[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Apparent Molal Expansibility of Electrolytes and the Coefficient of Expansibility (Thermal Expansion) as a Function of Concentration[1]

BY FRANK T. GUCKER, JR.

Several thermodynamic solute properties recently have been found to obey simple laws over a remarkably wide range of concentration. The apparent molal heat capacities, volumes and compressibilities of most electrolytes and of some non-electrolytes appear to be linear functions of the square root of the concentration from the most dilute solutions to those several molal or even more concentrated. These relationships were discovered, respectively, by Randall and Ramage,[2] Masson[3] and the present author,[4] who discussed their significance in a recent paper[5] which reviewed the earlier work. We will now define the apparent molal expansibility, which obeys a similar simple law, and show the use of this function in correlating the change of the coefficient of expansibility[6] of solutions with concentration.

The Apparent Molal Expansibility

If one mole of a solute is dissolved in V_1 cc. of solvent, and the resulting solution occupies a volume V cc., the apparent molal volume of the solute is defined by the equation

$$\Phi(V_2) = V - V_1 \tag{1}$$

Similarly, the apparent molal expansibility is defined as

$$\Phi(E_2) = \alpha V - \alpha_1 V_1 \tag{2}$$

where $\alpha = \frac{1}{V_0}\left(\frac{\partial V}{\partial T}\right)_P$ and α_1 are the coefficients of expansibility of solution and solvent, respectively. Eliminating V_1 between (1) and (2) and substituting c (the solute concentration in moles per liter) for $1000/V$ gives another useful equation

$$\Phi(E_2) = (1000/c)\,(\alpha - \alpha_1) + \alpha_1\Phi(V_2) \tag{3}$$

It also readily follows from differentiation of (1) that

$$\Phi(E_2) = (\partial\Phi(V_2)/\partial T)_P \tag{4}$$

Starting with Masson's linear relationship, at any temperature

$$\Phi(V_2) = \Phi^\circ(V_2) + ac^{1/2} \tag{5}$$

and differentiating with respect to temperature gives

$$\Phi(E_2) = \frac{\partial\Phi^\circ(V_2)}{\partial T} + \left[\frac{\partial a}{\partial T} - \frac{a}{2}\,(\alpha_1 + \Delta\alpha)\right] c^{1/2} \tag{6}$$

where $\Delta\alpha = \alpha - \alpha_1$. By (4), $\partial\Phi^\circ\ (V_2)/\partial T = \Phi^\circ(E_2)$. Since α_1 and $(\partial a/\partial T)$ are also constant, the only term within the brackets which changes with concentration is $(a/2)\,\Delta\alpha$; however, at least for most 1-1 electrolytes up to a concentration of several molal, this term is negligible so that we may write[7]

$$\Phi(E_2) = \Phi^\circ(E_2) + bc^{1/2} \tag{7}$$

Substituting in (3) the values of $\Phi(E_2)$ and $\Phi(V_2)$ from (5) and (7), gives a simple function of α itself

$$\alpha = \alpha_1 + Ac + Bc^{3/2} \tag{8}$$

where

$$A = \frac{\Phi^\circ(E_2) - \alpha_1\Phi^\circ(V_2)}{1000} \text{ and } B = \frac{b - \alpha_1 a}{1000} \tag{8'}$$

Equation (8) is analogous to that for densities developed by Root[8] and for coefficients of compressibility developed by the present author.[9]

The coefficients in (8) may be calculated directly from values of α at different concentrations by means of the function

$$F(\alpha) \equiv \frac{\alpha - \alpha_1}{c} = A + Bc^{1/2} \tag{9}$$

which is analogous to the $F(V)$ used by the author in calculating apparent molal volumes.[10]

Calculation of $\Phi(E_2)$ and α from Density Data

To illustrate the methods discussed above we have chosen the best available data for a number of electrolytes for which we need values of α in subsequent calculations.

In Fig. 1 the apparent molal volumes of potassium chloride in solutions of various concentrations are plotted against temperature. These are calculated by Geffcken[11] chiefly from the density data of Baxter and Wallace.[12] The concentrations refer strictly to 25°, but change

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(1) Paper presented before the Chicago meeting of the American Chemical Society, September 15, 1933.

(2) Randall and Ramage, THIS JOURNAL, **49**, 93 (1927).

(3) Masson, *Phil. Mag.*, [7] **8**, 218 (1929).

(4) Gucker, THIS JOURNAL, **55**, 2709 (1933).

(5) Gucker, *Chem. Rev.*, **13**, 111 (1933).

(6) This term, analogous to *compressibility*, is used in preference to the usual *thermal expansion*.

(7) For a similar development of the equation for the *apparent molal compressibility* see Geffcken, *Z. physik. Chem.*, **A167**, 240 (1934); and Scott, submitted to *J. Phys. Chem.*

(8) Root, THIS JOURNAL, **55**, 850 (1933).

(9) Gucker, *ibid.*, **55**, 2709 (1933).

(10) Gucker, *J. Phys. Chem.*, March, 1934.

(11) Geffcken, *Z. physik. Chem.*, **A155**, 1 (1931).

(12) Baxter and Wallace, THIS JOURNAL, **38**, 70 (1916).

only slightly over the range. All but two points lie along smooth curves. In these cases we have checked all the calculations, and the discrepancy seems to be in the original density data. We have therefore drawn the curves through the values of $\Phi(V_2)$ calculated from Geffcken's linear equations at the temperatures in question. The values for the 0.33 molal solution at 0°, and for the infinitely dilute solutions at all temperatures were calculated in the same way.

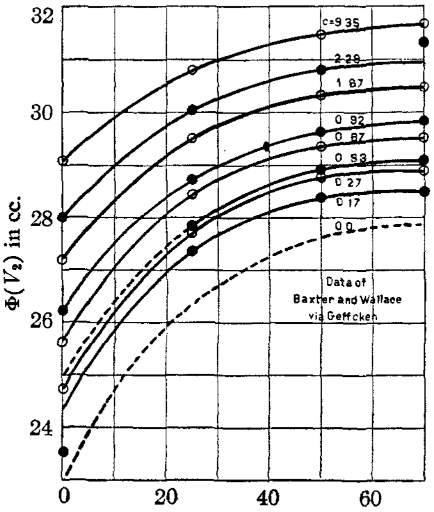

Fig. 1.—Apparent molal volumes of KCl solutions at different temperatures.

Similar plots of the apparent molal volumes of lithium chloride and sodium chloride were also made and values of $\Phi(E_2)$ at 0, 25 and 50° were obtained (using eq. 4) by graphical estimation of the tangents of the $\Phi(V_2)-t$ curves. These were plotted against $c^{1/2}$ and found to lie along straight lines, as shown in Fig. 2.[13] From the equations for the lines which best fitted the data, we calculated values of $\Phi(E_2)$ which were compared with the *observed* values. The numerical agreement in the case of potassium chloride at 25° is illustrated in Table I, while the equations for $\Phi(E_2)$ and the average differences between α observed and calculated are summarized in Table II. The agreement at 0° is not nearly so good as at the higher temperatures, because the steep tangents at the end of the curve are harder to estimate.

The use of $F(\alpha)$ is illustrated by the data for hydrochloric acid, sodium hydroxide and sodium sulfate at 25°. Values of α for the first two were calculated from the density data of the "International Critical Tables,"[14] at 10, 20, 30 and 40°, by the simplified least square method of the author and Dr. H. J. Brennen.[15] Those for sodium sulfate are taken from the careful dilatometer experiments of Gibson.[16]

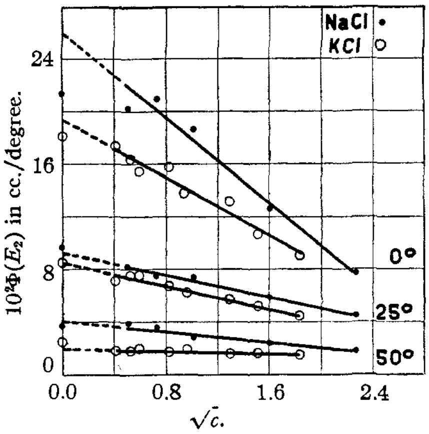

Fig. 2.—Apparent molal expansibilities at different temperatures.

TABLE I

$\Phi(E_2)$ FOR POTASSIUM CHLORIDE SOLUTIONS AT 25°

$c^{1/2}$	$10^2\Phi(E_2)$ Obs.[a]	$10^2\Phi(E_2)$ Calcd.[b]
0.000	8.5	8.5
.408	7.1	7.6
.521	7.5	7.4
.586	7.5	7.2
.818	6.7	6.7
.958	6.2	6.4
1.292	5.7	5.7
1.514	5.2	5.2
1.829	4.5	4.5

[a] Determined as $\partial\Phi(V_2)/\partial T$ from $\Phi(V_2)$-t curves.

[b] Calculated from equation $10^2\Phi(E_2) = 8.50 - 2.20c^{1/2}$.

In Fig. 3 values of $10^4F(\alpha)$ for these solutions are plotted against $c^{1/2}$. Hydrochloric acid shows excellent linearity over the whole range of the data. The agreement in the case of sodium hydroxide is only slightly less satisfactory up to 5 molal, above which the relationship fails.[17] The sodium sulfate data are represented by the

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[13] The lines for lithium chloride, which cross some of the others, are omitted to avoid confusion.

[14] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1928, 1st ed., Vol. III, pp. 54 and 79.

[15] Gucker and Brennen, THIS JOURNAL, 54, 886 (1932).

[16] Gibson, *J. Phys. Chem.*, 31, 496 (1927).

[17] However, the linear relationship for $\Phi(V_2)$ holds only up to 3 molal. Here, and in the case of the lithium chloride solutions at 25 and 50°, the linearity holds to appreciably higher concentrations for the *derivative* quantity. This is known to be true in other cases; for the apparent molal heat content (integral heat of dilution) is a linear function of $c^{1/2}$ only at extreme dilution; while the apparent molal heat capacity shows a linear relationship to high concentrations.

TABLE II

APPARENT MOLAL EXPANSIBILITIES AT DIFFERENT TEMPERATURES

Solute	0° $10^2\Phi(E_2)$	$10^6\Delta\alpha^a$	25° $10^2\Phi(E_2)$	$10^6\Delta\alpha^a$	50° $10^2\Phi(E_2)$	$10^6\Delta\alpha^a$
LiCl	$11.0 - 3.6c^{1/2}$	±0.3	$2.50 - 0.65c^{1/2}$	±0.2	$-2.40 + 0.42c^{1/2}$	±1
NaCl	$26.0 - 8.1c^{1/2}$	±6	$9.30 - 2.10c^{1/2}$	± .8	$4.10 - 1.0c^{1/2}$	±1
KCl	$19.3 - 5.5c^{1/2}$	±5	$8.50 - 2.20c^{1/2}$	± .5	$2.00 - 0.25c^{1/2}$	±0.5

[a] The *average* deviations in α corresponding to the difference between $\Phi(E_2)$ *observed* and *calculated*. Except for the equation for LiCl at 0°, which holds only up to $c = 2.8$, these equations hold over the whole experimental range; up to $c = 6.9$ for LiCl, $c = 4.8$ for NaCl and $c = 3.3$ for KCl.

linear equation with an average deviation of $\pm 1.9 \times 10^{-6}$ in α.

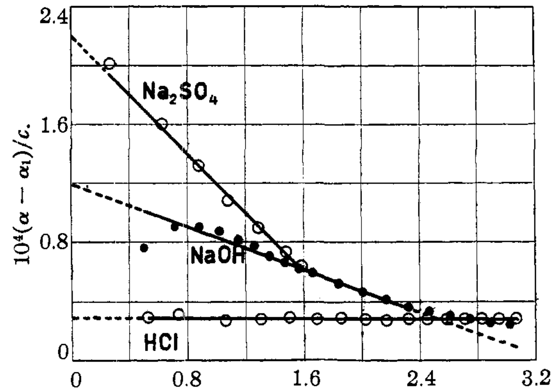

Fig. 3.—$10^4\ F(\alpha)$ against $\sqrt{c}$.

Equations for $\Phi(E_2)$ were calculated from those for $F(\alpha)$ by means of (8').[18] Thus, according to Gibson's data the apparent molal volume of sodium sulfate is a linear function of $c^{1/2}$ over the whole range mentioned above. Transforming his equation, where concentration is expressed in grams per cc., gives $\Phi(V_2) = 11.095 + 12.65_5 c^{1/2}$. Hence from (3), $10^2\Phi(E_2) = 22.19 - 9.33c^{1/2}$.

In Table III are summarized the apparent molal expansibilities of six 1-1 electrolytes and one 1-2 electrolyte at 25°; as well as the coefficients A and B in equation (8), from which α can be calculated directly.

General Characteristics of $\Phi(E_2)$

A study of Figs. 2 and 4 will show certain interesting regularities in the apparent molal expansibilities which parallel the other apparent molal properties.

All the solutes at 25° have positive values of $\Phi°(E)$ which are undoubtedly additive for the ions as in the case of the other apparent molal properties. All the slopes are negative, so that the increase in expansibility, per mole of solute, becomes *less* at higher concentrations. The slope is much greater for the 2-1 than for the 1-1 electrolytes; which, however, vary greatly among themselves. The order of *increasing* slope at 25° is HCl, LiCl, LiOH, NaCl, KCl, NaOH.

TABLE III

SUMMARY OF COEFFICIENTS FOR $\Phi(E_2)$ AND α AT 25°[a]

Solute	$\Phi(E_2) = \Phi°(E_2) + bc^{1/2}$ $10^2\Phi°(E_2)$	-10^2b	$\alpha = \alpha_1 + Ac + Bc^{3/2}$ 10^4A	-10^4B
HCl	3.4	0.02	0.29	0.004
LiCl	2.5_0	$.6_5$	.21	$.06_9$
LiOH[b]	4.5	1.8	.47	.19
NaCl	9.3_0	2.1_0	.89	$.21_6$
KCl	8.5_0	2.2_0	.78	$.22_6$
NaOH	11.7	3.5	1.19	.36
Na_2SO_4	22.1_9	9.3_3	2.19	$.96_6$

[a] The values of $\Phi°(V_2)$ and $\partial\Phi(V_2)/\partial c^{1/2}$ used in calculating $\Phi°(E_2)$ and b from A and B, or *vice versa* are taken from our previous article[19] except in the case of sodium sulfate previously cited, where we used Gibson's[18] values.

[b] The value of $\Phi(E_2)$ for LiOH was obtained by evaluating equations for $\Phi(V_2)$ at 30 and 20° from the "International Critical Tables" density data, and dividing the difference by 10 to obtain $\Delta\Phi(V_2)/\Delta T$. Values of α calculated by the least square method gave widely varying values of $\Phi(E_2)$. There appears to be some discrepancy in the density data, and this value must be considered rather tentative.

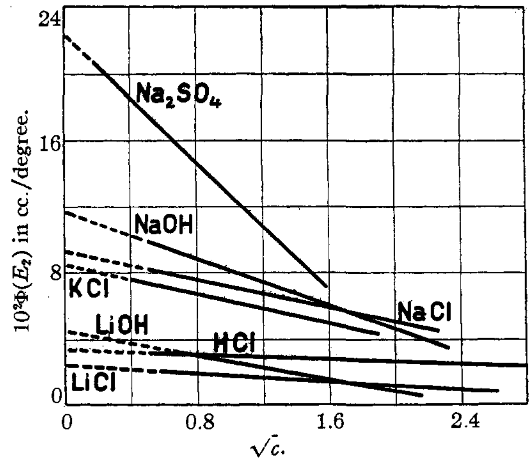

Fig. 4.—Apparent molal expansibilities at 25°.

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(18) Gibson, submitted to *J. Phys. Chem.* We wish to thank Dr. Gibson for privately communicating this result to us in advance of its publication.

With the single exception of lithium hydroxide (the value of which is in considerable doubt) this is the same order we found[19] for the increasing slope of the apparent molal volume curves, and also, with but three exceptions, for the apparent molal compressibility and heat capacity curves as well. This shows a striking similarity among these different properties.

The change of $\Phi(E_2)$ with temperature is also marked enough to deserve notice. In every case the curves at 0° are steeper and reach a larger $\Phi^\circ(E_2)$ value than those at the higher temperatures. In one or two instances (*cf.* lithium chloride here tabulated) $\Phi^\circ(E_2)$ becomes *negative* and the slope *positive* at 50°. In general, however, the effect of the solute is greater and varies most with concentration at the lower temperatures. Gibson[20] has already noted the marked effect of temperature over the range 25–40° in the case of the "fictive expansibility" of sodium sulfate.

Partial Molal Expansibility of Solute and Solvent

Two closely related thermodynamic properties, the partial molal expansibilities of solute and solvent, may be defined by the equations

$$\overline{E}_2 = \left(\frac{\partial E}{\partial n_2}\right)_{n_1,T,P} = \left(\frac{\partial \overline{V}_2}{\partial T}\right)_{n_1,n_2,P} \qquad (10)$$

$$\overline{E}_1 = \left(\frac{\partial E}{\partial n_1}\right)_{n_2,T,P} = \left(\frac{\partial \overline{V}_1}{\partial T}\right)_{n_1,n_2,P} \qquad (11)$$

The first of these quantities is closely related to the "fictive expansibility" which Gibson defined and used in the study of sodium sulfate previously mentioned. These quantities may be calculated from $\Phi(E_2)$ by means of the equations

$$\overline{E}_2 = \Phi^\circ(E_2) + \left[\frac{3000 - c\Phi^\circ(V_2)}{2000 + c^{3/2}\dfrac{\partial\Phi(V_2)}{\partial c^{1/2}}}\right]\frac{\partial\Phi(E_2)}{\partial c^{1/2}}\,c^{1/2} \qquad (12)$$

$$\overline{E}_1 = E_1^\circ - \frac{M_1}{d_1}\left[\frac{c}{2000 + c^{3/2}\dfrac{\partial\Phi(V_2)}{\partial c^{1/2}}}\right]\frac{\partial\Phi(E_2)}{\partial c^{1/2}}\,c^{1/2} \qquad (13)$$

where E_1° M_1 and d_1 are the molal expansibilities, molecular weight and density of the solvent.[21]

$\Phi(E_2)$ and the Debye–Hückel Theory

No theory as yet quantitatively accounts for all the apparent molal solute properties. Different workers have, however, derived from the limiting law of Debye and Hückel equations predicting the linearity of the apparent molal heat capacity, volume and compressibility of electrolytes. These equations were discussed in our previous article.[19] We can derive a similar equation for the apparent molal expansibility. Differentiating with respect to T the equation which Redlich and Rosenfeld,[22] derived for the partial molal volume gives the partial molal expansibility of an electrolyte, each molecule of which furnishes ν_i ions of charge z_i

$$\overline{E}_2 - \overline{E}_2^\circ = \frac{A}{2}\,\frac{(\Sigma\nu_i z_i^2)^{3/2}}{D^{3/2}\,T^{1/2}}\,f\,(D,P,V,T)c^{1/2} \qquad (14)$$

where $f\,(D,P,V,T) = -\frac{1}{2}\left[\frac{3}{D}\frac{\partial D}{\partial T} + \frac{1}{T} + \alpha\right]$

$$\left(\frac{3}{D}\frac{\partial D}{\partial P} - \beta\right) + \frac{\partial}{\partial T}\left[\frac{3}{D}\frac{\partial D}{\partial P} - \beta\right]$$

$$A = \left[\frac{\pi N^3\epsilon^6}{1000k}\right]^{1/2} = 2.457 \times 10^{14} \text{ (in c. g. s. units)}$$

D is the dielectric constant, and β the coefficient of compressibility of the solvent; T is the absolute temperature, N Avogadro's number, ϵ the charge of the electron and k Boltzmann's constant.

The equation predicts that, at least at low concentrations, $\overline{E}_2$ and hence also $\Phi(E_2)$ should be linear functions of $c^{1/2}$ and that the slopes should be *greater* for salts of higher valence type. We cannot evaluate f exactly, because $(\partial^2 D/\partial P\partial T)$ has not been determined. However, the *pressure* coefficients of β and of $(\partial \ln D/\partial P)T$ differ by only 10% and if we assume the temperature coefficients are equal

$$\frac{\partial}{\partial T}\left[\frac{3}{D}\frac{\partial D}{\partial P} - \beta\right] \simeq 2\frac{\partial\beta}{\partial T} = -2.5 \times 10^{-13}$$

whence, at 20°, $f = 4.3 \times 10^{-13}$ and

$$\overline{E}_2 - \overline{E}_2^\circ = 4.3 \times 10^{-13}\,(\Sigma\nu_i z_i^2)^{3/2}c^{1/2}$$

For a 1-1 electrolyte the predicted equation is

$$\Phi(E_2) = \Phi^\circ(E_2) + 8 \times 10^{-3}c^{1/2}$$

The Debye–Hückel theory therefore apparently predicts a *positive* slope, while all the actual slopes are *negative*. Only a study of the dielectric constant of water under pressure, over a wide range of temperature, can determine whether or not there is a real discrepancy between theory and fact.

At any rate, the Debye–Hückel theory cannot explain the individual slopes for particular electrolytes nor yet the *positive* value of $\Phi^\circ(E_2)$. The latter follows from the picture of the solvent water being under pressure due to the electrostrictive force of the ionic charge, for pressure increases α for water. The attempts of Evjen

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(19) Gucker, *Chem. Rev.*, **13**, 111 (1933).

(20) Gibson, *J. Phys. Chem.*, **31**, 496 (1927).

(21) For a discussion of these methods of calculation based on volume concentration and the derivation of the general equation of which (12) is a special case, see Ref. 10.

(22) Redlich and Rosenfeld, *Z. physik. Chem.*, **A155**, 65 (1931).

and Zwicky[23] to calculate this effect quantitatively are a step in the right direction, but do not yet account for the general linearity with $c^{1/2}$ or for the individuality of the lines.

It also seems unsafe to try to account for *all* the anomalous behavior of electrolytes on the basis of the free ions, since we showed[19] that the apparent molal volumes and compressibilities of sucrose and urea, from 30 to 70° obey the square root law. The same must be true of the apparent molal expansibilities of these substances, although the present density data do not warrant a numerical calculation.

Summary

We have defined the apparent molal expansibility of a solute, which is a linear function of the square root of the volume concentration for all the seven electrolytes studied.

The limiting value $\Phi^\circ(E_2)$ is more positive and the negative slope greater at low temperatures and for high valence type electrolytes.

Whenever the apparent molal expansion and volume each follows the square root law, the coefficient of expansibility (thermal expansion) $\alpha = \alpha_1 + Ac + Bc^{3/2}$.

We have derived equations by which the partial molal expansibility of solute and solvent may be calculated from $\Phi(E_2)$.

We have derived from the Debye–Hückel limiting law an expression which predicts the linearity of $\Phi(E_2)$ with $c^{1/2}$. An estimate of the coefficient, based on our present incomplete knowledge of the dielectric properties of water under pressure, indicates that the slope predicted at 20° is *positive* instead of *negative*.

The general theory of the apparent molal expansibility is incomplete but the order of increasing slopes of the $\Phi(E_2)$ lines here reported is shown to parallel that of the $\Phi(V_2)$, $\Phi(K_2)$ and $\Phi(C_{p2})$ lines.

EVANSTON, ILLINOIS RECEIVED NOVEMBER 6, 1933

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[23] Evjen and Zwicky, *Phys. Rev.*, **33**, 860 (1929).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

The Diffusion of Colloids and Colloidal Electrolytes; Egg Albumin; Comparison with Ultracentrifuge[1]

BY J. W. MCBAIN, C. R. DAWSON AND H. ALBERT BARKER

Colloids may diffuse quite as fast as ordinary molecules.[2] This is due to the influence of the oppositely charged ions which accompany all charged particles and drag them along just as hydrogen ions accelerate sulfate ions in the diffusion of sulfuric acid. Hence, ferric hydroxide or soaps may diffuse faster than sucrose.[3] These effects are diminished by the presence of other electrolytes or buffers, and they vanish at the isoelectric point. A number of investigators have arrived independently at the same formulation for diffusion of colloidal electrolytes and their admixtures with salts (at infinite dilution).

Under suitable conditions, diffusion through porous membranes of constant properties becomes one of the simplest, quickest and most accurate methods of determining particle size or molecular weight of many materials and substances of biological interest.

Egg albumin has been chosen for demonstrating some of the factors involved. It is one of the most thoroughly studied of colloids, and it forms clear, stable solutions which do not coagulate upon dialysis or the addition of moderate amounts of acid or base.

The experiments comprise a series with electrodialyzed egg albumin, brought to definite values of *P*H with hydrochloric acid or sodium hydroxide, diffusing into a solution of the same *P*H; and other series in which the egg albumin was not electrodialyzed and diffusion took place into water.

Experimental

The method and technique were those previously described,[4] in which diffusion cells ob-

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[1] Read at the meeting of the Pacific Intersectional Division at Salt Lake City, June 13, 1933.

[2] The contrary impression has been emphasized by the usual lecture demonstrations in which diffusion takes place into jellies or through colloidal diaphragms, thus introducing the wholly extraneous factor of ultrafiltration and sieve action.

[3] McBain and Liu, THIS JOURNAL, **53**, 59 (1931); M. E. Laing McBain, *ibid.*, **55**, 549 (1933); see also Hartley and Robinson, *Proc. Roy. Soc.* (London), **A134**, 20 (1931); Svedberg, *Kolloid-Z.*, **36**, Ergänzungsbd., p. 63 (1925), equations 13b and 14. We find for a ferric hydroxide sol ["Sol No. 20," McClatchie, *J. Phys. Chem.*, **36**, 2088 (1932)] a diffusion coefficient of 0.613 as compared with 0.46 for sucrose. The chlorine present diffused still faster than the iron. Herzog and Polotsky obtained similar high values for some dyes [*Z. Elektrochem.*, **17**, 680 (1911)].

[4] McBain and Liu, THIS JOURNAL, **53**, 59 (1931); M. E. Laing McBain, *ibid.*, **55**, 549 (1933); Dawson, *ibid.*, **55**, 432 (1933); McBain and Dawson, *ibid.*, **56**, 52 (1934).