evident not only in the greater velocity of inactivation of the amylase upon standing in heavy water at 25° but also in greater immediate losses of activity of the amylase upon dilution with heavy as compared with ordinary water.

The results obtained in comparable measurements with 50% heavy water, however, seem out of line. These are more variable but indicate greater inactivation of the enzyme in 50% heavy water than is obtained with either 99% heavy water or with ordinary water. In this connection it is of interest to note that Plantefol and Champetier[9] also report inconsistent results with the germination of *Narcissus papyraceus* in the presence of different concentrations of heavy water.

Summary

Working with highly purified heavy water and with highly purified preparations of pancreatic amylase, it has been found that (1) 100% heavy water has no marked influence upon the hydrolysis of starch by pancreatic amylase provided the conditions of the experiments are such as to minimize the deterioration of the enzyme and (2) that the inactivation of pancreatic amylase is more rapid and more pronounced when the amylase is held at 25° in highly purified heavy water than in similarly purified ordinary water.

NEW YORK, N. Y. RECEIVED NOVEMBER 12, 1935

---

[9] Plantefol and Champetier, *Compt. rend.*, **200**, 423 (1935).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

The Activity Coefficients of Lead Chloride in Aqueous Solutions of Barium Nitrate[1]

BY H. D. CROCKFORD AND H. O. FARR, JR.

Crockford and Thomas[2] derived from theoretical considerations the following expression for the mean distance of closest approach of the ions in dilute solutions of strong electrolytes.

$$\bar{a} = \frac{A_1 + A_2}{f_1 + f_2} \qquad (1)$$

wherein $A_1/f_1 = a_1$ and $A_2/f_2 = a_2$. In this expression a_1 and a_2 are the individual ion size parameter values for the two electrolytes and the f values are the frequencies of collisions. Hence the mean distance of closest approach in the solution containing the two electrolytes is a function of quantities depending upon the valence types of the electrolytes and the sizes of the individual ions concerned. It was shown by Crockford and Thomas[2] that the frequency of collision between the ions of a single electrolyte in dilute solutions is proportional to the square of the concentration. For two electrolytes the proportionality constants will be different but if they have small a values Crockford and Thomas have predicted that, due to compensating effects in the calculation of the individual frequencies, the following equation will be true

$$f_1 : f_2 :: C_1^2 : C_2^2 \qquad (2)$$

wherein C is the concentration of the electrolyte concerned. Consequently by means of equations (1) and (2) one can solve for the mean distance of closest approach if the two individual a values are known. Furthermore, if the ratio of the two concentrations is kept constant a constant value for the mean distance of closest approach should be obtained. Of course these considerations apply only to dilute solutions of strong electrolytes.

As a test of the above equations and in order to add to the general data concerning the a parameter of the Debye–Hückel theory a series of studies has been made with the cell.

$$\text{Pb–Hg(2 phase)} \mid PbCl_2(m_1)\ Ba(NO_3)_2(m_2) \mid \text{AgCl–Ag}$$

Three series of solutions have been studied: (I) a constant ratio of lead chloride and barium nitrate; (II) a constant molality of lead chloride and varying concentrations of barium nitrate; and (III) a constant molality of barium nitrate and varying concentrations of lead chloride. From the results have been calculated the activity coefficients of the lead chloride and the $\bar{a}$ parameter. The $\bar{a}$ values have also been calculated from existing data on the individual a values by means of equations (1) and (2).

Experimental Part

Purification of Materials.—Kahlbaum lead chloride was purified in a manner similar to that used by Crockford and Thomas.[2] C. P. grade of barium nitrate was purified as recommended by Hovorka and Rodebush.[3] The salt was crystallized three times from conductivity

---

[1] From a thesis presented by Mr. Farr to the faculty of the University of North Carolina as partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Crockford and Thomas, THIS JOURNAL, **55**, 568 (1933).

[3] Hovorka and Rodebush, *ibid*, **47**, 1614 (1925).

water, the crystals being finally dried at 140° for twenty-four hours, ground in an agate mortar, and kept in a vacuum desiccator. Before being used it was heated to 100° for several hours and cooled in the desiccator. Carefully purified mercury was twice redistilled. Tank nitrogen was purified by bubbling through alkaline permanganate, acid cuprous chloride, and alkaline pyrogallol. A very good grade of conductivity water was employed.

Preparation of Solutions.—Stock solutions of lead chloride were analyzed by precipitation of the chloride ion by means of silver nitrate. These stock solutions were diluted as required. The barium nitrate solutions were prepared by adding carefully weighed samples of the salt to solutions of lead chloride. These solutions could then be diluted to the proper concentrations. Flasks calibrated by the Bureau of Standards were used. By means of accurate density determinations the molalities could be calculated. Calibrated weights were of course used throughout the work.

Preparation of Electrodes.—For the silver–silver chloride electrodes platinum gauze 1.5 × 1.5 cm. was used. These electrodes were electrolyzed in a solution of potassium silver cyanide containing 10 g. of the salt per liter. These were plated four at a time for two hours, a current of 30 milliamperes being used. The anode was surrounded by a porous cup. The electrodes were then chloridized in 0.1 *M* hydrochloric acid. They gave an e. m. f. reproducible to at least 0.03 m. v. They were reddish-brown in color. A 6% amalgam by weight was prepared by dropping a known weight of oxide-free lead into an amalgam bulb through which was passing a stream of purified nitrogen. To this was then added the proper amount of purified mercury. The bulb was then kept at 125° until the amalgam became homogeneous. It was then introduced into the cell vessel from the amalgam bulb through a capillary opening.

Electrical Apparatus and Cell Vessel.—A Leeds and Northrup Type K potentiometer calibrated by the Bureau of Standards was used with a Leeds and Northrup No. 2500, Type R galvanometer. The electrical measuring apparatus was protected against electrical leak by equipotential shielding. The cell vessel, constructed of Pyrex glass, contained two sets of electrodes. A reservoir for the solution was attached. Before filling the vessel was carefully swept of air by means of a stream of purified nitrogen. E. m. f. readings easily reproducible to 0.03 m. v. were obtained with all but the most dilute solutions. With these a greater variation was found. The cell temperature was maintained constant at 25 ± 0.02° by means of a water thermostat.

Results and Calculations

Tables I, II and III give a summary of the experimental data together with the activity coefficients of the lead chloride and the $\bar{a}$ as calculated from the data.

The activity coefficients in the tables were calculated from the equation

$$E_{\text{mv}} + 88.7308\ (0.200687 + \log m) = E_0(\text{mv}) - 88{,}7308 \log f$$

TABLE I

Series I, m_1/m_2 constant

	m_1	m_2	E, v.		$\bar{a}$, Å.
1	0.01729	0.03575	0.51300	0.444	2.32
2	.01647	.03421	.51331	.463	2.45
3	.01235	.02564	.52125	.503	2.50
4	.01097	.02279	.52480	.516	2.49
5	.008227	.01709	.53328	.552	2.49
6	.004112	.008540	.55416	.642	2.55
7	.002056	.004270	.57640	.721	2.54
8	.001028	.002135	.59940	.794	2.67

TABLE II

Series II. Constant molality of $PbCl_2$ 0.019037

	m_2	E, v.		$\bar{a}$, Å
1	0.10025	0.51543	0.379	2.53
2	.08027	.51430	.390	2.49
3	.06069	.51223	.412	2.47
4	.04013	.50960	.441	2.41
5	.03030	.50872	.451	2.30
6	.02008	.50720	.469	2.20
7	.01003	.50520	.494	2.07
8	.00503	.50426	.507	1.95

TABLE III

Series III. Constant molality of $Ba(NO_3)_2$ 0.02004

	m_1 $PbCl_2$	E, v.	f	$\bar{a}$, Å.
1	0.02856	0.49501	0.429	2.09
2	.02141	.50371	.457	2.15
3	.01427	.51613	.500	2.33
4	.007136	.53924	.545	2.54
5	.003567	.56468	.563	2.53
6	.001784	.59110	.568	2.45
7	.000892	.61820	.562	2.31
8	.000446	.64640	.541	2.04

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 = 0.34320 volt calculated by La Mer, Gronwall and Greiff[4] from the data of Carmody[5] was used in the calculations.

The $\bar{a}$ values were calculated graphically according to the procedure outlined by La Mer, Gronwall and Greiff.[4] An attempt to employ the Debye first approximation for the calculation of a showed that for certain solutions a negative value was obtained, thus demonstrating the necessity of using the extended formula.

Discussion of Results

An inspection of the data shows that the activity coefficients increase with dilution in accordance with theory except for the last two points in series III. It is very difficult to obtain sufficiently accurate data in such concentrations so the error found is not surprising.

---

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

(5) Carmody, THIS JOURNAL, **51**, 2905 (1929).

An inspection of the $\bar{a}$ values in series I shows that the most probable value is 2.5 Å. It is to be noted that the values are quite constant except for the values for solutions 1 and 8. This is in agreement with equations (1) and (2). From this value of 2.5 Å. and the a value for silver chloride the value of a for barium nitrate was calculated. La Mer, Gronwall and Greiff[4] from the data of Carmody[5] have calculated that silver chloride should have an a value of 1.75 Å. With these values an a value of 2.68 Å. was found. La Mer, Gronwall and Greiff[4] have calculated from the freezing point data of Randall and Scott[6] a value of 3.1 Å. The agreement between their value and the one obtained by us is fair. It must be remembered that the use of freezing point data for such calculations is questionable.

To test the data of series II the $\bar{a}$ values were plotted against the molality of the barium nitrate. Except for solution 8 a smooth curve was obtained. The extrapolation of this curve to zero concentration gave a value of approximately 1.75 Å. This agrees with the value calculated by La Mer, Gronwall, and Greiff.[4]

When the same test is applied to the data of series III it is found that the last three values do not fit in well with the remainder of the series. When one considers how very small errors in the activity coefficient can affect the $\bar{a}$ value this is not surprising in these dilute solutions. Employing only the first five values an extrapolation to zero concentration gives a value of 2.68 Å. It is to be noted that this agrees exactly with that calculated from series I. It is of course obvious that this extrapolation is not accurate to more than ±0.02 Å.

As a further test of the data the $\bar{a}$ values for series II and III were calculated by equations (1) and (2) employing the values of 1.75 and 2.68 Å. for the a parameters of lead chloride and barium nitrate. Table IV gives these values along with the experimentally calculated data.

TABLE IV

	Series II		Series III	
	$\bar{a}$		$\bar{a}$	
	Exptl.	Calcd.	Exptl.	Calcd.
1	2.53	2.64	2.09	2.05
2	2.49	2.63	2.15	2.16
3	2.47	2.59	2.33	2.37
4	2.41	2.50	2.54	2.57
5	2.30	2.41	2.53	2.62
6	2.20	2.23	2.45	2.67
7	2.07	2.14	2.31	2.68
8	1.95	2.12	2.04	2.68

In most cases it is seen that the experimental and calculated values check quite closely.

In conclusion we wish to acknowledge our indebtedness to the Rockefeller Foundation for financial aid in purchasing part of the equipment used in the experimental work.

Summary

The activity coefficients of lead chloride in twenty-four solutions of barium nitrate have been determined. In series I the ratio of the molalities was kept constant. In series II and III the lead chloride and barium nitrate were respectively held constant.

From the activity coefficients the $\bar{a}$ parameters were calculated by means of the extended equation of La Mer, Gronwall and Greiff.

The values so obtained were used to check the equations of Crockford and Thomas concerning the ion size parameter in mixtures of electrolytes.

The need for the consideration of the $\bar{a}$ parameter value in mixtures of electrolytes at constant ratio of molalitity was demonstrated.

CHAPEL HILL, NORTH CAROLINA

RECEIVED SEPTEMBER 27, 1935

---

[6] Randall and Scott, THIS JOURNAL, **49**, 647 (1927).