frac{r}{k}\sin(kr)\,dr \rightarrow \int_0^L f(r)\,\frac{r}{k}\sin(kr)\,dr \tag{4.1}$$

and then, for the calculation of thermodynamic properties, the computed correlation function $g(r)_{\text{comp}}$ is continued by adding the asymptotic form $g(r)_{\text{asy}}$ for large r:

$$\begin{aligned} g(r) &= g(r)_{\text{comp}}, &&\text{for } r<L \\ &= g(r)_{\text{asy}}, &&\text{for } L<r, \end{aligned} \tag{4.2}$$

with the approximation that $g(r)$ has the limiting Debye–Hückel form

$$\ln g_{ij}(r)_{\text{asy}} = -\beta e_i e_j \exp(-\kappa r)/\epsilon r. \tag{4.3}$$

In Table VII some results are given for the ratio

$$R_{ij} = [g_{ij}(L)_{\text{comp}} - 1]/[g_{ij}(L)_{\text{asy}} - 1]. \tag{4.4}$$

These ratios are found to be surprisingly close to unity, but at least there is no evidence here for any important effect of the truncation on the correlation functions. In all the computations, κL is nearly constant[1] at 7.66, so $|g_{ij}(L)-1|$ varies from 5×10^{-5} at $0.1M$ ($L=73A$) to 1.5×10^{-4} at $1M$ ($L=23A$).

The effect of the continuation [Eq. (4.2)] on the computed thermodynamic properties is so small that the effect of any remaining uncertainty as to the correct asymptotic form of $g(r)$ is doubtless negligible. For example, the contribution of the assumed continuation to ϕ_v is $-\kappa^3\exp(-\kappa L)/24\pi c$ which amounts to -5.8×10^{-5} at $0.1M$ and -1.9×10^{-4} at $1M$.

Very recently Stell and Lebowitz[13] have devised a new equilibrium theory of ionic systems in which it is required to know the equilibrium properties (n-body correlation functions) of the corresponding discharged system. Then the properties of the ionic system can be calculated exactly at any concentration, although the results are expressed as power series in the "Coulomb length" $\lambda = 4\pi e^2/\epsilon kT$, where e is the electronic charge. One of their results which is very useful here is that, for sufficiently small λ but at *any* concentration,

$$\ln g_{ij}(r)_{\text{asy}} = -\beta e_i' e_j' \exp(-\kappa' r)/\epsilon r. \tag{4.5}$$

Here e_i' is a modified charge and κ' a modified Debye screening factor; both depend on properties of the discharged system as well as on the ionic charges. If the discharged anions are identical to the discharged cations, then $e_i' = e_i$ and $\kappa' = \kappa$.

Using the PY equation for the equation of state of a mixture of uncharged hard spheres[13] one may evaluate the right side of (4.5) for unsymmetrical models ($r_+ \neq r_-$). The result may be expressed as a ratio like R_{ij} but with the Stell–Lebowitz expression in the numerator. For the system $r_+ = 1.0$ Å; $r_- = 3.6$ Å, $c_2 = 1M$, one finds $R_{++} = 4.55$, $R_{+-} = 2.35$, and $R_{--} = 0.30$. If any of the variables c_2, $r_+ + r_-$, or $|r_+/r_- - 1|$ is reduced, then the R_{ij} becomes nearer to unity. The comparison of these R_{ij} values with those in Table VII, taken with the indications that the present HNC computations are rather accurate, leads to the conclusion that the small λ result given in Eq. (4.5) is not

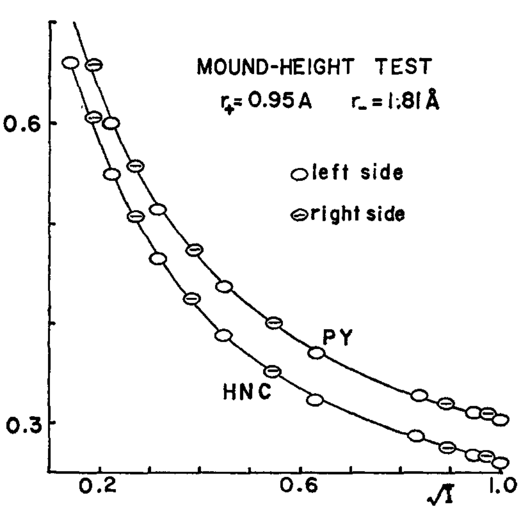

FIG. 5. Test of HNC and PY equations by Eq. (3.23). The ordinate for the PY equation has been raised by 0.5.

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[13] G. Stell and J. L. Lebowitz, J. Chem. Phys. 48, 3706 (1968).

TABLE VIII. Zeroth- and second-moment tests of HNC results.

System				1000 Δ_i 1000 Δ_i'			
r_+	r_-	d_{+-}	i	0.1	0.4	0.7	1.0 M
1.205	1.205	0	either	4	4	3	2
				4	−60	−15	−30
2.30	2.30	0	either	2	−1	−3	−4
				−15	−60	−80	−100
0.84	3.03	0	+	2	2	1	0
				−20	−90	−160	−240
			−	1	2	5	−7
				2	25	60	100
1.00	3.60	0	+	2	2	2	2
				−35	−150	−260	−360
			−	0	−5	−13	−9
				9	70	140	230
0.95	1.81	0.25kT	+	2	1	−1	−3
				6	−35	−65	−90
			−	2	1	−2	−4
				−4	−25	−45	−60

relevant to the system treated here (for which $\lambda/4\pi = 7.14$ Å).

B. Zeroth Moment

The quantity

$$G_{ij} = \int (g_{ij} - 1)\, d\mathbf{r} \tag{4.6}$$

which we call the zeroth moment of the correlation function appears in the compressibility equation for the free-energy function. From the grand-ensemble expression for G_{ij} as a fluctuation quantity and taking into account the strong resistance of a system of charges toward fluctuations which result in macroscopic deviations from electroneutrality, one finds that the deviation from electroneutrality of an ion plus its atmosphere

$$\Delta_i e_i \equiv e_i + \sum_{j=1}^{\sigma} c_j e_j G_{ij} \tag{4.7}$$

must vanish. Thus for electrolyte solutions there are some conditions on the zeroth moments of the correlation functions; these may be traced to the long range of the Coulomb potential. For a solution of a single electrolyte the resulting form is very simple: both of the following coefficients must vanish:

$$\Delta_+ = 1 + c_+(G_{++} - G_{+-}), \tag{4.8}$$

$$\Delta_- = 1 + c_-(G_{--} - G_{+-}), \tag{4.9}$$

and therefore, $G_{++} = G_{--}$ for symmetrical electrolytes ($c_+ = c_-$).

The Δ_i values obtained by the HNC equation for some typical systems are given in Table VIII. These include the effect of the continuation which contributes $-\exp(-\kappa L)(1+\kappa L) \sim -3.8\times 10^{-3}$ to Δ_i. The contribution, which is of the same size as Δ_i itself, is approximately constant, because the truncation at L is chosen so that κL is ~ 7.66 in every case.[1] Essentially the same results are obtained from the PY equation, while the $g(\Lambda)$ approximation, which serves as the starting point for the iterative solution of the integral equations, gives Δ_i values an order of magnitude larger. For the HNC equation the magnitude of Δ_i increases somewhat with the size of the ion cores.

It remains to inquire about the effect that these errors in g_{ij} make in the thermodynamic properties. The compressibility equation for a solution of a single electrolyte[1] can be written in the form

$$d \ln \gamma_\pm / d \ln c_2 = (\Gamma - 1 - \Gamma z)/(1 + \Gamma z), \tag{4.10}$$

$$\Gamma \equiv 1/cG_{+-}, \tag{4.11}$$

$$z \equiv \nu \Delta_+ \Delta_- / (\nu_+ \Delta_- + \nu_- \Delta_+), \tag{4.12}$$

where $\nu = \nu_+ + \nu_-$, ν_i is the number of ions of species i produced by one molecule of solute on complete dissociation, and $c = \sum c_i$. With one exception in the earlier work and here the compressibility equation has been used with the computed value of z, defined by Eq. (4.12). Since the exact value of z is known to be zero, one can obtain, for each system at each concentration, another value of $d\ln\gamma_\pm/d\ln c_2$ from Eq. (4.10) by setting $z=0$. The difference in values of $\ln\gamma_\pm$ obtained by the two methods, call it $\Delta\ln\gamma_+$, is a measure of the effect of the nonvanishing Δ_i on the thermodynamic properties.[14] It is found that the magnitude of this difference is less than 0.006 for all of the systems investigated here, with one exception, and is much smaller for most of them. The corresponding effect on the osmotic coefficient is smaller yet.

The exceptional case referred to in the preceding paragraph is the system for which $r_+=1.0$ Å, $r_-=3.6$ Å, and $c_2\sim 0.2M$. As may be seen from Table VIII, $\Delta_++\Delta_-$ passes through zero in this range. Therefore very large values of z are computed in this range. In this case, the value of $d\ln\gamma_\pm/dc_2$ reported (Table III) are obtained from Eq. (4.10) with $z=0$. It is very interesting that before the theory of the Δ_i had been given adequate consideration the computations for this system showed an anomaly near $0.2M$ in $d\ln\gamma_\pm/\partial c_2$ but none in ϕ (the latter from the virial equation). If this anomaly had not been removed as described here, it would contribute to the failure of the virial-compressibility self-consistency test for this system.

More generally, it may be remarked that the virial equation, since it involves integrals like Eq. (4.6) but with an additional factor $r(\partial u_{ij}/\partial r)$ in the integrand, depends less on $g(r)$ at large r than the compressibility equation does. Therefore the effect of nonvanishing Δ_i is a contribution to the virial-compressibility self-consistency test. Then this effect is not very important for the present HNC calculations.

C. Second Moment

Stillinger and Lovett[15] have recently discovered a condition on the second moment

$$G_{ij}'\equiv\int[g_{ij}(r)-1]r^2d\mathbf{r} \tag{4.13}$$

of the correlation functions in an ionic solution:

$$\Delta_i'\equiv 1+\frac{1}{6}\frac{\kappa^2}{e_i}\sum_{j=1}^{\sigma}c_je_jG_{ij}'=0. \tag{4.14}$$

This also derives from the long range of the Coulomb potential. For a solution of a single electrolyte we have [cf. Eqs. (4.8), (4.9)]

$$\Delta_+'=1+\tfrac{1}{6}\kappa^2c_+(G_{+\,+}'-G_{+\,-}'), \tag{4.15}$$

$$\Delta_-'=1+\tfrac{1}{6}\kappa^2c_-(G_{-\,-}'-G_{+\,-}'). \tag{4.16}$$

Values of Δ_i' from the present computations are given in Table VIII. Clearly the second-moment condition is only rather crudely obeyed by these computed correlation functions, but it is well worth noting that the continuation [Eq. (4.3)] contributes

$$-\exp(-\kappa L)(\kappa^3L^3+3\kappa^2L^2+6\kappa L+6)/6$$

which is as much as -52.2×10^{-3} and is approximately constant for the same reason that the continuation contribution to Δ_i is constant. Again there is little to choose between the HNC and PY equations, but either is markedly better than the $g(\Lambda)$ approximaton which serves as the starting point for the iterations.

V. DISCUSSION

It is concluded that the generally satisfactory picture that the familiar virial-compressibility consistency test gives when applied to these calculations is supported by all of the other criteria which are considered. In particular the adequacy of the HNC equation and its superiority over the PY equation for the present purpose are consistent with all of the observations.

For the systems considered here the highest concentration, $1M$, is less than a fifth of the concentration corresponding to close packing of the solute ions. It is therefore a rather low concentration on the scale often considered in the application of integral equation methods to nonionic systems, where the main result is that these methods fail badly at concentrations within a factor of 2 of the close-packing limit. The implications of this are not so serious for electrolyte solutions, because there is much to be learned from studies at lower concentrations and because at higher concentrations there is almost certainly going to be a substantial contribution from nonpairwise-additive terms in the direct potential for any model which is realistic enough to be useful in the effort to get a molecular interpretation of the macroscopic properties of ionic solutions. In fact, it can only be determined from careful study whether or not such effects are important even below $1M$.

One feature that has been studied and that is not described here is the appearance of extrema ("oscillations") in $g_{ij}(r)$ at some r greater than a_{ij}. Such oscillations are indeed observed in some of the computations described here. Another report is planned for these and some other features which are relevant to comparison with experiments on real systems.

ACKNOWLEDGMENTS

We are grateful to Dr. F. H. Stillinger and Professor J. Groeneveld for valuable discussions of the electroneutrality principle and its implications.

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[14] Strictly speaking, this refers to differences in the quantity $\ln\gamma_\pm(c_2)-\ln\gamma_\pm(0.1M)$, where c_2 is in the range 0.1–1M. We have set a bound for this range since the method described in Ref. 1 for the integration of $d\ln\gamma_\pm/dc_2$ cannot be applied to the $z=0$ limit of Eq. (4.10); as $c_2\rightarrow0$ the $\Delta(c)$ of Ref. 1 does not tend to zero when the $z=0$ limit of Eq. (4.10) is taken with the present computations.

[15] F. H. Stillinger and R. Lovett, J. Chem. Phys. **48**, 3858, 3869 (1968). See also F. H. Stillinger, Proc. Natl. Acad. Sci. **60**, 1138 (1968).[16]

[16] *Note added in proof.* Actually Stillinger and Lovett showed that $\Sigma c_ie_i^2\Delta_i'=0$, which for the 1–1 electrolyte case is the same as $\Delta_+'+\Delta_-'=0$. It is interesting that the individual Δ_i' values are about as nearly zero as their sum.