4. The inhibiting action of the products and its importance in obtaining a general kinetic equation for the reaction has been discussed.

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The Debye–Hückel Ion Size Parameter in Terms of Individual Ionic Radii. The Activity Coefficient of Lead Chloride in Solutions of Cadmium Nitrate[1]

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In the past the ion size parameter of the Debye–Hückel theory of solutions of strong electrolytes has been determined as a mean value for the ions of a given solution. If the parameter "a" could be calculated from the individual ionic radii and the result of this calculation verified experimentally, the physical meaning of the quantity "a" would take on added significance. It is the purpose of this paper to present this calculation and to give a preliminary test of its result.

Theoretical Calculation.—Consider a solution containing ions of kinds

$$1 \ldots i \ldots s$$

Let a_{ij} be the mean distance of closest approach for the ions of the i^{th} and j^{th} kinds, *i. e.*, the mean collision distance between the centers of the ions considered as spheres. Now if f_{ij} is the time average, or frequency, of collisions between the ions of the i^{th} and j^{th} kinds, then

$$\text{"}a\text{"} = \Sigma f_{ij}a_{ij}/\Sigma f_{ij} \qquad (1)$$

is the mean distance of closest approach for all ions in the solution, the summations being taken over all combinations of values of i and j. On the average for a large number of random collisions between any two ions the distances from the points of contact to their centers may be considered as the radii of spheres surrounding the ions; so that

$$a_{ij} = a_i + a_j$$

The quantities a_i and a_j depend presumably only upon the nature of the individual ions.

The following calculation of the frequency of collisions between the ions is based on the fundamental assumption of the Debye–Hückel theory: the effects between the ions may be attributed wholly to the electrical charges on them. Consider an ion of the i^{th} kind in a solution of

$$n_1 \ldots n_i \ldots n_s$$

moles of ions with valences

$$z_1 \ldots z_i \ldots z_s$$

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[1] The material for this paper was taken from a thesis submitted by Henry C. Thomas to the Faculty of the University of North Carolina in partial fulfilment of the requirements for the degree of Master of Science.

dissolved in a volume V of solution. The charge on an ion of the i^{th} kind is then $z_i\epsilon$, where ϵ is the charge on the electron. If $\mathrm{d}V$ is an elementary volume of solution at a distance r from an ion of the i^{th} kind, the time average of the number of ions of the j^{th} kind in $\mathrm{d}V$ is given by the Boltzmann relation

$$\frac{Nn_j}{V}\, e^{-z_j\epsilon\psi/kT}\, \mathrm{d}V$$

N is Avogadro's number per mole, Nn_j/V being the number of ions of the j^{th} kind per cubic centimeter of solution; ψ, the electrical potential in $\mathrm{d}V$; k, Boltzmann's constant; T, the absolute temperature; and e, the base of the natural logarithms. On changing to space polar coördinates and performing the indicated integration, there is obtained the number of ions of the j^{th} kind in a spherical shell of thickness $\mathrm{d}r$ surrounding and at a distance r from the i^{th} ion in question

$$\frac{Nn_j}{V}\, e^{-z_j\epsilon\psi/kT}\, r^2\mathrm{d}r \int_0^{\pi}\int_0^{2\pi} \sin\theta\, \mathrm{d}\theta\, \mathrm{d}\phi = 4\pi\, \frac{Nn_j}{V}\, e^{-z_j\epsilon\psi/kT}\, r^2\mathrm{d}r$$

In order to calculate the time average of collisions between the ion of the i^{th} kind and all the ions of the j^{th} kind, the above expression is integrated through a shell in contact with the i^{th} ion and of such thickness, $2a_j$, that all the ions of the j^{th} kind within the shell must be in contact with the i^{th} ion. Multiplying the resulting expression by the number of ions of the i^{th} kind per cubic centimeter, there is obtained the time average of all collisions per cubic centimeter between ions of the i^{th} and j^{th} kinds

$$f_{ij} = \frac{4\pi N^2}{V^2}\, n_i n_j \int_{a_i}^{a_i+2a_j} e^{-z_j\epsilon\psi/kT}\, r^2\, \mathrm{d}r$$

When this expression is summed over all pairs of kinds of ions in solution, the result is the time average, or frequency, of all collisions per cubic centimeter

$$\sum f_{ij} = \frac{4\pi N^2}{V^2} \sum_{i=1}^{s} \sum_{j=1}^{s} n_i n_j \int_{a_i}^{a_i+2a_j} e^{-z_j\epsilon\psi/kT}\, r^2\, \mathrm{d}r \qquad (2)$$

In order to obtain this expression in terms of the concentration of the dissolved compound we note that $n_i = \nu_i n$, where n is the number of moles of the compound in volume V of solution and ν_i the number of ions of the i^{th} kind to which one molecule of salt gives rise on ionization. The potential ψ at large distances from an ion is to be determined from the general solution of the Poisson–Boltzmann equation

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}\psi_i}{\mathrm{d}r}\right) = -\frac{4\pi\epsilon}{D}\sum_{j=1}^{s} \frac{Nn_j z_j}{V}\, e^{-z_j\epsilon\psi_i/kT}$$

However, in calculating the frequency of collisions only the potential near the surface of the ion is considered. The potential in this neighborhood will be largely due to the charge on the ion itself. Therefore no large error will be introduced if the potential is considered as arising wholly from the charge on the ion

$$\psi = \frac{z_i\epsilon}{D}\frac{1}{r} \tag{3}$$

where D is here the dielectric constant of the solvent. On making these substitutions the expression for the frequency becomes

$$\sum f_{ij} = 4\pi N^2 \left(\frac{n}{V}\right)^2 \sum_{i=1}^{s} \sum_{j=1}^{s} \nu_i\nu_j \int_{a_i}^{a_i+2a_j} e^{-z_iz_j\epsilon^2/DkTr}\, r^2\mathrm{d}r \tag{4}$$

Substituting (3) for the potential receives justification when it is observed that if the integral in (2) should contain concentration terms other than as a factor, the "a" value, see (1), would depend on the concentration of the solution. This is contrary to experimental knowledge. Were the potential determined by a solution of the Poisson–Boltzmann equation, concentration terms would enter otherwise than as a factor.

The frequency of collisions between the ions of a single salt in solution is then, in the region of dilute solutions, directly proportional to the square of the concentration.

For a solution of two salts the mean distance of closest approach will be given by an expression of the form

$$\text{“}\bar{a}\text{”} = \frac{A_1 + A_2}{f_1 + f_2} \tag{5}$$

Here A_1/f_1 = "a_1" and A_2/f_2 = "a_2"; the subscripts refer to the values for the individual salts. Expression (5) is the mean of "a_1" and "a_2" in which the separate values are weighted according to the corresponding collision frequencies. This expression may be considered as a close approximation to the value of "$\bar{a}$" given by (1), where the summations are carried over all combinations of i and j. We have now

$$f_1 = k_1\left(\frac{n_1}{V}\right)^2 = k_1c_1^2 \text{ and } f_2 = k_2\left(\frac{n_2}{V}\right)^2 = k_2c_2^2$$

where k is the coefficient of the concentration term in (4) and c is the molarity of the dissolved salt. Expression (5) shows that the "$\bar{a}$" value of a solution of two salts should remain constant if the ratio of the concentrations of the salts is held constant no matter what the total concentration may be. This fact is at once apparent when (5) is written in the form

$$\text{“}\bar{a}\text{”} = \frac{K_1c_1^2 + K_2c_2^2}{k_1c_1^2 + k_2c_2^2} = \frac{K_1b + K_2}{k_1b + k_2}$$

where $b = (c_1/c_2)^2$ = const. These considerations hold true, of course, only for dilute solutions of completely dissociated electrolytes.

Now the proportionality constants k_1 and k_2 will not in general be the same for different salts. If, however, the salts are of the same valence type, the difference between these constants will be determined solely by the integral in (4). In the following discussion, due to lack of any definite knowledge of the ionic radii, we will assume $k_1 = k_2$; so that

$$f_1/f_2 = (c_1/c_2)^2 \qquad (6)$$

A rough graphical integration of the function

$$r^2 e - z_1 z_2 \epsilon^2/DkTr$$

for a 1–2 salt in water at 25° shows that for values of r between 4 Å. and 10 Å. the difference between the integrals for similar types of salts should not be large. With expressions (5) and (6) it is a simple matter to calculate any one of "a_1," "a_2" or "$\bar{a}$," given two of them.

As an experimental test of the above ideas the results of measurements on the cell

$$\text{Pb–Hg (2 phase)} \mid PbCl_2(m_1),\ Cd(NO_3)_2(m_2) \mid \text{AgCl–Ag};\ m_1/m_2 = \text{const.}$$

have been applied. The "a" value of lead chloride has been calculated by La Mer, Gronwall and Greiff[2] from measurements by Carmody[3] on a similar cell containing only lead chloride. They find "a_1" = 1.75 Å. The "a" value for cadmium nitrate has been calculated by the present authors from freezing point measurements of Jones,[4] these being apparently the only available measurements on cadmium nitrate in sufficiently dilute solution. Too much reliance cannot be placed on the results of these calculations, based as they are on data of doubtful precision. Table I gives the results of these calculations.

TABLE I

Molarity	Δt_f obs.	Δt_f "a" = 8.0 Å.	Δt_f "a" = 11.5 Å.	Δt_f "a" = 14.0 Å.
0.001000	0.0054	0.0054	0.0054	0.0054
.002980	.0159	.0157	.0158	.0159
.004920	.0261	.0257	.0260	.0261
.006900	.0362	.0358	.0362	.0364
.00876	.0457	.0453	.0458	.0461
.02000	.1035	(.1000)	(.1038)	(.1046)

As may be seen the value "a_2" = 11.5 Å. gives the best agreement with the experimental data. The Debye first approximation for the osmotic deviation

$$\Theta = 0.764\sqrt{3c}\ \sigma(K\text{“}a\text{”})$$

was used in the calculation, the "a" value being sufficiently high to warrant the use of the simple equation.

Experimental Part

Purification of Materials.—Kahlbaum lead chloride was recrystallized three times from 0.006 N hydrochloric acid as recommended by Baxter and Grover.[5] The product

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[2] La Mer, Gronwall and Greiff, *J. Phys. Chem.*, **35**, 2245 (1931).

[3] Carmody, THIS JOURNAL, **51**, 2905 (1929).

[4] Jones, *Z. physik. Chem.*, **11**, 545 (1893).

[5] Baxter and Grover, THIS JOURNAL, **37**, 1051 (1915).

was carefully dried and ground. Kahlbaum cadmium nitrate was recrystallized three times from water. Carefully purified mercury was twice distilled as recommended by Hulett.[6] Commercial tank nitrogen was purified by passing it through a solution of acidified potassium permanganate and further treated according to Cowperthwaite and La Mer.[7]

Analytical.—The stock solution of lead chloride was analyzed by the potentiometric titration of the chloride using a silver–silver chloride indicator electrode and a 0.1 *N* calomel half cell with an ammonium nitrate–agar gel bridge. The cadmium nitrate solution was analyzed by electrolytic precipitation from an alkaline cyanide bath.

Preparation of Electrodes.—The silver–silver chloride electrodes were prepared according to the method described by Carmody.[8] The lead amalgam was prepared by dissolving Kahlbaum stick lead, "for analysis" grade, sufficient to make a 6% amalgam, in the purified mercury. After solution had been effected in an atmosphere of nitrogen, the amalgam was drawn into a Pyrex storage bulb similar to that described by La Mer and Parks.[9]

Preparation of Solutions.—The solutions for measurement were made up by diluting the analyzed stock solutions of lead chloride and cadmium nitrate using flasks calibrated to deliver by the Bureau of Standards.

Electrical Apparatus and Cell Vessel.—The potentiometer, which had been calibrated by the Bureau of Standards, was the Type K instrument of Leeds and Northrup. A Leeds and Northrup No. 2500, Type R, galvanometer was used. The standard cell, also calibrated by the Bureau of Standards, was of the Weston unsaturated type. The electrical measuring apparatus was protected against electrical leakage by equipotential shielding. The cell vessel, constructed of Pyrex glass, contained two sets of electrodes. The e. m. f. of each of the four combinations was measured. A reservoir for the solution was attached so that check measurements could be obtained without disturbing the electrodes or opening the cell to the air. The nitrogen served to stir the solution and preserve an inert atmosphere within the cell. No trouble was experienced in obtaining e. m. f. readings constant to 0.02 mv. The cell was placed in a water thermostat at 25 ± 0.02°. The Beckmann thermometer was compared with a thermometer calibrated by the Bureau of Standards.

Results and Calculations

Table II gives a summary of the experimental data together with the activity coefficient of the lead chloride, γ_s, calculated from the equation

$$E_{(\text{mv.})} + 88.725\,(0.2007 + \log m) = E_{0(\text{mv.})} - 88.725 \log \gamma_s$$

this being the equation for a chemical cell without transference after the constants for a 1–2 salt at 25° have been introduced. The value E_0 =

TABLE II

	m $PbCl_2$	m $Cd(NO_3)_2$	E. m. f., volts	γ_s
1	0.01633	0.01738	0.5174	0.420
2	.01020	.01086	.5295	.491
3	.006527	.006946	.5420	.555
4	.004665	.004965	.5516	.605
5	.003263	.003471	.5623	.655
6	.002040	.002170	.5767	.721

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(6) Hulett, *Phys. Rev.*, **23**, 314 (1911).

(7) Cowperthwaite and La Mer, THIS JOURNAL, **53**, 4333 (1931)

(8) Carmody, *ibid.*, **51**, 2901 (1929).

(9) La Mer and Parks, *ibid.*, **53**, 2040 (1931).

0.3432 volt calculated by La Mer, Gronwall and Greiff[2] from Carmody's[3] results was used in the calculations. The values given for the e. m. f. cannot be considered reliable to much better than 0.3 mv.

The values of γ_s here given are uniformly lower than those given by Carmody for lead chloride in solution alone.

The "$\bar{a}$" values for the four most dilute solutions have been calculated from the Debye first approximation for the activity coefficient

$$-\log \gamma_s = \frac{1.53636\,(-z_1z_2)\mathrm{K}}{1 + \text{“}\bar{a}\text{”}\mathrm{K}}$$

For solutions of a 1–2 salt in water at 25° $\mathrm{K} = 0.5686\sqrt{m}$; m is here the total molality. For solutions of this dilution it is unnecessary to distinguish between molality and molarity. Since cadmium nitrate and lead chloride are of the same valence type, the only effect which the presence of cadmium nitrate has on the calculations is to increase the value of K. In this connection see La Mer, Gronwall and Greiff,[2] p. 2282.

The results of these calculations are given in Table III.

TABLE III

No.	3	4	5	6
10^{-8} K	0.06599	0.05580	0.04666	0.03689
"$\bar{a}$," Å.	3.16	3.76	4.70	5.44

Discussion of Results

As is shown in Table III the "$\bar{a}$" values for mixed solutions of lead chloride and cadmium nitrate at constant ratio of concentration are not constant but increase with decreasing concentration. On the basis of our theoretical discussion this phenomenon would not be expected in such solutions of two strong electrolytes. In the case, however, of solutions containing cadmium and chloride ions this drift in the "$\bar{a}$" values may be accounted for very simply. It has long been recognized that cadmium chloride possesses many of the properties of a weak electrolyte. This salt may not be regarded as completely dissociated even at concentrations as low as 0.0005 m. The cadmium ion is presumably the component of cadmium nitrate which gives rise to its large, 11.5 Å., "a" value. If the cadmium ion is removed from the solution as undissociated cadmium chloride, it becomes in effect a part of the solvent and no longer exerts any influence on the mean distance of closest approach of the ions in the solution. As the dilution increases the cadmium chloride becomes more and more dissociated, and, due to the presence of more cadmium ion in solution, the "$\bar{a}$" value increases. A consequence of this idea is that the solution should have a "normal" "$\bar{a}$" value at infinite dilution. When the "$\bar{a}$" values given in Table III are plotted against the concentration, the values for the three most dilute solutions fall on a straight line. On extrapolating this line to zero concentration the limiting "$\bar{a}$" value is found to be 6.8 Å. Assuming the value of 6.8 Å. for the mean distance of closest approach of the mixed solutions, the value of 1.75 Å. for lead chloride and using expressions (5) and (6) the "a_2" for cadmium nitrate is calculated to be 11.3 Å. This calculated value is in excellent agreement with the value determined from the experimental work of Jones. It must be remembered that it depends upon the compensation effect ($k_1 = k_2$) in the calculation of the ratio of the frequencies of collision of the two salts and also upon a result obtained from an arbitrarily extrapolated curve. The first of these assumptions cannot be further tested with the data available. Similar and more extended experiments upon solutions of two completely dissociated electrolytes may settle this point.

According to the above result it may be stated that the physical meaning of the ion size parameter in the Debye–Hückel theory of solutions takes on added significance. The fact that this quantity may be used in a logical calculation of mean values is definite although indirect proof of its significance as a distance.

In conclusion we wish to acknowledge our indebtedness to the Rockefeller Foundation for financial aid which made possible the purchase of much of the equipment used in the experimental work.

Summary

A mathematical solution of the problem of the calculation of the mean distance of closest approach of the ions in dilute solutions of strong electrolytes is given. This quantity is obtained as a function of quantities depending upon the valence types of the dissolved compounds and the size of the individual ions.

The activity coefficients of lead chloride in solutions of cadmium nitrate have been determined at six concentrations. The ratio of the concentration of the lead chloride to that of the cadmium nitrate was held constant. The data obtained are used as a preliminary test of the above-mentioned theoretical calculation.

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