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Author(s): T. H. Lilley and C. C. Briggs
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Activity coefficients of calcium sulphate in water at 25 °C

BY T. H. LILLEY AND C. C. BRIGGS
Chemistry Department, The University, Sheffield S3 7HF, U.K.

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The activity coefficients of calcium sulphate in water up to the solubility limit have been determined at 25 °C by an electromotive force method utilizing cells involving a calcium ion-exchange membrane electrode and lead sulphate–lead amalgam electrodes. By appropriate integration of the activity coefficients, values for the osmotic coefficients of the solutions were obtained which are in good agreement with earlier measurements derived directly from freezing temperature measurements.

The standard electrode potential ($E^0_{\mathrm{PbSO_4|Pb(Hg)}}$) of $\mathrm{PbSO_4|Pb(Hg)}$ was obtained from the experimental measurements by the use of extrapolation functions based upon: (i) linearized solutions of the Poisson–Boltzmann equation in conjunction with an ion-association treatment and (ii) numerical integrations of the Poisson–Boltzmann equation. Both procedures agreed within the limits of experimental accuracy and gave $E^0_{\mathrm{PbSO_4|Pb(Hg)}} = -(352.6 \pm 0.4)\,\mathrm{mV}$ at 25 °C.

The thermodynamic solubility product of gypsum ($\mathrm{CaSO_4 \cdot 2H_2O}$), calculated from measurements on solutions at saturation, was found to be $(2.63 \pm 0.09)\,\mathrm{mol^2\,kg^{-2}}$.

INTRODUCTION

It is well known that the Debye–Hückel (D.–H.) treatment (or one of its semi-empirical modifications) will adequately represent the thermodynamic behaviour of simple, low charge type electrolytes in water at ambient temperatures, to molalities of about $0.1\,\mathrm{mol\,kg^{-1}}$. When electrolytes of higher charge type are considered those treatments based on the D.–H. approach become inadequate in the concentration range over which experimental measurements are possible and some other representation of solute non-ideality must be used. Two approaches have been used to treat this problem. Deviations from ideality for highly charged ions may be represented by using either non-linearized solutions to the D.–H. equation or by using a linearized D.–H. solution in conjunction with an assumed equilibrium between free and associated ions. There have been several discussions of this problem, based principally on the osmotic coefficient data obtained by Brown & Prue (1955) for the divalent metal sulphates. In this paper we describe the experimental determination of the activity coefficients of $\mathrm{CaSO_4}$ in water at 25 °C up to the solubility limit, by an e.m.f. method in which calcium ion-responsive electrode is used. The viability of such electrodes has been recently investigated (Briggs & Lilley

1974) and applied to thermodynamic investigations (Briggs & Lilley 1975*a*; Briggs *et al.* 1974). The solubility product of gypsum is evaluated and compared with some recent estimates.

EXPERIMENTAL

Materials

All solutions were prepared from laboratory distilled water which had been passed through a column of mixed strong acid and strong base ion-exchange resins (Permutit 'Bio-Deminrolit') immediately prior to use. Calcium sulphate dihydrate was Analar reagent grade. Its purity was checked by calcium analysis using EDTA (Briggs & Lilley 1974), by mass loss on ignition determinations and by powder X-ray diffraction. Stock solutions were prepared by mass and their concentrations checked by EDTA titration. Other solutions were prepared by mass from these stock solutions. Saturated solutions of the dihydrate were prepared by equilibration with excess of solid phase for a minimum of three weeks at 25 °C. The purification of calcium chloride and preparation of solutions has been described earlier (Briggs & Lilley 1974*a*). Analar lead nitrate was recrystallized from water. Solutions for use in electrolysis were prepared by adding deionized water to the recrystallized product and the mixture was equilibrated at 0 °C.

Lead sulphate was prepared from a stoichoimetric mixture of recrystallized lead nitrate and Analar sodium sulphate solutions. The precipitate was washed by decantation 16 times with deionized water.

The mercury used in electrolysis was purified as follows. High quality mercury was washed with a 15% sodium hydroxide solution. The NaOH solution was replaced at intervals until the aqueous phase remained almost clear after prolonged washing. After washing several times with deionized water, the washing process was continued with 1 M perchloric acid for four days, the acid solution being changed each day. The mercury was washed thoroughly with water, ethanol and ether and then triply distilled under vacuum. It was once again treated with one molar perchloric acid before finally washing with deionized water.

Amalgams containing about 4% lead were prepared electrolytically (Ives & Janz 1961; Briggs 1973).

'White Spot' nitrogen was passed through a tube of copper turnings maintained at about 520 °C in order to remove any traces of oxygen.

Apparatus

Cells

The design of cells used (figure 1) enabled oxygen to be excluded from the sulphate compartment but had the additional advantage that lead ions could be excluded from the calcium electrode compartment when desired.

Cells used for measuring calcium chloride activities have been described earlier (Briggs & Lilley 1974).

Electrodes

The calcium ion-responsive electrode, the silver–silver chloride electrodes and the measuring circuit and the thermostatting arrangement have been described earlier (Briggs & Lilley 1974). The lead amalgam–lead sulphate electrodes were prepared as described below.

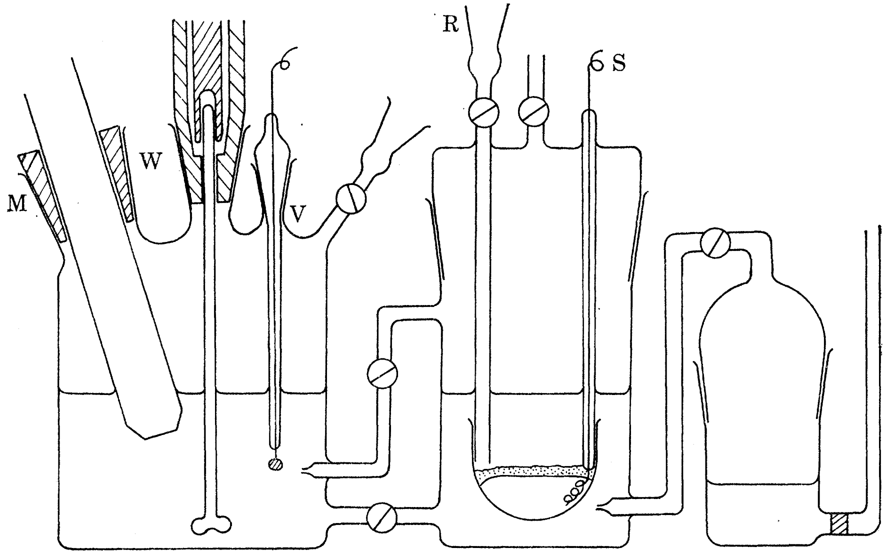

FIGURE 1. Diagrammatic representation of cells. The principal components are the calcium electrode (M), the stirrer (W), the Ag/AgCl electrode (V) and the Pb/$PbSO_4$ (electrode S).

Preparation of cells containing calcium sulphate

An amalgam storage reservoir was attached to the cell at R (see figure 1). The system was thoroughly flushed with nitrogen to remove oxygen and some lead amalgam transferred to the cell. A slurry of lead sulphate, in a calcium sulphate solution of the same molality as that to be investigated, was added to the cell through inlet R until a settled layer 2–3 mm thick was formed. The calcium electrode compartment was filled with calcium sulphate solution and nitrogen passed through it to remove all traces of oxygen.

Solution was then transferred to the lead amalgam-lead sulphate compartment using nitrogen pressure, until the solution level was the same in both compartments. The taps were then closed.

E.m.f. measurements

Two reference cells containing calcium chloride solutions and four test cells containing calcium sulphate solutions were used in each experiment. One of the reference cells was chosen to be used in transfer experiments with the test cells and the other reference cell was used to check that the calcium electrode was responding in a Nernstian manner (Briggs & Lilley 1974). Measurements were commenced on the test cells about 20 min after placing them in the air-thermostat. Subsequent measurements were made over the following few days.

Experimental conditions

The major differences in technique between these measurements and those described earlier (Briggs & Lilley 1974; Briggs *et al.* 1974) were

(i) Nitrogen was passed continuously through both compartments of the cells when e.m.f. measurements were made.

(ii) Excess liquid remaining on the calcium-ion electrode was removed by washing the electrode with the solution on which measurements were about to be made.

(iii) The use of the stirrer was discontinued except for the most dilute solution investigated.

RESULTS

The cells may be represented as

$$(\mathrm{Hg})\mathrm{Pb}|\mathrm{PbSO_4}\left|\begin{array}{c}\mathrm{CaSO_4}(m_1)\\ \mathrm{PbSO_4}(m_2)\end{array}\right|\left|\,\mathrm{CaSO_4}(m_1)\,\right\|\begin{array}{c}\text{Ca membrane}\\ \text{electrode}\end{array} \qquad \text{(i)}$$

and

$$\mathrm{Ag}|\mathrm{AgCl}|\mathrm{CaCl_2}(m_3)\ \|\ \text{Ca membrane electrode} \qquad \text{(ii)}$$

If m_2 is zero, the e.m.fs of cells (i) and (ii) are given by

$$E_{\mathrm{i}} = {}''E^0_{\mathrm{Ca}}{}'' - E^0_{\mathrm{PbSO_4|Pb(Hg)}} + (\tfrac{1}{2}k)\ln\{a(\mathrm{Ca^{2+}})\,a(\mathrm{SO_4}^{2-})\}, \qquad (1)$$

$$E_{\mathrm{ii}} = {}''E^0_{\mathrm{Ca}}{}'' - E^0_{\mathrm{AgCl|Ag}} + (\tfrac{1}{2}k)\ln\{a(\mathrm{Ca^{2+}})\,a^2(\mathrm{Cl^-})\}, \qquad (2)$$

where the non-constancy of the standard electrode potential of the calcium-ion-exchange membrane electrode is stressed by the quotation marks and $k = (RT/F)$.

The transfer potential (E_{T}) is given by

$$E_{\mathrm{T}} = E^0_{\mathrm{AgCl|Ag}} - E^0_{\mathrm{PbSO_4|Pb(Hg)}} + k\ln\{m_1\gamma(\mathrm{CaSO_4})\} - \tfrac{3}{2}k\ln\{4^{\frac{1}{3}}m_3\gamma(\mathrm{CaCl_2})\}. \qquad (3)$$

When dissolved lead sulphate is considered the transfer potentials are modified as discussed below and when $\mathrm{PbSO_4}$ is restricted to the lead amalgam–lead sulphate compartment, the transfer potential (E^*_{T}) is given by

$$E^*_{\mathrm{T}} = E^0_{\mathrm{AgCl|Ag}} - E^0_{\mathrm{PbSO_4|Pb(Hg)}} + \tfrac{1}{2}k\ln\{m_1(m_1+m_2)\,\gamma^2(\mathrm{CaSO_4})\} - \tfrac{3}{2}k\ln\{4^{\frac{1}{3}}m_3\gamma(\mathrm{CaCl_2})\} - E_j. \qquad (4)$$

The observed values of E^*_{T} for each solution are given in table 1. The reference calcium chloride solution was $0.03308\,\mathrm{mol\,kg^{-1}}$. When more than one cell was used for a given solution the mean of the results obtained from each cell and the overall mean of the transfer potential are given.

Effect of lead sulphate

The cells were usually used so that the calcium electrode compartment was maintained free of dissolved lead sulphate. Under these conditions the cell e.m.f. was modified by the presence of the lead sulphate in the lead amalgam–lead sulphate electrode compartment because

(i) the additional sulphate ions present gives rise to a correction term at the amalgam electrode of magnitude $\frac{1}{2}k \ln\{(m_1 + m_2)/m_2\}$ (see equation (4)).

TABLE 1. OBSERVED TRANSFER POTENTIALS AND CORRECTION TERMS

$10^4 m_1$ / mol kg^{-1}	N†	E_T / mV	σ§ / mV	E_j / mV	correction for Ca electrode / mV	correction for $PbSO_4$|Pb(Hg) electrode / mV	E_T* / mV	E'_T|| / mV	Δ¶ / mV
151.8	5	571.61	±0.08	< 0.005	0.01	0.01	571.62	324.73	±0.24
	9	571.45	±0.14				571.46	324.57	±0.30
	12	571.74	±0.05				571.75	324.86	±0.21
	26‡	571.61	±0.07				571.62	324.73	±0.23
99.80	6	564.31	±0.08	< 0.005	0.01	0.015	564.33	328.21	±0.24
	9	564.39	±0.03				564.40	328.28	±0.18
	15‡	564.35	±0.08				564.37	328.25	±0.24
59.97	13	555.32	±0.13	< 0.005	0.02	0.03	555.35	332.20	±0.29
33.36	5	544.59	±0.19	< 0.005	0.05	0.07	544.66	336.64	±0.36
	9	544.39	±0.03				544.46	336.44	±0.20
	14‡	544.46	±0.08				544.53	336.51	±0.25
20.03	12	534.71	±0.14	0.01	0.09	0.14	534.84	339.87	±0.34
11.09	9	522.37	±0.13	0.03	0.23	0.37	522.72	342.72	±0.40
6.576	19	511.48	±0.04	0.06	0.52	0.81	512.23	345.25	±0.42

† N is the number of independent transfers from a given solution.
‡ The total number of transfers for a given solution.
§ σ is the 95 % confidence limit of the mean transfer potential.
|| The reference $CaCl_2$ solution was of molality 0.03308 mol kg^{-1}.
¶ Δ is the estimated maximum error in E'_T.

(ii) The activity coefficient of sulphate ions in the amalgam compartment is changed. The effect is small compared to (i) and was consequently neglected.

(iii) A liquid junction is set up between the two compartments.

When lead sulphate is present in both compartments a liquid junction potential is no longer present but two other corrections are necessary.

1. The activity coefficient of calcium ions will be modified but this effect was neglected as in (ii) above.
2. The calcium electrode will respond to the presence of Pb^{2+} ions.

The importance of the various effects can only be calculated if the solubility of $PbSO_4$ in the calcium sulphate solutions is known. No experimental determinations could be found from a survey of the literature and it was necessary to estimate the required solubilities. The solubility of $PbSO_4$ in water at 25 °C is 1.49×10^{-4} mol kg^{-1} (Seidell 1958) and the solubility product can be obtained if the activity coefficient of the lead sulphate is estimated. It was found by Gardner & Glueckauf (1969) in their treatment of divalent sulphates that the variation of ionic activity coefficients was largely independent of the metal ion and, while our ultimate findings are somewhat at variance with those of these workers, we have used their estimates for the calculations involved in the overall correction terms.

The liquid junction potentials were estimated from the Henderson equation (see MacInnes 1939). (The concentration variation of transport numbers in the Henderson equation was estimated by using the Robinson & Stokes (1959) treatment.) The correction terms arising from the liquid junction potential and an estimate of the errors are given in table 1. Included in table 1 are the estimated correction terms arising from the additional sulphate, from the lead sulphate in the lead amalgam compartment and the term arising from the Pb^{2+} ion response of the calcium ion membrane electrode. This latter was calculated from the semi-empirical equation advocated by Ross (1967) using the parameters given by him.

The reason for choosing to measure cell e.m.f. values with the calcium electrode compartment free of lead sulphate is apparent from an inspection of table 1. The uncertainty in potential caused by the liquid junction potential is within experimental error at all calcium sulphate concentrations, but the uncertainty in the correction required to compensate for response of the calcium electrode to lead ions is significant at all concentrations used.

DISCUSSION

Initial treatment of results

Equation (4) may be re-expressed as

$$\begin{aligned} E'_{\mathrm{T}} &= E^{*}_{\mathrm{T}} - E^{0}_{\mathrm{AgCl|Ag}} - \tfrac{1}{2}k\ln\{m_1(m_1+m_2)\} + \tfrac{3}{2}k\ln\{4^{\frac{1}{3}}m_3\gamma(\mathrm{CaCl_2})\} + E_j \\ &= k\ln\gamma(\mathrm{CaSO_4}) - E^{0}_{\mathrm{PbSO_4|Pb(Hg)}}. \qquad (5) \end{aligned}$$

Table 1 gives values of E'_{T}. The standard potential of the Ag|AgCl electrode was taken as 222.4 mV (Ives & Janz 1961) and the activity of the calcium chloride reference solution was calculated by using Lietzke & Stoughton's (1962) parameters (Briggs & Lilley 1974).

A preliminary plot of E'_{T} against $m_1^{\frac{1}{2}}$ showed that the experimental results are considerably below the D.–H. limiting law.

It has been known for some considerable time that the Debye–Hückel treatment and its semi-empirical extensions are inadequate to represent the thermodynamic behaviour of electrolytes, other than those of the 1:1 charge type, in aqueous solutions at ambient temperatures and pressures. Two procedures have been used to deal with this problem. The first is that due to Bjerrum (1926) in which it is assumed that a certain fraction of ions are associated into ion-pairs at any particular concentration. The second procedure is to use an extended treatment based upon the Debye–Hückel electrostatic approach. Both of these have been investigated and applied to the present system.

Treatment of results by using the ion-pair concept

We assume that an equilibrium exists in solution between free ions and ions which are associated

$$\mathrm{CaSO_4 = Ca^{2+} + SO_4{}^{2-}}. \tag{6}$$

If the concentration of free calcium and sulphate ions is m_f then we may write the ion-association constant (K_D)

$$K_D = (m_\mathrm{f}\gamma_\mathrm{f})^2/\{(m_1 - m_\mathrm{f})\,\gamma^0\} \tag{7}$$

in which γ_f and γ^0 are the mean ionic activity coefficients of the free ions and the activity coefficient of the ion-pair respectively. It is assumed that the activity coefficient of the free ions may be represented by an equation of the extended Debye–Hückel type

$$\ln\gamma_\mathrm{f} = -\{|z_+ z_-|SI_\mathrm{f}^{\frac{1}{2}}\}/\{1 + (q/a_0)\,I_\mathrm{f}^{\frac{1}{2}}\} \tag{8}$$

in which I_f is the ionic strength of free ions

$$I_\mathrm{f} = 4m_\mathrm{f} \tag{9}$$

and the activity coefficient of the ion-pair is put equal to unity. Equations (7) and (8) contain two unknown terms K_D and q. Arbitrary values for K_D and q were chosen and for each pair of values equations (7), (8) and (9) were solved iteratively to give self-consistent values of m_f and γ_f. The apparent standard potential of the lead amalgam–lead sulphate electrode ($E^{0\prime}_{\mathrm{PbSO_4|Pb(Hg)}}$) was then calculated at each concentration by using

$$E^{0\prime}_{\mathrm{PbSO_4|Pb(Hg)}} = E^0_{\mathrm{AgCl|Ag}} - E_\mathrm{T} + \ln m_\mathrm{f}\gamma_\mathrm{f} - \tfrac{3}{2}k\ln\{4^{\frac{1}{3}}m_3\,\gamma(\mathrm{CaCl_2})\}. \tag{10}$$

The prime on the half-cell potential denotes that it will only become equal to the true value as the ionic strength approaches zero, because of inadequacies of the activity coefficient expressions.

The trend of the experimental results with ionic strength was the same as that obtained from ion-association model calculations (Lilley & Briggs 1975*a*) with a common intercept of -352.6 mV at zero ionic strength. Utilization of this allows the evaluation of K_D for chosen values of q. Examples of the results obtained are given in table 2.

Analysis of these results using the Bjerrum approach, in the same manner as that used by Brown & Prue (1955), leads to the values for the distance of closest approach (a) given in table 3. The error limits given for 'a' correspond to changes in E^0 of ± 0.2 mV. Values of q in the range $\frac{1}{2}q_B$ to q_B give an almost invariant distance of closest approach of about 0.38 nm. This is precisely the value predicted from the appropriate bond lengths (Gardner & Glueckauf 1971). The use of values for q lower than 0.38 nm give absurdly small 'a' values and $q = \frac{1}{2}q_B$ is probably the lowest value which can be sensibly used. This restriction is consistent with Guggenheim's view (1957) that small q values are unsuitable for use in the linearized D.–H. equation. (See also Lilley & Briggs 1975a.)

Comparison with the results obtained by Brown & Prue (1955) is complicated by the temperature difference between their measurements and our results. The temperature difference should not have a significant effect on the distance of closest approach but one would expect that K_D should be lower at 25 °C than at 0 °C by about $4 \times 10^{-4}\,\mathrm{mol\,kg^{-1}}$ (Pitzer 1972). The present analysis gives values of K_D and 'a' which are both higher than the corresponding values at 0 °C. The difference is not large and a standard electrode potential of -353.2 mV would give good agreement between the two sets of results. Other workers (Gardner & Glueckauf 1969, 1970; Pitzer 1972) have analysed the freezing temperature data of Brown & Prue (1955) assuming higher than pairwise association of ions. Although assumptions regarding higher association do not have a great effect at the low concentrations studied for $CaSO_4$ solutions, the results obtained are more concordant with the present analysis. Using $q = q_B$, Pitzer (1972) found $K_D = 0.0036\,\mathrm{mol\,kg^{-1}}$ and Gardner & Glueckauf (1969) using $q = (2/3)q_B$ obtained $K_D = 0.00428\,\mathrm{mol\,kg^{-1}}$, both at 0 °C.

TABLE 2. ION-PAIR DISSOCIATION CONSTANTS FOR $CaSO_4$

	$10^3K_D/(\mathrm{mol\,kg^{-1}})$		
q/nm	$E^0 = -352.6$ mV	$E^0 = -352.4$ mV	$E^0 = -352.8$ mV
0.357 ($\frac{1}{4}q_B$)	5.30	5.85	4.84
0.476 ($\frac{1}{3}q_B$)	5.01	5.50	4.60
0.714 ($\frac{1}{2}q_B$)	4.53	4.92	4.18
1.071 ($\frac{3}{4}q_B$)	4.00	4.31	3.73
1.428 (q_B)	3.64	3.90	3.41

TABLE 3. COMPARISON OF PRESENT RESULTS WITH THOSE OBTAINED FROM FREEZING TEMPERATURE MEASUREMENTS

present work (25 °C)			Brown & Prue (0 °C)		
q/nm	$\frac{10^3K_D}{\mathrm{mol\,kg^{-1}}}$	a/nm	q/nm	$\frac{10^3K_D}{\mathrm{mol\,kg^{-1}}}$	a/nm
1.428 (q_B)	3.64	0.393 ± 0.010	1.387 (q_B)	3.3	0.356
1.071 ($\frac{3}{4}q_B$)	4.00	0.381 ± 0.010			
0.714 ($\frac{1}{2}q_B$)	4.53	0.371 ± 0.009	0.694 ($\frac{1}{2}q_B$)	4.3	0.348
			0.50	5.0	0.341
0.476 ($\frac{1}{3}q_B$)	5.01	0.348 ± 0.009	0.40	5.4	0.326

A recent investigation of the association of $CaSO_4$ (Ainsworth 1973) from cells containing $CaSO_4$ and $CaCl_2$ leads to $K_D = 0.0049\,\mathrm{mol\,kg^{-1}}$ at 25 °C using $q = 0.501$ nm. A discussion of the method used and the results obtained is given elsewhere (Briggs & Lilley 1976a).

Treatment of results by using numerical solutions to the Poisson–Boltzmann equation

The most fruitful approach in the calculation of activity coefficients in dilute solutions has been *via* calculations of the mean electrostatic potential for a single fixed ion. The Poisson equation connecting the electrostatic potential at a central ion with the average distribution of surrounding charge is

$$\nabla^2\psi = \frac{-4\pi}{\epsilon}\sum_i ez_i\rho_i \exp\left[-W_i/kT\right]. \tag{11}$$

This equation is exact but several approximations to it have been used. Debye & Hückel (1923) equated $z_i e\psi$ to W_i, which is an approximation which is only valid when the charge distribution is always spherically symmetrical. Frank & Thompson (1959) showed that significant deviation from spherical symmetry was present for aqueous solutions of 1:1 electrolytes at concentrations as low as 10^{-4} mol kg^{-1}. With 2:2 electrolytes deviations from spherical symmetry occur at still lower concentration. Debye & Hückel (1923) approximated equation (11) further by linearization to give

$$\nabla^2\psi = \frac{-4\pi}{\epsilon}\sum_i \frac{e^2z_i^2}{kT}\rho_i\,\psi. \tag{12}$$

This approximation re-introduces a degree of physical self-consistency, but results in errors arising from the neglect of higher order terms. Other investigators (Müller 1927; Gronwall *et al.* 1928; Guggenheim 1957; Gardner & Glueckauf 1971) in treatments of 2:2 electrolytes have retained higher order terms in the exponential expansion, but have continued with the Debye–Hückel approximation that $W_i = z_i e\psi$. Outhwaite (1969) & Burly *et al.* (1971) have used a rather more sophisticated procedure in expressing equation (11) as

$$\nabla^2\psi = \frac{-4\pi}{\epsilon}\sum_i ez_i\rho_i\, V\exp\{-ez_i(\psi+\delta)/kT\} \tag{13}$$

in which V and δ are the excluded volume and fluctuation terms respectively (Kirkwood 1934). The deviation of V from unity is important for dilute solutions, but the fluctuation term is of significant magnitude only at the lowest concentrations used by us. The δ term may be obtained by using different closure approximations depending upon the number of fixed ions for which the potential is calculated. If a single fixed ion is considered then $\delta = 0$ and if $V = 1$ then the normal Poisson–Boltzmann (P.B.) equation results (equation (12)). Solutions to equation (13) have been obtained in which δ has been considered for two fixed ions in linearized (Outhwaite 1969) and in non-linearized (Burley *et al.* 1971, 1972) forms. These computations were performed by using both the Debye (1923) and Güntelberg (1926) charging processes. The results obtained were compared with Monte-Carlo calculations (Card & Valleau 1970) and were found to give better agreement than that obtained from the unmodified Poisson–Boltzmann equation. Self-consistency tests

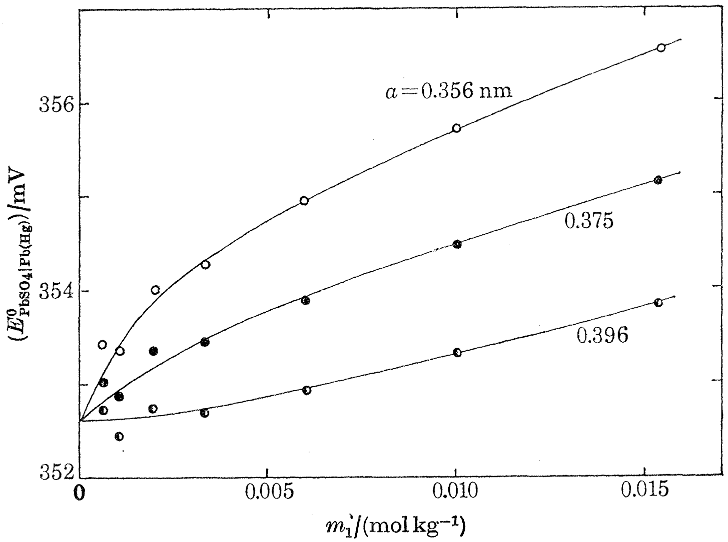

FIGURE 2. Use of modified P.–B. equation with Güntelberg charging process.

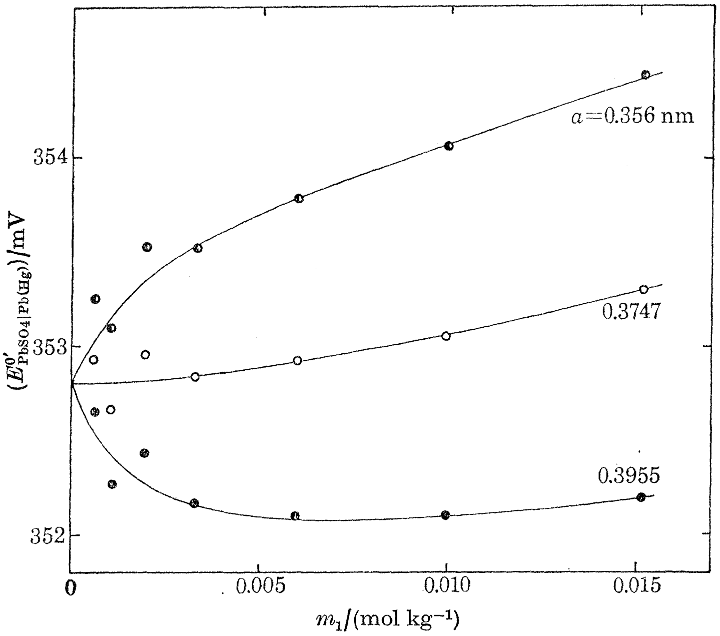

FIGURE 3. Unmodified P.–B. treatment with Güntelberg charging process.

were made by using the second moment condition (Stillinger & Lovett 1968) and by comparison of the results obtained from the Debye and Güntelberg charging processes. Both tests indicated that the modifications introduced were improvements. We have used the approach adopted by Burley *et al.* (1971, 1972) to calculate activity coefficients for 2:2 electrolytes in water at 25 °C. Calculations were

TABLE 4. MEAN MOLAL IONIC ACTIVITY COEFFICIENTS AT 25 °C

	$-\ln\gamma^{\text{elec}}$						$-\ln\gamma^{\text{exp}}$	
$\frac{10^4 m_1}{\text{mol kg}^{-1}}$	D.-H.	P.B.D.	m.P.B.D.	P.B.G.D.H.	P.B.G.K.G.	m.P.B.G.	this work	G.G.
151.8	0.8725	1.0246	1.0748	1.0689	1.0858	1.1326	1.085 ± 0.018	1.149
99.80	0.7415	0.8896	0.9271	0.9285	0.9383	0.9756	0.947 ± 0.020	0.997
59.97	0.6027	0.7399	0.7656	0.7702	0.7752	0.8029	0.790 ± 0.020	0.830
33.36	0.4695	0.5881	0.6043	0.6091	0.6113	0.6296	0.626 ± 0.019	0.656
20.03	0.3748	0.4739	0.4842	0.4891	0.4903	0.5014	0.496 ± 0.023	0.526
11.09	0.2865	0.3626	0.3684	0.3721	0.3726	0.3786	0.384 ± 0.025	0.393
6.576	0.2247	0.2819	0.2852	0.2880	0.2882	0.2914	0.286 ± 0.026	0.303

γ^{elec} is the electrostatic contribution to the activity coefficient estimated by different methods.

P.B.G.D.H. and P.B.G.K.G. denote the use of the Poisson–Boltzmann approach using the Debye–Hückel and the Kirkwood–Glueckauf approximations (see Gardner & Glueckauf 1971). The other acronyms are described in the text.

γ^{exp} is the experimental activity coefficient with G.G. indicating the Gardner & Glueckauf (1970) treatment of the osmotic coefficient results of Brown & Prue (1955).

performed by using the normal Poisson–Boltzmann equation with the Debye charging process (P.B.D.) and the modified equation (equation (13)) using the Debye charging process (m.P.B.D.) and the Güntelberg charging process (m.P.B.G.). The results of Gardner & Glueckauf (1971) were used for the normal Poisson–Boltzmann equation with a Güntelberg charging process (P.B.G.). The values chosen for the distance of closest approach were 0.356, 0.375 and 0.396 nm. The calculated activity coefficients were then incorporated in equation (5). Some of the results obtained are shown in figures 2 and 3. Smooth curves were drawn through the results obtained and although the differences between the various treatments are clearly significant, and intercept at zero concentration of $CaSO_4$ of -352.6 mV results for the m.P.B.G. m.P.B.D. and P.B.D. treatments and the slightly different value of -352.8 mV for the P.B.G. treatment. In all cases the marked non-linearity of the curves makes the precision of the intercept difficult to assess. In table 4 we compare the results obtained for the calculated activity coefficients using the above treatments for a distance of closest approach of 0.396 nm. The discrepancies between the Güntelberg and Debye charging processes, for both the unmodified and modified treatments shows that all are imperfect. A decision as to which set is best is unnecessary for our purpose since all treatments give good agreement when used to obtain values for the required standard electrode potential. The difference between the value derived using the P.B.G. treatment (-352.8 mV) and that derived from all other treatments (-352.6 mV) including the ion-pairing approach discussed above is within the estimated error of our experiments.

CONCLUSIONS

Standard potential of the $PbSO_4|Pb(Hg)$ *electrode*

The value we obtain for $E^0_{PbSO_4|Pb(Hg)}$ is -352.6 (± 0.4) mV at 25 °C. The estimated uncertainty of 0.4 mV includes contributions from the extrapolation methods used, uncertainties in the activity coefficients of $CaCl_2$ in the reference cells (Briggs & Lilley 1974*a*) and possible systematic errors. The cell

$$Pb(Hg)|PbSO_4|Na_2SO_4 . 10H_2O|Na_2SO_4(satd)|HgSO_4|Hg$$

has been investigated several times at 25 °C (Henderson & Stegman 1918; Mellon & Henderson 1920; Ishikawa & Hagisawa 1934; Harned & Hamer 1935; LaMer & Carpenter 1936) and the mean value obtained for the cell potential was 964.65 mV with a maximum difference of 0.06 mV. The cell

$$Pt|H_2|H_2SO_4|HgSO_4|Hg$$

has been investigated, and earlier work assessed, by Covington and co-workers (1965) and they estimate the standard cell potential to be 612.5 mV with an uncertainty of at least 0.3 mV. Combination of the results from the above two cells gives $E^0_{PbSO_4|Pb(Hg)} = -352.15(\pm 0.36)$ mV, where the error limits are minimum values. The agreement between this result and our value of -352.6 (± 0.4) mV is satisfactory.

Stoichiometric activity and osmotic coefficients of $CaSO_4$

Stoichiometric coefficients for calcium sulphate were calculated from equation (3) by using $E^0_{PbSO_4|Pb(Hg)} = -352.6\,mV$. The results obtained are given in table 4. The error limits shown correspond to an uncertainty of $\pm 0.4\,mV$ in the standard electrode potential. Values of the activity coefficients obtained by Gardner & Glueckauf (1970) were interpolated as a function of temperature and concentration from table 3 of their paper and are included in table 4. The results obtained by Pitzer (1972) using a similar analysis to that of Gardner & Glueckauf (1970) are almost identical to these latter results at low concentrations but are slightly higher at the two highest concentrations.

Comparison of the present results with those obtained earlier (Gardner & Glueckauf 1970), shows that at the two lowest concentrations, the results agree within our estimated experimental error. At higher concentrations the two sets of results deviate, but inclusion of error limits on Glueckauf's results would probably enable the differences to be reconciled.

Appropriate Gibbs–Duhem integrations of the activity coefficients were performed (Briggs 1973) and osmotic coefficients obtained. Those calculated agree, within experimental error, with the results of Brown & Prue (1955).

Thermodynamic solubility product of gypsum

The thermodynamic solubility product for the dissolution process

$$CaSO_4.2H_2O\text{ (solid)} = Ca^{2+}(aq.) + SO_4{}^{2-}(aq.) + 2H_2O$$

is defined by

$$K_{sp} = a(Ca^{2+})\,a(SO_4{}^{2-})\,a^2(H_2O) = m_s\gamma_s^2 a_s^2(H_2O), \tag{19}$$

where m_s is the solubility of calcium sulphate in water and the subscript s on the activity coefficient and the water activity indicates these are the values at the salt solubility limit. Substituting into equation (19) the component terms $m_s = 1.518 \times 10^{-2}\,mol\,kg^{-1}$ (Briggs 1973) $\gamma_s = 0.338(\pm 0.006)$ and

$$a_s(H_2O) \simeq \exp -0.036 m_s \phi_s = 0.9995 \text{ gives } K_{sp} = 2.63(\pm 0.09) \times 10^{-5}\,mol^2\,kg^{-2}.$$

We believe that the solubility is accurate, but any error in the measured solubility is irrelevant since its prior use in calculating γ_s exactly compensates for any error. Gardner & Glueckauf (1970, 1971) and Glueckauf (1969) have estimated K_{sp} using less direct approaches than that given here based upon the osmotic coefficient data of Brown & Prue (1955), and the values obtained were 2.49×10^{-5}, 2.26×10^{-5} and $2.23 \times 10^{-5}\,mol^2\,kg^{-2}$. Estimates of the errors on these results were not given.

Further discussions of the thermodynamic behaviour of $CaSO_4$ have been and will be given elsewhere (Briggs & Lilley 1976*a*, *b*; Glueckauf & Lilley 1976).

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