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Reviews

Critical Evaluation of the Thermodynamic Properties of Aqueous Calcium Chloride. 1. Osmotic and Activity Coefficients of 0−10.77 mol·kg^{-1} Aqueous Calcium Chloride Solutions at 298.15 K and Correlation with Extended Pitzer Ion-Interaction Models

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Isopiestic vapor-pressure measurements were performed at 298.15 K for $CaCl_2$(aq) solutions at 66 molalities from (4.3235 to 10.253) mol·kg^{-1}, using H_2SO_4(aq) as the reference standard, with emphasis given to the accurate characterization of the osmotic coefficients near and above saturation. Published isopiestic molalities, direct vapor pressures, and emf results for $CaCl_2$(aq) have been critically reevaluated and recalculated in an internally consistent manner. This critically-assessed database was used to evaluate the parameters of Pitzer's equations and various extended forms at 298.15 K and 0.1 MPa. Neither the standard equations nor empirically extended versions were able to represent the thermodynamic results over more than part of the molality range without large cyclic systematic deviations. It was possible, however, to obtain essentially quantitative agreement between experiment and model over the full molality range if (1) the presence of $CaCl^+$(aq) ion pairs was included explicitly and (2) higher-order virial terms were included. One such quantitative model is presented here in detail. Without these higher-order virial terms the same model is able to represent the $\phi(CaCl_2)$ fairly well only to about 8 mol·kg^{-1}. The osmotic coefficient of $CaCl_2$(aq) goes through a minimum around 0.11 mol·kg^{-1}, which is followed by a regular increase with molality to a broad maximum in the supersaturated molality region where $\phi(CaCl_2)$ is nearly constant at 3.169−3.173 from about (8.5 to 9.5) mol·kg^{-1}. It then decreases slightly by about 0.3% at higher molalities.

Contents

1. Introduction

Seawater and most natural groundwaters contain low concentrations of Ca^{2+} ions along with much higher concentrations of Cl^- ions [91-cle/whi]. In many of these waters the concentration of Ca^{2+} is limited by the presence of SO_4^{2-} ions, with (depending on temperature) gypsum, $CaSO_4·2H_2O$(cr), or anhydrite, $CaSO_4$(cr), being the solubility limiting phase. However, a number of highly-saline sulfate-deficient natural brines are known that contain relatively high concentrations of Na^+, Ca^{2+}, and Cl^- ions, along with lesser amounts of other ions including Mg^{2+}, K^+, HCO_3^-, SO_4^{2-}, and Br^- [90-har, 94-bot/gre]. Some of these brines contain the equivalent of several mass percent of $CaCl_2$. Generally, the mass fraction of Na is several times larger than that of Ca, although in some brines the relative amounts are reversed.

Hypersaline chloride brines from deep mines and deep bore holes [87-fra/fri, 87-guh/kan, 87-vov] are known that contain from 22 to 127 g of calcium per liter, which is equivalent to molar concentrations of $CaCl_2$(aq) of (0.55 to 3.2) mol·dm^{-3}. Fluid inclusions in minerals such as in dolomites and sphalerites also may contain considerable concentrations of $CaCl_2$ [87-hay/kes]. This field has been surveyed by Bischoff et al. [96-bis/ros] who reference numerous examples of other highly-concentrated Ca-rich brines, including one type that is so concentrated that it is equivalent to fused antarcticite, $CaCl_2·6H_2O$.

In 1945 Stokes [45-sto] suggested that solutions of $CaCl_2$(aq) would be suitable as an isopiestic reference standard at 298.15 K since $CaCl_2$ is widely available in fairly high purity and is quite soluble in water, and its solutions

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readily supersaturate. These $CaCl_2(aq)$ solutions can be used for the determination of water activities down to $a_w \approx 0.17$. This is considerably below the lower limits of a_w for the reference standards NaCl(aq) and KCl(aq) of 0.75 and 0.84, respectively [65-rob/sto]. The other major isopiestic reference standard used at low water activities/ high molalities is $H_2SO_4(aq)$, which is thermodynamically well characterized down to about $a_w = 0.026$ [65-rob/sto, 76-rar/hab, 91-rar/pla, 95-cle/bri]. However, $H_2SO_4(aq)$ is too corrosive to be used in most of the isopiestic sample cups available for the early studies, which were usually made of silver or gold-plated silver. Stokes therefore suggested $CaCl_2(aq)$ as a less-corrosive alternative reference standard for isopiestic studies. This application requires that the osmotic and activity coefficients of $CaCl_2(aq)$ be known with high accuracy.

Thermodynamic activity data for $CaCl_2(aq)$ at 298.15 K have been reviewed critically by Rard et al. [77-rar/hab] and Staples and Nuttall [77-sta/nut]. Their analyses indicate that some freezing temperature depression and emf measurements are available that accurately characterize the activities of $CaCl_2(aq)$ at low molalities. However, the majority of published emf data appear to be quite inaccurate, especially those involving a calcium amalgam electrode. Likewise, very few of the direct vapor pressure measurements for $CaCl_2(aq)$ are accurate. Thus the most reliable and extensive thermodynamic activity data above about 0.1 $mol \cdot kg^{-1}$ are from isopiestic measurements relative to the other isopiestic standards. As discussed by Rard and Platford [91-rar/pla], this dependence of the water activities on isopiestic comparison to the other reference standards makes $CaCl_2(aq)$ a secondary rather than a primary reference standard.

Graphically smoothed values of the osmotic coefficients ϕ of $CaCl_2(aq)$ at 298.15 K and round molalities were provided by Stokes [45-sto] up to 10.5 $mol \cdot kg^{-1}$, which, with only minor modification, formed the basis of the tabulated values of Robinson and Stokes [65-rob/sto]. Later reviews by Rard et al. [77-rar/hab] and Staples and Nuttall [77-sta/nut] incorporated thermodynamic data published after Stokes' original study. There is a maximum difference in $\phi(CaCl_2)$ between these evaluations of $\approx 0.6\%$, with better agreement over most of the molality range.

Attempts have been made to provide reliable thermodynamic models for $CaCl_2(aq)$ from 273.15 to 373.15 K. Ananthaswamy and Atkinson [85-ana/atk] anchored their model to the recommended results of Rard et al. [77-rar/hab] at 298.15 K, and Smith-Magowan et al. [87-smi/gar] included the evaluated database of Staples and Nuttall [77-sta/nut] in their model. In spite of the reasonably good agreement of these two models at 298.15 K, there are substantial differences at the upper and lower temperature limits. For example, at 7.0 $mol \cdot kg^{-1}$ and 373.15 K, Ananthaswamy and Atkinson report $\phi(CaCl_2) = 2.268$ whereas Smith-Magowan et al. report $\phi(CaCl_2) = 2.417$, which is a difference of 6.5%. This is an unacceptably large uncertainty for a reference standard. Pitzer and Shi [93-pit/shi] have compared these two models graphically at (298.15 to 363.15) K. Rard and Archer [95-rar/arc] used the isopiestic equilibrium molalities of Voigt et al. at 373.4_5 K [90-voi/dit], for solutions of NaBr(aq) equilibrated against $CaCl_2(aq)$, to back-calculate $\phi(CaCl_2)$ at this temperature using their own extended Pitzer model to calculate $\phi(NaBr)$. The derived $\phi(CaCl_2)$ agree much better with those calculated from the model of Ananthaswamy and Atkinson than with those from the model of Smith-Magowan et al. at higher molalities, although there are some significant differences.

Brendler and Voigt [94-bre/voi] reported that osmotic coefficients for several electrolytes, including $CaCl_2(aq)$, from their isopiestic measurements using $MgCl_2(aq)$ as the reference standard, were not consistent with those reported by the high-temperature group at Oak Ridge National Laboratory using NaCl(aq) as the reference standard. However, Holmes et al. [94-hol/bus] have shown that these discrepancies are largely eliminated when this calculation is reversed and the high-temperature isopiestic results from their two laboratories are compared on a consistent basis using NaCl(aq) as reference standard directly, or are compared indirectly through use of LiCl(aq) and KCl(aq) osmotic coefficients referenced through $\phi(NaCl)$. This implies that the reported discrepancies are largely an artifact from the use of inconsistent reference standard osmotic coefficients and not from errors in the isopiestic measurements.

The equations of Pitzer [91-pit] are among the most widely used for representing the thermodynamic properties of aqueous solutions of single electrolytes and their mixtures to high ionic strengths. Harvie and Weare [80-har/wea] showed that Pitzer's equations could also be used to model reliably the solubilities of brine salt mixtures and to predict correctly the precipitation sequences as water is evaporated from their solutions. This has led to the extensive use of Pitzer's equations to model the solubilities of numerous natural brines and other mixtures of soluble inorganic electrolytes [82-har/eug, 84-har/mol, 86-fel/wea, 88-mol, 90-spe/mol, 91-pab/pit].

Pitzer and Mayorga [73-pit/may] provided parameters for Pitzer's equations for the osmotic and activity coefficients of $CaCl_2(aq)$ at 298.15 K, which were based on fitting of experimental data only to about 2.5 $mol \cdot kg^{-1}$. Phutela and Pitzer [83-phu/pit] later reevaluated the parameters using experimental activities up to 4.457 $mol \cdot kg^{-1}$ but noted that increasing the molality range being fitted resulted in a considerable degradation in the quality of the fit to $\phi(CaCl_2)$ below 1 $mol \cdot kg^{-1}$, which implies the predicted activity coefficients are significantly less accurate. Harvie and Weare [80-har/wea] and Ananthaswamy and Atkinson [82-ana/atk] have also pointed out that the model of Pitzer and Mayorga yields large errors when extrapolated to calculate osmotic or activity coefficients at higher molalities. In contrast, Phutela and Pitzer [83-phu/pit] found that thermodynamic data for $MgCl_2(aq)$ could be represented with the same type of Pitzer equation up to 4 $mol \cdot kg^{-1}$ without such difficulties and that extrapolations of these equations to higher molalities give much better agreement between experiment and model for $\phi(MgCl_2)$ than for $\phi(CaCl_2)$.

Several attempts have been made to extend the range of validity of the Pitzer equation fits for $CaCl_2(aq)$ by inclusion of higher-order virial terms containing cubic, quartic, etc., powers of the stoichiometric molality of $CaCl_2(aq)$. This approach was first applied by Rogers [82-rog] at 298.15 K, later by others to 373.15 K [85-ana/atk, 87-smi/gar], and more recently, in a modified form, to about 523 K [94-pit/oak]. The most comprehensive of the Pitzer-equation-based models is that of Holmes et al. [94-hol/bus]. Although Holmes et al. did not use higher-order virial terms, they included a $\beta^{(2)}_{MX}$ term in Pitzer's equation that is equivalent to assuming the presence of moderate amounts of complex formation. This $\beta^{(2)}_{MX}$ was not a least-squares parameter derived from their global model fits but was evaluated from the formation constants for $CaCl^+(aq)$ reported by Frantz and Marshall [82-fra/mar] from conductivity measurements at high temperatures and pressures. Their model [94-hol/bus] is applicable to quite high temperatures and pressures but is limited to molalities below 4.6 mol·kg^{-1}.

Clegg et al. [92-cle/pit] have refitted the Staples and Nuttall [77-sta/nut] database for $CaCl_2$(aq) at 298.15 K with a mole fraction composition based model. That model exhibited systematic cyclic deviations about the experimental data when fitted to the full molality range.

There is an obvious need for an improved model to represent the thermodynamic properties of $CaCl_2$(aq) quantitatively to the highest molalities and as a function of temperature. As indicated by the extensive reference list of published thermodynamic properties given by Holmes et al. [94-hol/bus], several additional heat capacity, enthalpy of dilution, and isopiestic studies have been published since the earlier reviews [65-rob/sto, 77-rar/hab, 77-sta/nut, 85-ana/atk, 87-smi/gar]. These, together with earlier results and the new isopiestic results reported here, should provide a much more accurate database to constrain such modeling efforts.

Our original goals were (1) to provide more accurate isopiestic data for $CaCl_2$(aq) to supersaturated molalities at 298.15 K and (2) to obtain a model extension of Pitzer's equations that would accurately represent the available experimental thermodynamic data for $CaCl_2$(aq) over the full molality range and from the freezing temperatures of the solutions to about 383 K. New isopiestic results are presented here for $CaCl_2$(aq) from (4.3235 to 10.253) mol·kg^{-1}. During the course of the modeling calculations, however, it became clear that it is necessary to consider explicitly the formation of ion pairs in these solutions in order to obtain a quantitative thermodynamic model above about 4.5 mol·kg^{-1}. Unfortunately, the formation constant $K(CaCl^+)$ is very poorly known in this temperature region, and the reported values of $K(CaCl^+)$ below 383 K appear to be quite uncertain. Consequently, we have limited the present report to an application of Pitzer's equations and extended models for the osmotic and activity coefficients of $CaCl_2$(aq) at 298.15 K. A model equation is presented here that represents the more accurate osmotic and activity coefficients to near experimental accuracy, even in the supersaturated molality region. We will consider the temperature dependence of these equations at some later time.

2. Experimental Section

The isopiestic vapor pressure measurements were performed at Lawrence Livermore National Laboratory at the temperature (298.15 ± 0.00$_5$) K (IPTS-68) in one of our stainless-steel isopiestic chambers with sample cups of tantalum metal [85-rar]. A detailed description of this experimental method is given by Rard and Platford [91-rar/pla]. Air was removed, with a vacuum pump, from the isopiestic chambers in four to six stages prior to starting each isopiestic equilibration. Samples of a solution of H_2SO_4(aq) were used as the isopiestic reference standard.

We modified the copper block of this isopiestic chamber part way through the series 1 experiments, after the first 24 equilibrations had been performed. A fanlike device was added to the center of the top of the copper heat-transfer block that contains the sample cups; this provides some stirring of the vapor phase to assist in the transport of water vapor between the various samples as they are equilibrated. See the description by Rard [96-rar, 97-rar] for more details. These "fans" are a modified version of a device used in Albright's laboratory as described by Mitchell et al. [92-mit/but].

Solution samples were allowed to equilibrate in the isopiestic chamber for periods ranging from (6 to 24) days, and consistent results were obtained that did not depend on the equilibration time. Molalities up to 10.253 mol·kg^{-1} were investigated successfully. On the basis of reported solubilities [32-hep, 33-bas/bar, 37-var/mis, 58-lin, 87-smi/gar], the solubility of $CaCl_2·6H_2O$(cr) at 298.15 K falls somewhere in the range (7.278 to 7.462) mol·kg^{-1}, which indicates that our measurements extend nearly 3 mol·kg^{-1} into the supersaturated molality region. We did one continuous series of measurements (part of series 1) lasting almost five months at supersaturated molalities without encountering crystallization. Although molalities of $CaCl_2$(aq) as high as 10.253 mol·kg^{-1} were achieved, a second such attempt to go above 10 mol·kg^{-1} (series 2 experiments) resulted in one of the $CaCl_2$ samples becoming completely solid.

In the majority of the isopiestic experiments, the molalities of the solutions were increased from those of the preceding experiment by adding an extra sample cup containing a few drops of concentrated H_2SO_4(aq). This H_2SO_4(aq) acted as a "trap" for the water. However, in several experiments the direction of the concentration changes was reversed by diluting the samples with H_2O(l). This was done to recheck the consistency with earlier measurements. In all cases agreement is excellent. Furthermore, the isopiestic equilibrium molality ratio $m(H_2SO_4)/m(CaCl_2)$ for the series 1 and 2 experiments agrees to within about 0.12%, except for one of the series 2 experiments with $m(CaCl_2) = 8.9672$ mol·kg^{-1} where the discrepancy is somewhat larger. The molality ratio $m(H_2SO_4)/m(CaCl_2)$ for that one experiment is about 0.22% above a smoothed curve through the other results.

Water for the solution preparations and for diluting samples was purified by ion exchange followed by distillation. All apparent solution masses ("weights") were converted to masses, as were those of $CaSO_4$(s), which was used as the gravimetric weighing form for the molality analyses of the $CaCl_2$(aq) stock solution. Assumed values of the molar masses were 98.074 g·mol^{-1} for H_2SO_4, 110.986 g·mol^{-1} for $CaCl_2$, and 136.138 g·mol^{-1} for $CaSO_4$.

The stock solution of H_2SO_4(aq) was prepared by mass dilution of a concentrated stock solution with purified water. Its molality was determined to be (0.999 32 ± 0.000 59) mol·kg^{-1} by mass titration of four samples with standardized NaOH(aq) using phenolphthalein as the endpoint indicator. This value agrees well with a calculated molality of 0.999 42 mol·kg^{-1} obtained from a similar analysis of the concentrated stock solution and the mass dilution results. Here and below, the reported stock solution molality uncertainties are estimated standard deviations. The mean of these two analyses, 0.999 37 mol·kg^{-1}, was accepted.

The $CaCl_2$(aq) stock solution was prepared by reaction of Mallinckrodt Primary Standard $CaCO_3$(s) and HCl(aq). This solution was filtered and then adjusted to its equivalence pH, which had been determined previously by potentiometric pH titration. Concentrations of impurities in this $CaCO_3$(s) were determined by direct current arc optical emission spectroscopy, and the detailed results were reported by Rard and Archer [95-rar/arc]. On the basis of that analysis, the $CaCl_2$ is actually equivalent to a mixture of 99.885 mol % $CaCl_2$, 0.057 mol % $SrCl_2$, 0.013 mol % NaCl, 0.012 mol % $MgCl_2$, 0.007 mol % each of $BaCl_2$, SiO_2, and $AlCl_3$, and 0.012 mol % of other impurities. Because the main impurity ($SrCl_2$) has nearly identical water activities as $CaCl_2$(aq) solutions, its presence should have an insignificant effect on the osmotic coefficient determinations.

Table 1. Isopiestic Molalities of Aqueous H_2SO_4 and $CaCl_2$ Solutions and Osmotic Coefficients of $CaCl_2$ at 298.15 K (IPTS-68)[a]

$m(H_2SO_4)/(mol\cdot kg^{-1})$	$m(CaCl_2)/(mol\cdot kg^{-1})$	$\phi(CaCl_2)$	$m(H_2SO_4)/(mol\cdot kg^{-1})$	$m(CaCl_2)/(mol\cdot kg^{-1})$	$\phi(CaCl_2)$
Series 1					
6.8598 ± 0.0027	4.4922 ± 0.0006	2.3781	11.695 ± 0.006	7.5334 ± 0.0014	3.1277
6.9374 ± 0.0022	4.5364 ± 0.0004	2.3965	11.944 ± 0.002	7.7242 ± 0.0019	3.1404
7.1689 ± 0.0028	4.6706 ± 0.0001	2.4492	12.212 ± 0.003	7.9388 ± 0.0004	3.1499
7.3671 ± 0.0029	4.7849 ± 0.0001	2.4936	12.474 ± 0.008	8.1459 ± 0.0024	3.1598
7.4836 ± 0.0032	4.8525 ± 0.0001	2.5190	12.646 ± 0.005	8.2890 ± 0.0028	3.1633
7.7358 ± 0.0027	4.9973 ± 0.0011	2.5737	12.785 ± 0.006	8.4060 ± 0.0011	3.1656
8.0121 ± 0.0030	5.1555 ± 0.0001	2.6321	12.962 ± 0.007	8.5552 ± 0.0026	3.1684
8.2703 ± 0.0028	5.3049 ± 0.0011	2.6842	13.153 ± 0.006	8.7236 ± 0.0013	3.1686
6.5693 ± 0.0019	4.3235 ± 0.0001	2.3097	13.345 ± 0.010	8.8938 ± 0.0003	3.1684
7.8648 ± 0.0014	5.0704 ± 0.0003	2.6016	13.493 ± 0.009	9.0238 ± 0.0041	3.1688
8.1880 ± 0.0037	5.2546 ± 0.0004	2.6691	13.659 ± 0.003	9.1705 ± 0.0067	3.1688
8.5605 ± 0.0014	5.4715 ± 0.0005	2.7415	13.908 ± 0.000	9.3927 ± 0.0063	3.1682
8.8232 ± 0.0017	5.6264 ± 0.0012	2.7895	14.053 ± 0.002	9.5340 ± 0.0022	3.1639
9.1082 ± 0.0041	5.7963 ± 0.0014	2.8390	14.109 ± 0.009	9.5732 ± 0.0022	3.1673
9.3781 ± 0.0046	5.9597 ± 0.0007	2.8830	14.407 ± 0.003	9.8501 ± 0.0023	3.1630
9.5877 ± 0.0017	6.0878 ± 0.0009	2.9155	14.539 ± 0.010	9.9742 ± 0.0009	3.1608
9.7745 ± 0.0006	6.2049 ± 0.0008	2.9423	14.649 ± 0.002	10.089 ± 0.000	3.1554
9.8263 ± 0.0033	6.2388 ± 0.0023	2.9489	14.845 ± 0.008	10.253 ± 0.000[b]	3.1584
10.053 ± 0.002	6.3800 ± 0.0009	2.9807	10.358 ± 0.000	6.5868 ± 0.0004	3.0142
10.266 ± 0.000	6.5198 ± 0.0002	3.0064	10.589 ± 0.002	6.7396 ± 0.0018	3.0404
10.461 ± 0.003	6.6518 ± 0.0011	3.0274	10.545 ± 0.002	6.7089 ± 0.0009	3.0362
10.676 ± 0.004	6.7987 ± 0.0014	3.0493	10.766 ± 0.001	6.8604 ± 0.0013	3.0581
10.907 ± 0.004	6.9544 ± 0.0011	3.0729	10.967 ± 0.000	7.0002 ± 0.0000	3.0766
11.058 ± 0.004[c]	7.0626 ± 0.0018[c]	3.0851	9.8016 ± 0.0028	6.2219 ± 0.0022	2.9461
11.250 ± 0.004	7.2053 ± 0.0000	3.0981	9.8600 ± 0.0015	6.2599 ± 0.0010	2.9537
11.407 ± 0.008	7.3157 ± 0.0019	3.1110	8.7250 ± 0.0028	5.5695 ± 0.0002	2.7712
Series 2					
9.8179 ± 0.0029	6.2348 ± 0.0008	2.9471	12.462 ± 0.002	8.1357 ± 0.0021	3.1596
9.8754 ± 0.0008	6.2719 ± 0.0007	2.9547	12.989 ± 0.002	8.5791 ± 0.0016	3.1684
8.7372 ± 0.0020	5.5801 ± 0.0006	2.7718	13.454 ± 0.007	8.9672 ± 0.0006	3.1766
9.4096 ± 0.0014	5.9824 ± 0.0004	2.8863	13.930 ± 0.005	9.4073 ± 0.0008	3.1698
10.674 ± 0.002	6.7958 ± 0.0004	3.0498	14.413 ± 0.013	9.8471 ± 0.0030	3.1657
11.475 ± 0.001	7.3718 ± 0.0016	3.1130	14.388 ± 0.006	9.8227[d]	3.1664_5
$11.975_5 \pm 0.003$	7.7527 ± 0.0009	3.1402	7.9002 ± 0.0006	5.0919 ± 0.0012	2.6085

[a] Reported molality pairs are those of $CaCl_2(aq)$ and $H_2SO_4(aq)$ in isopiestic equilibrium. With one exception, the reported molalities are the average from duplicate samples. Osmotic coefficients of the $H_2SO_4(aq)$ reference standard solutions were calculated with the equation and parameters of Rard et al. [76-rar/hab] for molalities >6.1 mol·kg^{-1} and of Clegg et al. [94-cle/rar] for those ≤ 6.1 mol·kg^{-1}. Results for each series are reported in the actual order that they were measured, starting with the three left-hand columns from top to bottom, and followed by the three right-hand columns from top to bottom. Different samples of each stock solution were used for each series. [b] These two samples of supersaturated $CaCl_2(aq)$ were liquid when removed from the isopiestic chamber for weighing, but both became completely solid after being cooled to the laboratory temperature of ≈292 K. The $CaCl_2$ samples were redissolved before the next equilibration was started. [c] After this equilibration was complete, the copper heat-transfer block was modified by addition of a fanlike device to provide some stirring of the vapor phase as the chamber was rocked back and forth during the isopiestic equilibrations. It was present during the remaining equilibrations of the first series and for all of the second series of equilibrations. [d] This molality is for a single sample because the other $CaCl_2$ sample solidified during this equilibration; the solid sample was redissolved before the next equilibration was started.

The molality of the $CaCl_2(aq)$ stock solution was determined three separate times by conversion of samples to anhydrous $CaSO_4$. For these molality analyses, samples of the stock solution were weighed directly into three empty but previously weighed porcelain crucibles. Equal amounts of a slight excess of ≈2.5 mol·dm^{-3} $H_2SO_4(aq)$ were then added to each of these crucibles and to an otherwise empty tare crucible. The four crucibles were placed on a hot plate and heated gradually until evaporation of H_2O and HCl was complete and fuming of SO_3 had commenced. They were then transferred to a preheated box furnace, and the temperature was increased gradually until after fuming ceased. The following day the crucibles were removed from the furnace, cooled for 1 h in a desiccator, weighed, and returned to the furnace. Numerous replicate weighings were done in the same manner on different days at this same temperature and at several other temperatures ranging from (673 to 973) K. There was no significant variation of the calculated molality with the furnace temperature.

Results from the three molality analyses of the $CaCl_2$(aq) stock solution are: $(6.6068 \pm 0.001\,8_5)$ mol·kg^{-1} (November 1990−January 1991), (6.6058 ± 0.0017) mol·kg^{-1} (June−July 1991), and (6.6068 ± 0.0029) mol·kg^{-1} (October−December 1994). The statistically-weighted mean of these three analyses, (6.6063 ± 0.0011) mol·kg^{-1}, was accepted.

Table 1 contains a listing of the experimental isopiestic molalities of $CaCl_2(aq)$ and of the $H_2SO_4(aq)$ reference standard solutions. Reported values are the mean molalities for duplicate samples, along with the deviation of the individual molalities from their corresponding average. The majority of deviations are 0.04% or less. However, there were a few experiments where the deviations were larger, ranging up to 0.073% for $CaCl_2(aq)$ and up to 0.090% for $H_2SO_4(aq)$. Osmotic coefficients of the $CaCl_2(aq)$ solutions were calculated from the isopiestic molalities and the osmotic coefficients ϕ of $H_2SO_4(aq)$. These $\phi(H_2SO_4)$ were calculated with the equation and parameters of Rard et al. [76-rar/hab] for molalities > 6.1 mol·kg^{-1} and those of Clegg et al. [94-cle/rar] for ≤ 6.1 mol·kg^{-1}. This table contains the results of 66 experiments with $CaCl_2(aq)$ molalities ranging from (4.3235 to 10.253) mol·kg^{-1}. An additional 41 experiments were reported elsewhere [95-rar/arc] for $CaCl_2(aq)$ molalities ranging from (2.7682 to 4.4579) mol·kg^{-1}, determined with samples of the same stock solutions as used here. Taken together, these 107 data points constitute a thorough reinvestigation.

3. Critical Reanalysis of Literature Data

3.1. General Considerations of Corrections. Thermodynamic data considered in this review were published between 1902 and 1995. During this period there have been numerous minor revisions to the molar masses of the elements (including a change from the use of the normal isotopic abundance of oxygen to the use of carbon 12 to define the mole) and to the international temperature scales, redefinitions and refinement of some units and fundamental constants, and improvements in the accuracy of the properties of pure water. In this section we consider the nature and magnitude of many of the corrections that must be applied to earlier data to bring them into conformity with current values and standards.

Before any attempt was made to model these thermodynamic properties, all of the thermodynamic data were recalculated *when necessary and to the extent possible* to bring them into conformity with accepted modern values of these fundamental quantities. Unfortunately, in many cases, inadequate information was presented to allow the recalculations to be made rigorously (e.g., molar masses are rarely reported) or an "educated guess" had to be made as to what values may have been used. It is commonplace for scientists to continue to use older molar masses or temperature scales for many years after they are superseded, but the publications frequently do not report which values were actually used.

Numerical values of the molalities and molarities obviously depend on the molar mass assumed for $CaCl_2$. However, to correct properly the reported molalities or molarities requires that the method used to analyze the concentration of the stock solution also be reported, since similar corrections are required there also. The most commonly used gravimetric weighing techniques for analyzing solutions of $CaCl_2$(aq) involve precipitation of AgCl(s) or $CaSO_4$(s). However, in a few cases, dehydration, precipitation of the oxalate CaC_2O_4(s), or mass titration with EDTA were used. Between 1925 and the present, the molar masses of $CaCl_2$, AgCl, $CaSO_4$, etc., have varied by about 0.01% on the average. Thus, it was only necessary to recalculate the reported molarities or molalities if the concentrations of $CaCl_2$ were reported to five or more figures, and only if the method for analyzing the concentration was reported and the corresponding thermodynamic measurements appeared to be precise enough to warrant this change. In very few cases was this correction needed.

Rossini [56-ros, 74-ros] and Stimson [55-sti] have discussed the changes in the value of the conversion factor for calorie to joule, which is now fixed at 4.1840 $J\cdot cal^{-1}$. In the past this conversion factor has varied from 4.185 to 4.186 05 (international J)$\cdot$(international cal)$^{-1}$ to 4.1867 or 4.1868 J$\cdot$(international cal)$^{-1}$. In addition, in the United States from about 1930 to about 1948 the "dry" calorie was in common use with 4.1833 (international J)$\cdot$("dry" cal)$^{-1}$. Furthermore, calorimeters were sometimes calibrated with water, and values for the heat capacity of water have changed with time because of these redefinitions of the conversion factor and because of refinements in the experimental measurements for water. Older calorimetric data were corrected to the modern values of these quantities. However, in some cases where insufficient experimental information was reported, it was necessary to make an "educated guess" as to what value was used.

Although we have already reanalyzed the available calorimetric data for $CaCl_2$(aq) in a consistent manner, they will not be discussed in the present report, which is limited to a comparison of Pitzer-equation-based models for osmotic and activity coefficients at 298.15 K. The calorimetric data will be discussed in a second report in which the temperature dependences of the Pitzer parameters are determined. Similiarly, the calculation of osmotic coefficients from freezing temperature depression measurements [02-jon/get, 07-jon/pea, 58-lin, 60-tim, 75-gib/fon, 90-oak/bod] will be reported at that time.

Most of the thermodynamic data for $CaCl_2$(aq) were measured when the international temperature scale of 1927 (ITS-27) or the international practical temperature scales of 1948 (IPTS-48) and 1968 (IPTS-68) were in use. Below 630 °C the ITS-27 and IPTS-48 temperature scales are identical. A few of the studies were done prior to the to the ITS-27 scale; their temperatures presumably refer to the normal hydrogen scale of 1887, which is not as well defined as the more recent ones. The IPTS-48 and IPTS-68 temperature scales differ by 0.008_5 K at 298.15 K and by $0.000 \le \delta T \le 0.011$ K between 273 and 383 K [92-gol/wei].

Most of the thermodynamic properties being reviewed, such as emfs or heat capacities, are not sufficiently sensitive functions of temperature or are not known precisely enough for corrections to be required for the minor differences between temperature scales. However, the calculation of osmotic coefficients from vapor pressures requires that both the vapor pressure of the solution and of pure water refer to the same temperature scale, since any inconsistency can yield significant errors, especially at low molalities. The absolute value of the error due to an inconsistent choice of temperature scale for pure water is given by

$$|\delta(m\phi)| = (m_w/\nu) \ln\{P_w^\circ(\text{IPTS-68})/P_w^\circ(\text{IPTS-48})\} \qquad (1)$$

where m is the molality of $CaCl_2$(aq), $m_w = (1000\ g\cdot kg^{-1}/18.0153\ g\cdot mol^{-1}) = 55.5084\ mol\cdot kg^{-1}$ is the molality of water in the solution, $\nu = 3$ is the stoichiometric ionization number for $CaCl_2$, and P_w° is the vapor pressure of pure water. Using the vapor pressures for water for these two temperature scales as tabulated by Wexler and Greenspan [71-wex/gre] gives a value of $|\delta(m\phi)|$ equal to 0 at 273.15 K, 0.0095 at (298.15 and 323.15) K, 0.0054_5 at 348.15 K, and 0 at 373.15 K. Clearly $\delta\phi$ is quite significant at the temperatures of interest for this review, and it increases as the molality decreases since it depends on $1/m$.

3.2. Isopiestic Data. Numerous isopiestic vapor-pressure studies have been reported for $CaCl_2$(aq) relative to a variety of other reference standards, and they constitute the largest body of data that characterize the thermodynamic activities of these solutions. The most important issues to be considered here are the accuracy and precision of the individual data sets, the accuracy and consistency of the osmotic coefficients of the other reference standards, and the recalculation and correction of earlier published isopiestic results to bring them into conformity with the best current evaluations for the osmotic coefficients of the other reference standards.

Table 2 contains a summary of all of the isopiestic studies which we are aware of that contain equilibrium molalities which can be used to derive osmotic coefficients for $CaCl_2$(aq) solutions, and involve another reference standard or some other binary solution whose osmotic coefficients are sufficiently well characterized to serve as a provisional standard. Listed are the molality range of $CaCl_2$(aq) investigated, the number of experimental data points, and the electrolyte solution(s) used as isopiestic reference standard(s).

Some of these studies had the explicit goal of characterizing $\phi(CaCl_2)$ or of intercomparing several of the reference standards [40-rob, 45-sto, 71-chi/pla, 73-pla, 77-rar/spe, 78-

Table 2. Summary of Available Isopiestic Results for Aqueous $CaCl_2$ Solutions in Chronological Order

molality range/ (mol·kg^{-1})	T/K	no. of points	reference standard	relative weight^a	ref
0.0887−2.202	298.15	29	KCl	0.0	40-rob
0.0908−2.981	298.15	29	NaCl	1.0	45-sto
2.951−10.771	298.15	42	H_2SO_4	1.0 (4)	45-sto
1.7850	298.15	1^b	KCl	1.0	60-sae/spe
2.5579−2.8284	298.15	3	NaCl	0.0	62-shu/mak
1.776−2.959	298.15	5	NaCl	0.0	65-kir/luk
1.057−1.988	298.15	6	KCl	1.0	66-kir/luk
0.3702−2.8500	298.15	16	NaCl	1.0	66-rob/bow
1.254−2.069^c	298.15	4	NaCl	0.25	67-kir/luk
1.254−2.069^c	298.15	4	KCl	0.25 (1)	67-kir/luk
0.4948−2.1195	298.15	9	KCl	1.0	68-rob/cov
≈0.1−7.0	288.15	?^{d}	H_2SO_4	0.0	71-chi/pla
0.4959−2.874^e	273.15	7	NaCl		73-pla
0.4959−0.7840^e	273.15	2	KCl		73-pla
0.7840−6.972^e	273.15	21	H_2SO_4		73-pla
1.145−2.947	298.15	4	NaCl	0.75	75-pla
0.4798−2.1694^f	298.15	78	KCl	0.5	76-spe/web
2.6341−8.8254	298.15	60	H_2SO_4	1.0	77-rar/spe
0.8012−3.2485^g	382.0	22	NaCl/KCl		78-hol/bae
0.8237−3.2289^g	413.8	19	NaCl/KCl		78-hol/bae
0.8559−3.9426^g	445.4	20	NaCl/KCl		78-hol/bae
0.7940−3.9568^g	474.0	17	NaCl/KCl		78-hol/bae
1.4934−2.9772^e	298.15	20	NaCl	1.0	81-rar/mil
2.0201−2.2491^e	298.15	2	KCl	1.0	81-rar/mil
1.4934−3.9625^e	298.15	23	H_2SO_4	1.0	81-rar/mil
2.6546−2.9761	298.15	4	NaCl	1.0	83-mac/bat
0.7139−1.2789	298.15	11	KCl	0.0	84-ves/kap
0.2438−2.7648^h	323.15	20	NaCl		86-dav/duc
0.2438−2.7648^h	323.15	20	LiCl		86-dav/duc
3.1040−12.022	323.15	27	LiCl		86-duc/hol
2.5602−2.7593	298.15	2	NaCl	1.0	86-mac/bat
0.35081−3.3754^h	373.4_5	15	NaCl		88-grj/voi
0.35081−3.8659^h	373.4_5	12	LiCl		88-grj/voi
0.3600−3.0057	318.15	24	NaCl		89-gil/cal
0.1081−5.6594	273.15	20	LiCl		89-pen/gil
0.9580−3.1555	373.4_5	8	KCl		90-fan/grj
1.1144−5.9770	373.4_5	26	LiCl		90-voi/hau
4.7219−7.2592	428.7	7	LiCl		94-bre/voi
0.5438−3.7105	443.92	36	NaCl		94-hol/bus
0.5964−3.8129	473.61	36	NaCl		94-hol/bus
0.4074−4.0883	498.27	30	NaCl		94-hol/bus
0.5311−4.3720	498.72	25	NaCl		94-hol/bus
0.4898−4.5041	523.20	33	NaCl		94-hol/bus
0.4299−4.8131	524.12	23	NaCl		94-hol/bus
2.7682−3.0200^i	298.15	4	NaCl	1.0	95-rar/arc
2.7682−4.4579	298.15	41	H_2SO_4	1.0	95-rar/arc
4.3235−10.253	298.15	66	H_2SO_4	1.0	Table 1

[a] Relative weights are assigned only to the isopiestic data sets measured at 298.15 K and not at other temperatures because this review is restricted to 298.15 K. The numbers in parentheses are the number of data points from that study that were given zero weight in the least-squares fits. Their molalities are (2.951, 3.072, 3.362, and 3.715) mol·kg^{-1} [45-sto] and 2.069 mol·kg^{-1} [67-kir/luk]. [b] Other sets of equilibrium molalities are given in this report, but they are the same as some of the results given by Spedding et al. [76-spe/web]. [c] The same $CaCl_2$(aq) solutions were equilibrated simultaneously with both NaCl(aq) and KCl(aq). [d] The actual number of data points is unknown since only smoothed results were presented at round values of the molality. Childs and Platford used both H_2SO_4(aq) and urea(aq) as reference standards. [e] Several of these equilibrations involved $CaCl_2$(aq) solutions equilibrated simultaneously against two of the reference standards. [f] The isopiestic molalities are "buried" in their extensive listing of isopiestic results for rare earth chlorides. However, the results for $CaCl_2$(aq) are tabulated in Table I of Rard et al. [77-rar/hab]. [g] These same $CaCl_2$(aq) solutions were equilibrated simultaneously with both NaCl(aq) and KCl(aq). [h] These same $CaCl_2$(aq) solutions were equilibrated simultaneously with both NaCl(aq) and LiCl(aq). [i] These four $CaCl_2$(aq) solutions were equilibrated simultaneously with both NaCl(aq) and H_2SO_4(aq).

hol/bae, 81-rar/mil, 84-ves/kap, 86-dav/duc, 86-duc/hol, 88-grj/voi, 89-gil/cal, 89-pen/gil, 94-bre/voi, 94-hol/bus, 95-rar/arc], including the present study. In other cases isopiestic measurements were performed for some other aqueous electrolyte or mixture in which two or more of the reference standards were used simultaneously, and which yield some $\phi(CaCl_2)$ values over a more or less restricted concentration interval [60-sae/spe, 62-shu/mak, 65-kir/luk, 66-kir/luk, 66-rob/bow, 67-kir/luk, 68-rob/cov, 75-pla, 76-spe/web, 83-mac/bat, 86-mac/bat, 90-fan/grj, 90-voi/hau]. Since there are such a large number of different studies from a number of different laboratories using four different reference standards, sufficient isopiestic results are available (especially at 298.15 K) to provide a good statistical measure of the uncertainty of $\phi(CaCl_2)$.

The most commonly used isopiestic reference standards for aqueous solutions, other than $CaCl_2$(aq), are NaCl(aq), KCl(aq), and H_2SO_4(aq) [65-rob/sto, 91-rar/pla]. However, in several of the studies listed in Table 2, LiCl(aq) was used at (273.15, 323.15, 373.4_5, or 428.7) K [86-dav/duc, 86-duc/hol, 88-grj/voi, 89-pen/gil, 90-voi/hau, 94-bre/voi].

The osmotic coefficients of $CaCl_2$(aq) were recalculated from the isopiestic equilibrium molalities using the fundamental equation for isopiestic equilibrium

$$\phi(CaCl_2) = \nu^* m^* \phi^* / 3m(CaCl_2) \qquad (2)$$

where the asterisk denotes the property for an isopiestic reference standard. The ionization numbers for the reference electrolytes are stoichiometric, i.e., assume complete dissociation, and thus are $\nu^* = 2$ for NaCl(aq), KCl(aq), and LiCl(aq), and $\nu^* = 3$ for H_2SO_4(aq).

As noted in the previous section, there have been changes in the molar masses of $CaCl_2$(aq) and the other reference standards of about 0.01% during the different times that isopiestic data have been reported. This affects the equilibrium molalities by about 0.01% at low molalities and about 0.02% at the highest molalities. Typical precision for isopiestic molalities is about (0.05 to 0.1)%. Equation 2 indicates that the calculation of $\phi(CaCl_2)$ depends on the ratio of the molalities of reference standard to $CaCl_2$(aq), and thus there is a partial compensation for the switch between oxygen and carbon 12 scales to define molar masses. Consequently, it was judged unnecessary to correct published isopiestic molalities for changes in molar masses.

Osmotic coefficients of NaCl(aq) were taken from the critical review of Archer [92-arc], with due account taken of corrections to some of their equations [94-cle/rar, 95-rar/arc]. That review appears to yield the most comprehensive and accurate values for ϕ^*(NaCl) and which agree at 298.15 K to within 0.003 of values from previous reviews [65-rob/sto, 72-ham/wu]. Values of $\phi^*(H_2SO_4)$ were calculated from the equation and parameters of Clegg et al. [94-cle/rar] for molalities ≤ 6.1 mol·kg^{-1} and from Rard et al. [76-rar/hab] for molalities > 6.1 mol·kg^{-1}.

Preliminary calculations were performed with ϕ^*(KCl) at 298.15 K taken from Hamer and Wu [72-ham/wu] and which agree to 0.0012 with tabulated values of Robinson and Stokes [65-rob/sto]. Pabalan and Pitzer [88-pab/pit] have published Pitzer equations for KCl(aq) applicable to high temperatures. They constrained their equation with the high-temperature isopiestic data of Holmes et al. [78-hol/bae] and with published low- and high-temperature calorimetric data. Neither freezing temperature nor emf measurements were considered by Pabalan and Pitzer, and it not clear which isopiestic and vapor pressure data were included in their evaluation at low and intermediate temperatures. Thus we are unsure which data constrained their equation in most of the temperature region of interest.

An examination of the $\phi(CaCl_2)$ at 298.15 K calculated from isopiestic measurements using NaCl(aq) and KCl(aq) as reference standards indicates that values determined with NaCl(aq) were generally systematically higher than those determined with KCl(aq) by up to 0.5% for the higher quality studies when ϕ^*(KCl) was taken from the equation of Hamer and Wu [72-ham/wu] and ϕ^*(NaCl) was taken from the equation of Archer [92-arc], although there was some overlap in values. Differences of a similar magnitude are also present for isopiestic values of ϕ(NaBr) at 298.15 K as determined relative to the same two reference standards, according to the critically reanalyzed literature results [95-rar/arc]. Differences between results for ϕ(H_2SO_4) [94-cle/rar] relative to these same two reference standards are less clear cut, mainly because some of the isopiestic data for that system are substandard.

The selected source of osmotic coefficients for NaCl(aq) is a detailed and up-to-date critical analysis of thermodynamic data for this system [92-arc], and we have confidence in the calculated ϕ^*(NaCl). Thus it appears that the osmotic coefficients of Hamer and Wu for KCl(aq) [72-ham/wu] need to be updated to make them more consistent with the other reference standards. Archer [96-arc] has reevaluated ϕ^*(KCl) and supplied us with values of the Pitzer equation parameters at 298.15 K. Archer's evaluation for KCl(aq) was accepted since it is consistent with his evaluation for NaCl(aq) and because it eliminates most of the inconsistency between these two reference standards.

LiCl(aq) was used as a provisional isopiestic reference standard in several studies at temperatures of (273.15, 323.15, and 343.4$_5$) K [86-dav/duc, 86-duc/hol, 88-grj/voi, 89-pen/gil, 90-voi/hau]. The most reliable source of ϕ^*(LiCl) values appears to be Gibbard and Scatchard [73-gib/sca]. Their deviation plots indicate that the reliability of their model is about 0.002−0.003 at low temperatures but that the scatter in the better quality osmotic coefficients around room temperature is $\approx$0.02. This latter value is about a factor of 10 larger than for NaCl(aq) or KCl(aq). Rard and Platford [91-rar/pla] also pointed out that equilibrium molalities of LiCl(aq) are inherently about twice as uncertain as those of the other reference standards. This is because modern commercial samples of LiCl are frequently highly depleted in lithium 6, whereas in many of the earlier studies the lithium was of normal isotopic abundance. The lithium isotopic composition of any particular LiCl sample is unknown. Thus LiCl(aq) seems to us to be an unfortunate choice for a reference standard.

Initial calculations of ϕ^*(LiCl) from their equations [73-gib/sca] gave results that were correct at 298.15 K but that were clearly incorrect at all other temperatures. All subsequent issues of the *Journal of Chemical and Engineering Data* were examined, but no errata was located. We ultimately traced the problem to a missing minus sign between the curly brace and the parenthesis on the first line of their eq 4. This was discovered by rederiving this equation using the general expression for "*D*" given by them elsewhere [74-gib/sca] and assuming that τ and t are actually the same quantity. We also note that their tabulated coefficients $D_3^{(3)}$, $D_4^{(3)}$, and $D_5^{(3)}$ for LiCl(aq) are mislabeled as $D_3^{(2)}$, $D_4^{(2)}$, and $D_5^{(2)}$, respectively.

There are a large number of isopiestic studies at 298.15 K, and thus comparisons can be made to assign preliminary weights to the various data sets to be used in subsequent modeling efforts. Values of ϕ($CaCl_2$) at this temperature vary as a function of molality from about 0.85 at the minimum to 3.17 at the maximum, which is a ratio of 3.7. Thus a rejection or weighting criterion based upon the absolute size of the deviations from a least-squares based model would have a disproportional effect on weighting of ϕ($CaCl_2$) in the different molality regions. The precision of isopiestic experiments is typically about (0.05 to 0.1)% of the molalities of the electrolyte being studied and of the reference standard [91-rar/pla], or (0.1 to 0.2)% in their equilibrium molality ratio. There are enough isopiestic studies with each of the three reference standards NaCl(aq), KCl(aq), and H_2SO_4(aq) to allow meaningful graphical comparisons of the isopiestic molality ratio $m^*/m(CaCl_2)$ separately for each reference standard. These plots have the added advantage that slight inconsistencies between the osmotic coefficients of the different reference standards have no effect on these comparisons since the molality ratios for each reference standard are compared separately. We estimate the reference standards have uncertainties in ϕ^* ranging from (0.1 to 0.3)% depending on the molality.

Several expanded-scale plots of $m^*(KCl)/m(CaCl_2)$ were made at 298.15 K over different molality regions for the available data [40-rob, 60-sae/spe, 66-kir/luk, 67-kir/luk, 68-rob/cov, 76-spe/web, 81-rar/mil, 84-ves/kap]. These comparisons indicated that most values of $m^*(KCl)/m(CaCl_2)$ fall within 0.2% of a smoothed curve drawn through the more concordant data sets [60-sae/spe, 66-kir/luk, 68-rob/cov, 76-spe/web, 81-rar/mil]. However, the early results of Robinson [40-rob] are quite scattered and generally are too low by about (0.2 to 0.8)%, and those of Vesala et al. [84-ves/kap] are too high by (0.7 to 2.0)%. Furthermore, three of the four points of Kirgintsev and Luk'yanov from their 1967 study [67-kir/luk] are about 0.4% high. Those same four experiments also involved equilibrations with NaCl(aq) solutions, and the $m^*(NaCl)/m(CaCl_2)$ ratio is also high by about this amount (see below); this implies that their $CaCl_2$(aq) solution is the source of this discrepancy.

According to Stokes [45-sto], Robinson's data [40-rob] are in error because of significant contamination of the $CaCl_2$(aq) by alkali metal chloride. This is a quite plausible explanation, and thus Robinson's results were not included in the modeling calculations. Similarly, the $m^*(KCl)/m(CaCl_2)$ values of Vesala et al. [84-ves/kap] are so much higher than all of the other studies that they either must have had serious contamination of one of their solutions or else erred in their molality analysis. Their results were also rejected. Three of Kirgintsev and Luk'yanov's four values from their 1967 study [67-kir/luk] were given reduced weight in the least-squares fits, and the fourth point was weighted zero. The results from the study of Spedding et al. [76-spe/web] are slightly lower than the more concordant results using KCl(aq) as reference standard and were also given reduced weight.

Similar comparisons of $m^*(NaCl)/m(CaCl_2)$ at 298.15 K were made over different molality regions for the available data sets [45-sto, 62-shu/mak, 65-kir/luk, 66-rob/bow, 67-kir/luk, 75-pla, 81-rar/mil, 83-mac/bat, 86-mac/bat, 95-rar/arc]. Most values of $m^*(NaCl)/m(CaCl_2)$ fall within 0.2% of a smoothed curve through the more concordant data sets [45-sto, 66-rob/bow, 75-pla, 81-rar/mil, 83-mac/bat, 86-mac/bat, 95-rar/arc]. However, the molality ratios from the studies of Shul'ts et al. [62-shu/mak] and from Kirgintsev and Luk'yanov [65-kir/luk, 67-kir/luk] are generally about (0.2 to 0.5)% high, and their results were given reduced or zero weight in the least-squares fits. Robinson and Bower's [66-rob/bow] results are generally in good agreement with most of the other studies, except for their two highest molality experiments which have slightly high molality ratios.

Values of $m^*(H_2SO_4)/m(CaCl_2)$ at 298.15 K are available from several studies [45-sto, 77-rar/spe, 81-rar/mil, 95-rar/arc] including the present one and extend about (3.4 ± 0.1) mol·kg^{-1} into the supersaturated region. For $m(CaCl_2) \approx$ (2.6 to 6.0) mol·kg^{-1} the results from all of these studies are in excellent agreement, about 0.15% in $m^*(H_2SO_4)/$-

Table 3. Summary of Other Vapor-Pressure Results (Nonisopiestic) for Aqueous $CaCl_2$ Solutions for Temperatures $\leq$ 523 K in Chronological Order

molality range/(mol·kg^{-1})	T/K	no. of points	method[a]	relative weight[b]	ref
0.255−9.248	343.05−363.15	42	dvp		13-per/pri
2.3345−12.731	331.17−414.07	40	btd		21-bak/wai
0.183−13.774	313.15−353.15	98	svp?		27-har/per
0.199−7.278	298.15	14	dpd	0.0	32-hep
0.000809−0.315	373.151−373.561	9	btd		35-pla
0.2489−9.239	291.15	28	svp		36-lan
7.342	298.15	1	svp?	0.0	37-var/mis
0.3043−7.0308	298.15−318.15	8	dvp	1.0	40-bec/new
3.019−3.036	298.15	4	bte	0.75	47-sto
0.25−6.0	298.15	13	btne	0.25	65-pet
2.9573−7.8767	292.852−362.079	52	svp	0.0	72-jak/van
0.05066−0.06083	298.15	2	vpo	0.0	74-amd
0.246−5.536	423−523[c]	21	svp		80-zar/lvo
5.07−25.8	523[c]	7	svp		84-ket/uru
0.5−5.7	473−523[c]	42	svp		84-woo/cre
0.9568−5.002	322.7−402.7	38	svp		85-sak/hak
9.251	523[c]	1	svp		87-uru/val
1.002−7.885	303.15−343.15	40	svp		91-pat/tri

[a] For the experimental method: "dvp" denotes dynamic vapor pressure measurement, "btd" denotes boiling temperature determination, "dpd" denotes dew point determination, "svp" denotes static vapor pressure measurement, "bte" denotes bithermal equilibration (this method is sometimes referred to as the bithermal isopiestic method), "btne" denotes the bithermal method operated in the nonequilibrium mode, and "vpo" denotes vapor-pressure osmometry. [b] Only results at 298.15 K were assigned weights for the reported least-squares calculations. Some individual values were assigned zero weight; see Table 4 for weights assigned to individual osmotic coefficients. [c] Results at higher temperatures are also reported. Ketsko et al. [84-ket/uru] also reported vapor pressures for saturated solutions containing a solid phase of uncertain composition.

$m(CaCl_2)$, except for the four lowest molality experiments of Stokes [45-sto] which are higher by about 0.3%. Above 6.0 mol·kg^{-1} the various studies agree to within 0.35% in this molality ratio, with better agreement over certain molality intervals. Although the molality ratio for the series 2 experiment from Table 1 with $m(CaCl_2) = 8.9672$ mol·kg^{-1} falls about 0.2% above the curve for the other experiments of that table, it is within the range of the other published studies. Osmotic coefficients above 10 mol·kg^{-1}, Table 1 and ref [45-sto], are fairly scattered, which is not unexpected given the high molalities and the high degree of supersaturation of $CaCl_2$(aq).

3.3. Nonisopiestic Vapor-Pressure Data. Vapor pressures of $CaCl_2$(aq) solutions have been determined by a number of more-or-less direct methods. Table 3 summarizes those studies for which vapor pressures are reported at temperatures ≤ 523 K. Isopiestic vapor pressure studies are not listed here since they are already given in Table 2.

A variety of techniques were used for these determinations. Many were made by the static vapor-pressure method (direct measurement of the vapor pressure of a degassed solution) [36-lan, 72-jak/van, 80-zar/lvo, 84-ket/uru, 84-woo/cre, 85-sak/hak, 87-uru/val, 91-pat/tri], by the dynamic vapor pressure method (determination of the mass of water vapor from a solution required to saturate a known volume of flowing gas) [13-per/pri, 40-bec/new], or by the simultaneous determination of the vapor pressure and boiling temperature of a solution [21-bak/wai, 35-pla]. A few vapor pressures have been reported by Stokes [47-sto] using the bithermal equilibrium (bithermal isopiestic) method. In this method, reservoirs of solution and of pure solvent are in contact through a common vapor phase; the solution reservoir is kept at a fixed temperature, and the pure solvent reservoir is cooled until the distillation of solvent ceases. Petit [65-pet] used a variant of this method involving determination of the initial rate of distillation of solvent when the solution and the pure solvent were kept at different temperatures, but this nonequilibrium method appears to be much less precise than the normal bithermal equilibrium method. Vapor pressures have also been reported using dew point determinations [32-hep], which are not very precise measurements, and by vapor pressure osmometry [74-amd], in which the molalities of the solutions are not accurately known. Most of these methods have been described by Rard and Platford [91-rar/pla].

In general, values of $\phi(CaCl_2)$ derived from direct vapor-pressure measurements are significantly less reliable than values determined from isopiestic measurements, especially at lower molalities. This can be understood by considering the equation used to calculate osmotic coefficients from the experimental vapor pressures [91-rar/pla]

$$\phi = -(m_w/\nu mRT)\{RT\ln(P_w/P_w^\circ) + B_2(T)(P_w - P_w^\circ) + V_w(P_w - P_w^\circ)\} \quad (3)$$

where P_w is the vapor pressure of water vapor above a solution of molality m, P_w° the vapor pressure of pure water at the same temperature, T the temperature in kelvin, R the gas constant, $B_2(T)$ the second virial coefficient of water vapor (pressure form of the virial expansion), which is a function of temperature but not pressure, and V_w the partial molar volume of water in the solution, which is a function of molality, temperature, and pressure. To maintain consistency with the evaluation for H_2SO_4(aq) [94-cle/rar], $R = 8.3144$ J·K^{-1}·mol^{-1}.

For dilute solutions, the second and third terms on the right-hand side of eq 3 become negligible and $\phi \approx -(m_w/\nu m)\ln(P_w/P_w^\circ)$. Under this condition, ϕ becomes the ratio of two quantities that both approach zero, and it becomes highly uncertain at low molalities. For this reason, vapor-pressure measurements (other than isopiestic) at molalities below about 1 mol·kg^{-1} are rarely accurate or precise enough to yield meaningful values of ϕ.

Only the vapor pressures determined at $T \leq 383.15$ K were reanalyzed. At these temperatures, the last term of eq 3 is negligible compared to the two preceding terms and also compared to experimental error: $\{V_w(P_w^\circ - P_w)\}/RT \leq 5 \times 10^{-7}$ at 273.15 and $\leq 6 \times 10^{-5}$ at 373.15 K [91-rar/pla]. The first term of eq 3 inside the curly braces dominates over the second term at all of these temperatures.

Values of P_w° were taken from the tables of Wexler and Greenspan [71-wex/gre] for temperatures 273.15 K ≤ T ≤

373.15 K, calculated from their equation at 373.15 K < T ≤ 375 K, and from Haar et al. [84-haa/gal] at T > 375 K. The evaluation of Haar et al. has a much wider range of applicability and is probably slightly more accurate. However, differences between these values of P_{w}° are quite small for $T \leq 375$ K (<1 Pa for $T \leq 333$ K; ≤2.9 Pa for $T \leq 373.15$ K), and the results of Wexler and Greenspan are more convenient to use since they are given for both the IPTS-48 and IPTS-68 temperature scales. Values of $B_2(T)$ were taken from Table 1 of Rard and Platford [91-rar/pla] for $T \leq 373.15$ K and from Haar et al. at $T > 373.15$ K; these values are consistent to within 8 $\mathrm{cm^3 \cdot mol^{-1}}$ (1.7%) at 373.15 K, and this small difference has a negligible effect on the calculated values of ϕ.

Table 4 contains all of the derived $\phi(\mathrm{CaCl_2})$ for measurements at $T = 298.15$ K. In general, these $\phi(\mathrm{CaCl_2})$ are very close to those calculated by Rard et al. [77-rar/hab] at higher molalities, but some have larger differences at lower molalities where $\phi(\mathrm{CaCl_2})$ is more sensitive to the selected value of P_{w}°. These differences are due to refinements in the values of P_{w}° and $B_2(T)$ used for the calculations. Relative weights are assigned to each calculated $\phi(\mathrm{CaCl_2})$.

In general, the values of $\phi(\mathrm{CaCl_2})$ in this table are much less precise and much less accurate than the majority of the isopiestic data. The highest quality $\phi(\mathrm{CaCl_2})$ values in Table 4 are those of Bechtold and Newton at (3.0334 and 7.0308) $\mathrm{mol \cdot kg^{-1}}$ [40-bec/new] and the four values of Stokes [47-sto], which are consistent with the isopiestic values of $\phi(\mathrm{CaCl_2})$ within experimental precision. Bechtold and Newton's results at 0.3043 $\mathrm{mol \cdot kg^{-1}}$ are discrepant, which is not surprising because of the considerable sensitivity of $\phi(\mathrm{CaCl_2})$ to minor errors in P_{w} and P_{w}° at low molalities.

Values of $\phi(\mathrm{CaCl_2})$ from Hepburn [32-hep] are lower than the isopiestic results by (10 to 15)% below 1 $\mathrm{mol \cdot kg^{-1}}$ but are scattered around the isopiestic results by about (0.5 to 2.5)% at higher molalities. This results from the poor precision of the dew points. Amdur's [74-amd] vapor pressure osmometry results are (1.5 to 2.0)% from the isopiestic $\phi(\mathrm{CaCl_2})$. Both data sets were given zero weight. Derived $\phi(\mathrm{CaCl_2})$ from the nonequilibrium bithermal measurements of Petit [65-pet] are systematically high and scattered below about 3.0 $\mathrm{mol \cdot kg^{-1}}$ but are in moderately good agreement with isopiestic data at higher molalities. The lower molality results of this study were weighted zero.

Varasova et al. [37-var/mis] reported the vapor pressure of a saturated $\mathrm{CaCl_2(aq)}$ solution at 298.15 K. The derived value of $\phi(\mathrm{CaCl_2})$ is in excellent agreement with available isopiestic data, but this agreement must be accidental since Varasova et al. only reported the vapor pressure to two significant figures.

Jakli and Van Hook [72-jak/van] determined vapor pressures of three different solutions of $\mathrm{CaCl_2(aq)}$ as a function of temperature, which can be interpolated to yield $\phi(\mathrm{CaCl_2})$ at 298.15 K. The authors found that their experimental results were quite discrepant from isopiestic results at 298.15 K and attributed this discrepancy to their solution preparation method (addition of purportedly anhydrous $\mathrm{CaCl_2}$ and water). They assumed that their $\mathrm{CaCl_2}$ actually contained some residual moisture and estimated this water content by normalizing their two lower molalities to agree with $\phi(\mathrm{CaCl_2})$ from Robinson and Stokes [65-rob/sto]. However, their calculated corrected highest molality results then yielded $\phi(\mathrm{CaCl_2})$ values that fell about 5% below those of Robinson and Stokes. This suggests that residual water in their $\mathrm{CaCl_2(s)}$ was not their only source of error, and their data [72-jak/van] were likewise rejected.

Table 4. Osmotic Coefficients of Aqueous $\mathrm{CaCl_2}$ Solutions at 298.15 K Derived from Nonisopiestic Vapor-Pressure Measurements

$m(\mathrm{CaCl_2})$/ $(\mathrm{mol \cdot kg^{-1}})$	$(P_{\mathrm{w}}/P_{\mathrm{w}}^{\circ})^{a}$	$\phi(\mathrm{CaCl_2})$	relative weight	ref
0.199	0.989 32^{b}	0.9969	0.0	32-hep
0.284	0.986 38^{b}	0.8921	0.0	32-hep
0.344	0.986 38^{b}	0.7365	0.0	32-hep
0.494	0.979 92^{b}	0.7586	0.0	32-hep
0.635	0.972 91^{b}	0.7991	0.0	32-hep
0.796	0.963 06^{b}	0.8737	0.0	32-hep
1.000	0.951 59^{b}	0.9168	0.0	32-hep
1.504	0.909 61^{b}	1.1639	0.0	32-hep
1.985	0.861 37^{b}	1.3891	0.0	32-hep
2.495	0.810 42^{b}	1.5568	0.0	32-hep
2.990	0.751 83^{b}	1.7629	0.0	32-hep
4.004	0.620 11^{b}	2.2056	0.0	32-hep
5.826	0.399 08^{b}	2.9145	0.0	32-hep
7.278	0.294 50^{b}	3.1052	0.0	32-hep
7.342	0.290_5	3.11_6	0.0	37-var/mis
0.3043	0.986 33	0.8357	0.0	40-bec/new
3.0334	0.745 83	1.7865	1.0	40-bec/new
7.0308	0.309 64	3.0825	1.0	40-bec/new
3.019	0.747 14^{c}	1.7843	0.75	47-sto
3.021	0.747 14^{c}	1.7831	0.75	47-sto
3.024	0.747 14^{c}	1.7813	0.75	47-sto
3.036	0.745 60^{c}	1.7868	0.75	47-sto
0.25	0.988 45	0.8588	0.0	65-pet
0.50	0.976 83	0.8664	0.0	65-pet
0.75	0.959 44	1.0200	0.0	65-pet
1.0	0.942 01	1.1037	0.0	65-pet
1.5	0.903 41	1.2512	0.0	65-pet
2.0	0.860 76	1.3852	0.0	65-pet
2.5	0.807 55	1.5798	0.0	65-pet
3.0	0.749 96	1.7723	0.25	65-pet
3.5	0.685 22	1.9959	0.0	65-pet
4.0	0.623 63	2.1817	0.25	65-pet
4.5	0.559 68	2.3837	0.25	65-pet
5.0	0.498 26	2.5752	0.25	65-pet
6.0	0.390 33	2.8983	0.25	65-pet
0.05066^{d}	0.997 599^{e}	0.8780	0.0	74-amd
0.06083^{d}	0.997 237^{e}	0.8416	0.0	74-amd

[a] Vapor pressures of pure water were taken from Wexler and Greenspan [71-wex/gre], who report critically assessed values from (273.15 to 373.15) K at every 0.1 K for the IPTS-48 and IPTS-68 temperature scales. At 298.15 K, $P_{\mathrm{w}}^{\circ} = 3.1670$ kPa on IPTS-27 and IPTS-48 and $P_{\mathrm{w}}^{\circ} = 3.1686$ kPa on IPTS-68. [b] Values of P_{w} were recalculated from the reported "dew point" temperatures [32-hep] using Wexler and Greenspan's [71-wex/gre] assessed vapor pressures for IPTS-48. [c] Values of P_{w} were recalculated from the reported temperatures of the reservoir of pure water in bithermal equilibrium with the $\mathrm{CaCl_2(aq)}$ solution [47-sto] using Wexler and Greenspan's [71-wex/gre] assessed vapor pressures for IPTS-48. [d] These are the molalities reported by Amdur [74-amd]. The experimental measurement amounts to a determination of the temperature increase of a drop of this solution in contact, through the vapor phase, with a drop of pure water. Since water is absorbed by the solution during this measurement, the actual molality must be less that this. However, since the same type of error occurred during the calibration of their apparatus, there may be some partial compensation. [e] Their apparatus was calibrated [69-amd] with solutions of NaCl(aq) and KCl(aq), with the water activities of those solutions being taken from the tabulated values of Robinson and Stokes [65-rob/sto]. Thus these are a_{w} values rather than $(P_{\mathrm{w}}/P_{\mathrm{w}}^{\circ})$.

A preliminary assessment of the accuracy and precision of $\phi(\mathrm{CaCl_2})$ at $T \neq 298.15$ K was made with direct plots of $\phi(\mathrm{CaCl_2})$ against molality at various constant temperatures. For example, values of $\phi(\mathrm{CaCl_2})$ at 313.15 K were reported by Harrison and Perman [27-har/per] and Patil et al. [91-pat/tri], and the values of Bechtold and Newton [40-bec/new] can be interpolated accurately to this temperature. Values of $\phi(\mathrm{CaCl_2})$ from Bechtold and Newton and from Patil et al. are fairly consistent, whereas those of Harrison and Perman are both very scattered and lower by up to 0.3 in $\phi(\mathrm{CaCl_2})$, i.e. by up to 10%. Zero weights were

Table 5. Summary of Available Emf Results for Aqueous $CaCl_2$ Solutions in Chronological Order

molality range/($mol \cdot kg^{-1}$)	T/K	no. of points	cell type	relative weight[a]	ref
0.005−0.05[b]	290−291	6	G (eq 13)		24-tam
0.01−3.502	298.15	13	A (eq 7)	0.0	25-luc
0.01−2.586	298.15	11	H (eq 14)	0.2	25-luc
0.0099−0.0994[b]	289−296	59	K (eq 26)		26-dru/luf
0.0099−3.2702	298.15	11	A (eq 7)	0.0	29-fos
0.009921−0.9301	298.15	9	A (eq 7)	0.0	30-sca/tef
0.025−0.05	≈288−291	2	G (eq 13)		31-shi
0.0032−3.867[b]	298.15	7	L.a (eq 27)	0.0	32-has/jel
0.000625−0.01[c]	303.15	4	D (eq 10)		32-mas
0.001−0.005[c]	303.15	4	F (eq 12)		32-mas
0.00125−0.01[c]	303.15	3	H (eq 14)		32-mas
0.0018207−0.097003	298.15	6	H (eq 14)	1.0 (1)	37-she/mac
0.0029934−0.075054	288.15−308.15	27	H (eq 14)	0.4	46-mcl/gor
0.0010−0.080	298.15	8	B (eq 8)	0.0	59-sah
?[d]	298.15	?[d]	C (eq 9)	0.0	62-jak/tan
8.8×10^{-6}−4.49	298.15	9	I (eq 22)	0.0	67-ros
1.00×10^{-5}−3.11	298.15	23	I (eq 22)[e]	0.1	70-sha
0.005828−0.09680	298.15−343.15	34	E (eq 11)	0.4 (1)	71-mus/pag
0.0010275−0.295890	298.15	6[f]	J (eq 23)	1.0	74-bri/lil

[a] Only results at 298.15 K and not at other temperatures were assigned weights for the reported least-squares calculations because this review is restricted to 298.15 K. The numbers in parentheses are the number of data points from that study that were given zero weight in the least-squares fits. These molalities are 0.060 084 $mol \cdot kg^{-1}$ [37-she/mac] and 0.019 32 $mol \cdot kg^{-1}$ [71-mus/pag]. [b] The reported concentration units for these three studies [24-tam, 26-dru/luf, 32-has/jel] are molarities, not molalities. [c] The concentration units for this study are uncertain since Masaki [32-mas] sometimes referred to the concentrations as molarities and sometimes as molalities. [d] Only the evaluated standard potentials were reported [62-jak/tan]; consequently both the number of data points and the experimental emfs are unknown. [e] Shatkay [70-sha] also reported emfs for four other cells that contained either KCl or KNO_3 salt bridges. Since the emfs for those cells contain liquid junction potentials, they were not analyzed. [f] Briggs and Lilley [74-bri/lil] performed measurements with these solutions at their "natural" pH's and for samples to which a small amount of NaOH(aq) had been added. There was no significant variation of the emf with pH. Numerous replicate measurements (4 to 14 determinations) were made of each emf.

consequently assigned to all data from Harrison and Perman [27-har/per]. However, the $\phi(CaCl_2)$ of Patil et al. [91-pat/tri] at 1.002 $mol \cdot kg^{-1}$ appear to be quite high at all temperatures.

Comparisons of $\phi(CaCl_2)$ at various temperatures from the studies of Perman and Price [13-per/pri] and Patil et al. [91-pat/tri] indicated a general consistency of better than 0.1 in $\phi(CaCl_2)$ between these studies except at low molalities where agreement is poorer. A plot of the $\phi(CaCl_2)$ at constant molality as a function of temperature from the study of Baker and Waite [21-bak/wai] indicated an internal consistency of about 0.01. None of these studies yields $\phi(CaCl_2)$ as precise as the isopiestic results.

Values of $\phi(CaCl_2)$ from vapor pressure measurements at $T \neq 298.15$ K will be compared in greater detail in our second paper, when the temperature dependence of the model equations for $CaCl_2(aq)$ are reported.

3.4. Emf Data. There are 16 publications that report experimental emfs for solutions of $CaCl_2(aq)$. Most of these were restricted to 298.15 K [25-luc, 29-fos, 30-sca/tef, 32-has/jel, 37-she/mac, 59-sah, 62-jak/tan, 67-ros, 70-sha, 74-bri/lil]; two others were variable-temperature studies that also included measurements at 298.15 K [46-mcl/gor, 71-mus/pag]; the rest were done at 303.15 K [32-mas], (290 to 291) K [24-tam], or (289 to 296) K [26-dru/luf]. Shibata [31-shi] reported emfs for only two $CaCl_2(aq)$ concentrations at (288 to 291) K.

These emf studies were made with a large variety of different cells: some containing both calcium ion and chloride ion responsive electrodes including double cells with a reference electrode compartment containing a fixed reference molality of $CaCl_2(aq)$; several types of concentration cells without transference containing either calcium-responsive or chloride-responsive electrodes; cells with transference containing chloride-responsive electrodes. These anion-responsive electrodes were silver/silver chloride or mercury/mercurous chloride (calomel) electrodes, whereas the cation-responsive electrodes were usually calcium amalgam or a liquid membrane ion-exchange electrode. However, two studies were done with cation-responsive electrodes of the "third kind", i.e., with lead/lead oxalate/calcium oxalate [59-sah] or lead/lead carbonate/calcium carbonate electrodes [62-jak/tan].

Table 5 contains a summary of the available emf studies with their molality, temperature or temperature range, and the cell type. Several data sets were not reanalyzed. Jakuszewski and Taniewska-Osińska [62-jak/tan] only reported extrapolated $E°$ values and not the experimental emfs. In several of the studies [26-dru/luf, 32-has/jel], including four of the five series of measurements by Shatkay [70-sha], salt bridges were used and thus the emfs include contributions from liquid-junction potentials (ljp). Because the values of these ljp are unknown, these data sets could not be reanalyzed in a rigorous fashion.

3.4.1. Corrections for Solubilities. Solubility corrections are sometimes required for the dissolution of electrode material into solutions used for emf measurements, since they may affect the emf at low molalities of solute. For example, dissolution of calcium amalgam and calcium oxalate electrodes adds excess Ca(II) ions to the solution, whereas dissolution of silver chloride and mercurous chloride yields additional chloride ions. At low enough molalities this additional source of ions could constitute a significant fraction of their total concentration. Correction of the standard potential for the presence of Ca(II) ions produced by reaction of Ca(Hg) with water is not possible because the dissolution reaction does not produce a saturated solution of $CaCl_2(aq)$ or $Ca(OH)_2(aq)$ under the experimental conditions and because the pH continuously increases with time:

$$\mathrm{Ca(amalgam)} + 2\mathrm{H_2O(l)} \rightleftarrows \mathrm{Ca^{2+}(aq)} + 2\mathrm{OH^-(aq)} + \mathrm{H_2(g)} \quad (4)$$

Dissolution of mercurous chloride, $Hg_2Cl_2(cr)$, in water or aqueous chloride solutions does not produce a saturated solution containing just $Hg_2Cl_2(aq)$ and its dissociation products, but rather the $Hg_2^{2+}(aq)$ that forms undergoes partial dismutation by the following reaction:

$$\mathrm{Hg_2^{2+}(aq) \rightleftarrows Hg^{2+}(aq) + Hg(aq)} \tag{5}$$

The predominant species in solutions of $Hg_2Cl_2(aq)$ containing excess chloride is $HgCl_4^{2-}(aq)$ [80-mar], but significant amounts of $Hg(OH)_2(aq)$, $HgCl_2(aq)$, $Hg(OH)^+(aq)$, $HgCl^+(aq)$, $Hg_2^{2+}(aq)$, and $Hg_2(OH)^+(aq)$ are also present [61-hil/ive, 80-mar].

According to the critical review of Clever et al. [85-cle/joh], the equilibrium solubility of metallic mercury in air-free water is $(3.03 \pm 0.12) \times 10^{-7}$ mol·kg^{-1} at 298.15 K. They also tabulated numerous experimental values for the solubility of pure $HgCl_2(cr)$ in water, which range from (0.257 to 0.273) mol·kg^{-1} at 298.15 K. This is about 5 orders of magnitude larger than the solubility of $Hg_2Cl_2(cr)$ [80-mar], and thus $HgCl_2(cr)$ will not become the solubility-limiting phase in these solutions. The solubility of $HgCl_2(cr)$ in concentrated solutions of $CaCl_2(aq)$ and other chloride salts is increased by factors of about 10 to 20 over that in pure water [33-bas/bar, 39-tho] owing to the formation of chloride complexes such as $HgCl_4^{2-}(aq)$.

Richards and Archibald [02-ric/arc] studied the solubility of $Hg_2Cl_2(cr)$ in (0.36 to 4.50) mol·dm^{-3} $CaCl_2(aq)$ containing some liquid Hg at (298.15 ± 0.05) K. They analyzed their solutions for the total mercury ion concentrations by precipitation as the insoluble HgS(s). The HgS(s) is extremely insoluble, and its precipitation causes the equilibrium given by eq 5 to shift essentially completely to the right [66-cot/wil]. Richards and Archibald reported their results as the mass of HgS(s) precipitated, as the volume of solution analyzed, and as the mass of $HgCl_2$ per liter of solution. The latter value results from reporting the concentrations formally as if the dissolved mercury was present solely as $HgCl_2(aq)$. Molar concentrations calculated by us from their reported masses of HgS and volumes of solution were identical in all cases to those we calculated from their masses of $HgCl_2$ per liter of solution. We note that the method used by Richards and Archibald to analyze the dissolved mercury content of their solutions gives just the half of the mercury that was precipitated as HgS(s), but not the other half which was converted to metallic mercury. However, for estimating the effect on the emf for a cell containing a solution of $CaCl_2(aq)$ saturated with calomel, this is irrelevant since only the concentration of "extra" chloride ion in the solutions is significant, and this is the same no matter whether the concentrations are reported as "$HgCl_2$" or as "Hg_2Cl_2".

We calculated the corresponding molalities of $CaCl_2(aq)$ and $HgCl_2(aq)$ from the molar concentrations derived from the data in ref 02-ric/arc assuming that the densities are the same as for solutions of pure $CaCl_2(aq)$, with the density of $CaCl_2(aq)$ solutions being calculated from the equation of Rard and Miller [79-rar/mil]. These results are reported in Table 6. Garrett et al. [42-gar/nob] reported molalities of $Hg_2Cl_2(aq)$ in solutions of $CaCl_2(aq)$ from reanalysis of these same data. Their derived molalities of $CaCl_2(aq)$ are in reasonable agreement with the values in Table 6, but their molalities of $Hg_2Cl_2(aq)$ are (10 to 22)% higher than can be accounted for by their use of an assumed different chemical species (Hg_2Cl_2 as opposed to $HgCl_2$). Marcus [80-mar] reported molar concentrations of dissolved mercury in their Table 5.2 for the five lower concentration $CaCl_2(aq)$ solutions of Richards and Archibald, which are about 35% higher than our values.

Let ΔE be the estimated difference in emf between two hypothetical reversible cells, one containing $CaCl_2(aq)$ only and the other containing $CaCl_2(aq)$ saturated with Hg_2Cl_2. This ΔE is then given by $\Delta E = (RT/2F) \ln[m'(\mathrm{Ca}^{2+})m'(\mathrm{Cl}^-)^2\gamma_{\mathrm{Ca}}'(\gamma_{\mathrm{Cl}}')^2/m(\mathrm{Ca}^{2+})m(\mathrm{Cl}^-)^2\gamma_\pm{}^3]$. Here the primed quantities refer to the solutions saturated with $Hg_2Cl_2(cr)$ and the unprimed quantities refer to its absence. Since the contribution of chloride ion from dissolution of Hg_2Cl_2 to the total chloride ion concentration is ≤0.055% for all solutions studied by Richards and Archibald [02-ric/arc], we can assume $\gamma_{\mathrm{Ca}}'(\gamma_{\mathrm{Cl}}')^2 \approx \gamma_\pm{}^3$ and thus $\Delta E \approx (RT/F) \ln[m'(\mathrm{Cl}^-)/m(\mathrm{Cl}^-)]$. This calculation indicates that ΔE correction ranges from (0.006 to 0.014) mV, which is negligible compared to experimental error in the emf studies. Values of the solubility of Hg_2Cl_2 were estimated graphically for (0.01 to 0.25) mol·kg^{-1} solutions of $CaCl_2(aq)$, on the basis of the reported solubilities of Richards and Archibald [02-ric/arc] at higher concentrations of $CaCl_2(aq)$ and its solubility in pure water [80-mar]. These solubilities were used in turn to estimate ΔE. These results are also given in Table 6 and indicate that the correction to the emf from dissolution of Hg_2Cl_2 is negligible in this molality region also.

Table 6. Summary of Solubilities of $Hg_2Cl_2(cr)$ in Solutions of Aqueous $CaCl_2$ (Reported as Molalities of $HgCl_2$) at 298.15 K and the Correction to the Emf of Reversible Cells

$m(\mathrm{CaCl_2})$/(mol·kg^{-1})	$m(\mathrm{HgCl_2})^a$/(mol·kg^{-1})	ΔE^b/mV
	Richards and Archibald [02-ric/arc]	
0.36_4	8.2×10^{-5}	0.006
0.50_7	1.2×10^{-4}	0.006
1.02_8	3.1×10^{-4}	0.008
1.29_4	4.45×10^{-4}	0.009
1.85_0	8.93×10^{-4}	0.012
2.48_3	1.28×10^{-3}	0.013
3.19_9	1.75×10^{-3}	0.014
4.43_5	2.16×10^{-3}	0.013
5.25_9	2.22×10^{-3}	0.011
	Estimated Values	
0.01	9.6×10^{-6}	0.025
0.02	1.1×10^{-5}	0.014
0.03	1.2×10^{-5}	0.010
0.04	1.3×10^{-5}	0.008
0.05	$1.4_5 \times 10^{-5}$	0.007
0.06	1.6×10^{-5}	0.007
0.08	1.9×10^{-5}	0.006
0.10	2.2×10^{-5}	0.006
0.15	3.2×10^{-5}	0.005
0.20	4.2×10^{-5}	0.005
0.25	5.3×10^{-5}	0.005

[a] The reported molalities of "$HgCl_2$" account for only half of the mercury from dissolution of $Hg_2Cl_2(cr)$, as a consequence of the method of analysis. However, the molalities of chloride ion produced by this dissolution are correctly given by $2m(\mathrm{HgCl_2})$. [b] Values of $\Delta E \approx (RT/F) \ln[m'(\mathrm{Cl}^-)/m(\mathrm{Cl}^-)]$ are the estimated differences in emf between two hypothetical reversible concentration cells without transference, one containing $CaCl_2(aq)$ only and the other containing $CaCl_2(aq)$ saturated with $Hg_2Cl_2(cr)$.

The dissolution of AgCl(cr) in water at 298.15 K can be written as

$$\mathrm{AgCl(cr) \rightleftarrows Ag^{+}(aq) + Cl^{-}(aq)} \tag{6}$$

for which the thermodynamic solubility product is $K(\mathrm{AgCl}) = a(\mathrm{Ag}^+)\cdot a(\mathrm{Cl}^-)$. A value of $K(\mathrm{AgCl}) = 1.8 \times 10^{-10}$ (on the molality scale) is available at 298.15 K from the careful study of Jonte and Martin [52-jon/mar]. They noted that the complexes $AgCl^0(aq)$ and $AgCl_2^-(aq)$ also were present in the water solution and in solutions containing low concentrations of chloride ion. Lietzke and Stoughton [57-lie/sto] suggested that the higher-order silver chloride complexes with three and four chlorides may be needed to explain the large increase in solubility of AgCl(cr) when higher concentrations of chloride salts or HCl(aq) are present.

The solubilities of AgCl(s) in solutions of (0.175 to 5.00) mol·dm^{-3} $CaCl_2$(aq) have been reported for temperatures around 298 K and exhibit an approximately 20-fold increase with increasing $CaCl_2$(aq) concentration [11-for, 21-for/col]. However, Jonte and Martin [52-jon/mar] noted that the method used for solubility determination in these earlier studies, determination of the silver concentration at which opalescence was detected [11-for, 21-for/col], yields values ca. 35% higher than equilibrium solubilities for AgCl(cr). Thus the reported "solubilities" [11-for, 21-for/col] are likely to be overestimated. Solubilities of AgCl(cr) in KCl(aq) solutions [42-gar/nob] suggest that the concentration of chloride produced by dissolution of AgCl(cr) in aqueous solutions of chloride salts is probably slightly lower than from dissolution of Hg_2Cl_2(cr), at least at low and intermediate concentrations of chloride. The corrections to the emfs of reversible cells saturated with AgCl will be slightly less than for solutions saturated with Hg_2Cl_2 and thus be negligible.

The solubility of calcium oxalate CaC_2O_4(cr) in water has been summarized by Linke [58-lin] and is between (4 and 7) × 10^{-5} mol·dm^{-3} at 298.15 K. No values were reported by Linke for its solubility in solutions of $CaCl_2$(aq), but measurements in solutions of other chloride salts indicate a significant salting-in effect. These data suggest that the molar solubilities of CaC_2O_4(cr) and Hg_2Cl_2(cr) in $CaCl_2$(aq) solutions will be quite similar in magnitude, and thus the correction to the emf of the cell with a CaC_2O_4(cr) electrode [59-sah] can also be neglected.

3.4.2. Results for Various Cells. In 1940 Robinson [40-rob] noted that his isopiestic results and water activities calculated from freezing temperature depression measurements were fairly consistent with each other, whereas activity coefficients of $CaCl_2$(aq) derived from three separate emf studies with cells containing a calcium amalgam electrode [25-luc, 29-fos, 30-sca/tef] were quite discrepant, with the differences increasing rapidly with concentration. Robinson concluded that the calcium amalgam electrode was probably not reversible.

One problem with the calcium amalgam electrode has already been described above, eq 4, and involves reaction of the calcium metal with water at the amalgam surface to produce $Ca(OH)_2$(aq). This alters the total Ca^{2+}(aq) concentration and the solution pH and depletes calcium from the electrode surface. However, this effect can be reduced significantly by use of streaming amalgam electrodes [30-sca/tef]. The emf measurements can also be disturbed by dissolved oxygen in the $CaCl_2$(aq) solutions, which causes direct oxidation of the calcium metal.

Lucasse [25-luc], Fosbinder [29-fos], and Scatchard and Tefft [30-sca/tef] did their emf experiments using a "double cell" of the type

$$\mathrm{Ag(cr)|AgCl(cr)|CaCl_2(aq,}m_\mathrm{r}\mathrm{)|Ca}_x\mathrm{Hg(l)|CaCl_2(aq,}m\mathrm{)|AgCl(cr)|Ag(cr)} \quad \text{(cell A)} \quad (7)$$

using streaming (flowing) amalgam electrodes. These emf determinations were made with two solutions of $CaCl_2$(aq), one with molality m_r which served as a reference solution. Thus their emf measurements were for a concentration cell without transference. Scatchard and Tefft compared their emfs to those of the other two studies and showed that, in general, the emfs were consistent to about ±1 mV with a few points deviating by from (2.0 to 2.6) mV.

Butler [68-but] reexamined emf measurements for various cells containing different aqueous electrolytes that yield standard potentials for the calcium amalgam electrode, reextrapolated these experimental emfs in a consistent manner to yield $E°$ values, and applied consistent corrections for liquid junction potentials, etc. Butler concluded that the standard potential of the calcium amalgam electrode in aqueous solutions is $E° = -(1.996 \pm 0.002)$ V. This uncertainty of 2 mV is too large for the emfs to yield accurate activity coefficients for $CaCl_2$(aq) solutions. The available emf measurements for cells containing $CaCl_2$(aq) were not always consistent nor were they of the highest quality. For example, Butler's values of $E°$ derived from the data of Fosbinder [29-fos] were scattered by over 1 mV and were systematically low, and those derived from the measurements of Drucker and Luft [26-dru/luf] were even more scattered.

Rard et al. [77-rar/hab] used the Gibbs−Duhem equation to derive osmotic coefficients for $CaCl_2$(aq) solutions from various emf studies. The resulting $\phi(CaCl_2)$ were generally consistent with values calculated by them from isopiestic and freezing temperature depression measurements. However, three of the four sets of emf values that were inconsistent with all other activity data involved calcium amalgam electrodes and showed systematic positive deviations for $\phi(CaCl_2)$. The emf data of Fosbinder [29-fos] and of Lucasse [25-luc] were extremely discrepant from the isopiestic and freezing temperature results, with the differences increasing rapidly with molality, whereas those of Scatchard and Tefft [30-sca/tef] showed deviations that initially increase with the molality of $CaCl_2$(aq) but then decrease. They [77-rar/hab] did not discuss the emf study of Drucker and Luft [26-dru/luf].

The $\phi(CaCl_2)$ derived from the emf measurements of Sahay [59-sah] for a cell of the "third kind" with a calcium oxalate electrode also showed large systematic deviations but in the opposite direction. The cell used by Sahay is

$$\mathrm{Pb}_x\mathrm{Hg(l?)|PbC_2O_4(s)|CaC_2O_4(s)|CaCl_2(aq,}m\mathrm{)|AgCl(cr)|Ag(cr)} \quad \text{(cell B)} \quad (8)$$

Sahay did not specify the concentration of lead in the amalgam. Thus it is not known whether the lead amalgam was unsaturated or saturated or whether it was single-phase or two-phase. A different type of cell of the "third kind" was used by Jakuszewski and Taniewska-Osińska [62-jak/tan]:

$$\mathrm{Pb(cr)|PbCO_3(s)|CaCO_3(s)|CaCl_2(aq,}m\mathrm{)|Hg_2Cl_2(cr)|Hg(l)} \quad \text{(cell C)} \quad (9)$$

It is impossible to judge the precision and accuracy of this study because the $CaCl_2$(aq) solution molalities and the emfs were not reported.

On the basis of the information presented in the preceding four paragraphs, it appears that the emfs reported in five of the studies [25-luc, 26-dru/luf, 29-fos, 30-sca/tef, 59-sah] are quite inaccurate due to electrode problems, and thus they are rejected. Masaki [32-mas] performed four emf measurements for dilute solutions of $CaCl_2$(aq) using a concentration cell with transference containing two calcium amalgam electrodes:

$$\mathrm{Ca}_x\mathrm{Hg(l)|CaCl_2(aq,}m_1\mathrm{)|CaCl_2(aq,}m_2\mathrm{)|Ca}_x\mathrm{Hg(l)} \quad \text{(cell D)} \quad (10)$$

Since these measurements were done at (303.15 ± 0.05) K rather than 298.15 K, and because of the general unreliability of the calcium amalgam electrode, these emfs were not analyzed.

Mussini and Pagella [71-mus/pag] studied emfs for the following cell

$$\mathrm{Pt(cr)|Ca}_x\mathrm{Hg(l)|CaCl_2(aq,}m\mathrm{)|AgCl(cr)|Ag(cr)|Pt(cr)} \quad \text{(cell E)} \quad (11)$$

where measurements were performed from (298.15 to 343.15) K. The amalgam concentration for the experiments at 298.15 K was fixed at a calcium mole fraction of $x = 0.003\,21$. Their experiments involved the use of flowing amalgams with the concentration of calcium in the amalgam being determined just before and just after the emf measurements. This appears to be the only accurate emf study for $CaCl_2$(aq) with a cell using a calcium amalgam electrode. However, the precision of their emfs is about ±0.4 mV, which is lower that for some of the emfs determined for concentration cells with transference; see below.

Four emf studies involved cells with a mercurous chloride/mercury metal electrode (calomel) [24-tam, 31-shi, 70-sha] or a concentration cell with transference using two calomel electrodes [32-mas]. The concentration cell used by Masaki [32-mas] is

$$\mathrm{Hg(l)|Hg_2Cl_2(cr)|CaCl_2(aq,}m_1\mathrm{)|CaCl_2(aq,}m_2\mathrm{)|Hg_2Cl_2(cr)|Hg(l)} \quad \text{(cell F)} \quad (12)$$

where a solution junction was present between the two solution compartments. The counter electrodes in Tamele's [24-tam] and Shibata's [31-shi] studies were calcium amalgam electrodes whereas Shatkay [70-sha] used a liquid membrane ion-exchange electrode. Tamele's and Shibata's cells were of the type

$$\mathrm{Ca}_x\mathrm{Hg(l)|CaCl_2(aq,}m\mathrm{)|Hg_2Cl_2(cr)|Hg(l)} \quad \text{(cell G)} \quad (13)$$

Tamele's measurements were done at (290 to 291) K, Shibata's at (288 to 291) K, Masaki's at (303.15 ± 0.05) K, and Shatkay's at (298.15 ± 0.1) K.

Hills and Ives [61-hil/ive] have reviewed the calomel electrode in detail. Although this electrode is now routinely used for emf measurements, this has not always been the case. They pointed out that in most of the studies prior to 1922, dissolved oxygen was assumed to affect the electrode potentials only at low chloride concentrations, whereas oxidation of mercury by dissolved oxygen to form Hg_2Cl_2(s) is now known to occur at all concentrations, thus making at least some of the earlier emf measurements of doubtful reliability. The calomel electrode also behaves rather erratically when a thick layer of Hg_2Cl_2(cr) is present on the mercury metal but is more stable and reproducible when only a thin layer of Hg_2Cl_2(cr) is present. Electrolytically generated calomel generally gives high potential readings which are very slow to "decay" to the equilibrium emfs and which are very prone to formation of a yellow oxychloride compound. Other difficulties with the calomel electrode are discussed by Hills and Ives. The methods and precautions necessary to prepare a reliable calomel electrode for accurate emf measurements were not worked out in detail until the 1950s, and the reliability of earlier emf measurements with this electrode can legitimately be questioned. Because of this, and because the emfs were not measured at 298.15 K, the earlier studies of Tamale [24-tam], Shibata [31-shi], and Masaki [32-mas] were not analyzed.

Emfs were reported in four studies for concentration cells with transference using pairs of silver chloride/silver electrodes. Lucasse [25-luc] performed measurements from (0.01 to 2.586) mol·kg^{-1} at (298.15 ± 0.01) K, Masaki [32-mas] from (0.00125 to 0.01) mol·dm^{-3} at 303.15 K, Shedlovsky and MacInnes [37-she/mac] from (0.001 815 3 to 0.096 540) mol·dm^{-3} at 298.15 K, and McLeod and Gordon [46-mcl/gor] from about (0.003 to 0.075) mol·kg^{-1} at (288.15, 298.15, and 308.15) K. The electrochemical cells used in these studies are

$$\mathrm{Ag(cr)|AgCl(cr)|CaCl_2(aq,}m_\mathrm{r}\mathrm{)|CaCl_2(aq,}m\mathrm{)|AgCl(cr)|Ag(cr)} \quad \text{(cell H)} \quad (14)$$

where m_r is a reference solution molality. The ratio of the activity of $CaCl_2$(aq) at the molality m to its activity at m_r is given by

$$\ln\{a(\mathrm{CaCl_2},m_\mathrm{r})/a(\mathrm{CaCl_2},m)\} = (2F/RT)\int_{E_\mathrm{r}}^{E}(\mathrm{d}E/t_+) \quad (15)$$

where t_+ is the cation transference number. The most reliable cation transference numbers for $CaCl_2$(aq) are those of Longsworth [35-lon] at 298.15 K and of Keenan et al. [45-ken/mcl] at (288.15, 298.15, and 308.15) K. Rard et al. [77-rar/hab] gave a least-squares representation of these t_+ at 298.15 K that is valid to 0.0985 mol·kg^{-1}. Since there are no more recent values of t_+ of equivalent or superior quality, their equation was accepted. The higher-molality results of Lucasse [25-luc] for cells with transference, m = (0.1612 to 2.586) mol·kg^{-1}, were not analyzed since accurate transference numbers are not available at these molalities. Molar concentrations reported in some of the emf studies [37-she/mac, 67-ros] were converted to molalities using the density equation reported by Rard and Miller [79-rar/mil]. Only the emfs measured at 298.15 K will be discussed here.

We note that Staples and Nuttall [77-sta/nut] reanalyzed the emfs of Lucasse [25-luc] from (0.1612 to 2.586) mol·kg^{-1} for cells with transference using the values of t_+ reported by Lucasse. However, since those t_+ were derived by Lucasse from the same emf measurements (along with the emfs for a cell without transference, using a calcium amalgam electrode, which both we and Staples and Nuttall judged to be unreliable), the calculations of Staples and Nuttall involved circular reasoning. Since Staples and Nuttall assigned the resulting relative activity coefficients zero weight in their least-squares fit, their final results were not compromised.

If the emfs for cells with transference are measured relative to a fixed reference solution molality, $E_\mathrm{r} = 0$ when $m = m_\mathrm{r}$. The integral in eq 15 can thus be rewritten as $\int_{\mathrm{Er}}^{E}(\mathrm{d}E/t_+) = \int_0^E(1/t_+ - 1/t_+')\mathrm{d}E + \int_0^E(\mathrm{d}E/t_+')$ where t_+' is the cation transference number at the reference solution molality. Equation 15 then becomes

$$\begin{aligned}\ln\{a(\mathrm{CaCl_2},m_\mathrm{r})/a(\mathrm{CaCl_2},m)\} &= (2F/RT)\left[\int_0^E(1/t_+ - 1/t_+')\mathrm{d}E + \int_0^E(\mathrm{d}E/t_+')\right] \\ &= (2F/RT)\left[\int_0^E(1/t_+ - 1/t_+')\mathrm{d}E + (E/t_+')\right] \quad (16)\end{aligned}$$

For Lucasse's [25-luc] emfs for cells with transference and with the emfs adjusted so that m_r = 0.080 53 mol·kg^{-1}, Rard et al. [77-rar/hab] obtained the least-squares equation

$$\int_0^E(1/t_+ - 1/t_+')\mathrm{d}E = 0.767\,971\,3E^{1.5} - 5.135\,592\,8E^{1.75} + 5.113\,399\,15E^{2.0} \quad (17)$$

Similarly, from the results of Shedlovsky and MacInnes [37-she/mac] with their emfs adjusted so that m_r = 0.097 003 mol·kg^{-1}, Rard et al. obtained

$$\int_0^E (1/t_+ - 1/t_+')\mathrm{d}E = 0.905\ 752\ 6E^{1.5} - 6.064\ 508\ 9E^{1.75} + 6.212\ 265\ 5E^{2.0} \quad (18)$$

These equations were accepted for this review. We note that Rard et al. did not report the least-squares parameters for eqs 17 and 18, but we have extracted them from their original computer printout.

Analysis of the emfs of McLeod and Gordon [46-mcl/gor] is slightly more complicated since their reference molality varied from experiment to experiment. Most of their reference molalities fall in the range (0.024 802 to 0.025 025) $\mathrm{mol \cdot kg^{-1}}$, with one value at 0.028 786 $\mathrm{mol \cdot kg^{-1}}$. This last measurement is somewhat discrepant from the other emfs, and the reference molality is possibly a misprint for $m_r = 0.024\ 786\ \mathrm{mol \cdot kg^{-1}}$, but being unsure of that we did not include this experiment in the evaluation of the first integral of eq 16.

We decided to recalculate the results of McLeod and Gordon [46-mcl/gor] to a constant reference molality of $m_r^* = 0.025\ \mathrm{mol \cdot kg^{-1}}$. Let E^* be the emf that would be obtained if a concentration cell were set up between one of the actual reference solutions of molality m_r and cation transference number t_+' and a solution with the selected constant reference molality having $m_r^* = 0.025\ \mathrm{mol \cdot kg^{-1}}$ and cation transference number t_+^*. Then, the following equation is obtained

$$\ln\{a(\mathrm{CaCl_2}, m_r^*)/a(\mathrm{CaCl_2}, m)\} = \ln\{a(\mathrm{CaCl_2}, m_r^*)/a(\mathrm{CaCl_2}, m_r)\} + \ln\{a(\mathrm{CaCl_2}, m_r)/a(\mathrm{CaCl_2}, m)\} = (2F/RT)\left[\int_0^{E^*} (1/t_+' - 1/t_+^*)\mathrm{d}E + (E^*/t_+^*) + \int_0^E (1/t_+ - 1/t_+')\mathrm{d}E + (E/t_+')\right] \quad (19)$$

Values of E are known for all of the experiments and t_+, t_+', and t_+^* can be calculated using the equation of Rard et al. [77-rar/hab]. However, E^* is not an experimentally determined quantity. Furthermore, since only one or two emfs were measured for any particular reference molality m', there will not be enough points to allow an analytical function to be obtained for $(1/t_+ - 1/t_+')$, which is required for our method of analysis. Thus, some approximations will be necessary to evaluate the right-hand side of eq 19.

For an equivalent reversible concentration cell without transference, the activity coefficients of Rard et al. [77-rar/hab] yield $E^* \le 0.26$ V for the reference molalities used by McLeod and Gordon [46-mcl/gor] excluding the dubious one. For the actual concentration cell with transference, the emfs are smaller than for a cell without transference, so it is likely that $E^* \le 0.15$ V. The t_+' and t_+^* are very close in numerical value: $t_+^* = 0.4151_9$ and $0.4151_8 \le t_+' \le 0.4152_7$. Consequently, $\int_0^{E^*}(1/t_+' - 1/t_+^*)\mathrm{d}E + (E^*/t_+^*) = \int_0^{E^*}(\mathrm{d}E/t_+') \approx E^*/t_+^*$, where $E^*/t_+^* \le 0.4$ mV. For four of the experiments m_r is very close to m_r^* so E^*/t_+^* will be significantly smaller than 0.4 mV. Clearly, $\int_0^{E^*}(1/t_+' - 1/t_+^*)\mathrm{d}E + (E^*/t_+^*) \ll \int_0^{E}(1/t_+ - 1/t_+')\mathrm{d}E + (E/t_+')$, and the first two terms inside the square brackets of eq 19 can be neglected.

The quantity that needs to be evaluated is thus $\int_0^{E}(1/t_+ - 1/t_+')\mathrm{d}E + (E/t_+')$. Any particular reference solution of molality m_r was used for only one or two emf measurements. Clearly, there are not enough experimental points to evaluate the coefficients of equations of the form of eqs 17 and 18 directly. However, since t_+' and t_+^* are nearly equal, $\int_0^{E}(1/t_+ - 1/t_+^*)\mathrm{d}E + (E/t_+')$ should be an excellent approximation for $\int_0^{E}(1/t_+ - 1/t_+')\mathrm{d}E + (E/t_+')$. The "working equation" for analyzing the emfs of Mc Leod and Gordon [46-mcl/gor] then becomes

$$\ln\{a(\mathrm{CaCl_2}, m_r^*)/a(\mathrm{CaCl_2}, m)\} \approx (2F/RT)\left[\int_0^E (1/t_+ - 1/t_+^*)\mathrm{d}E + (E/t_+')\right] \quad (20)$$

Some of the solutions studied by McLeod and Gordon [46-mcl/gor] had molalities higher than m_r^*, and some were lower; as a consequence the experimental emfs have both positive and negative values. Polynomial equations like eqs 17 are 18 cannot be used when the emf is negative. Consequently, 0.015 V was added to each emf so that all would have positive values. The integral in eq 20 then becomes

$$\int_0^E (1/t_+ - 1/t_+^*)\mathrm{d}E = \int_{0.015}^{E+0.015} (1/t_+ - 1/t_+^*)\mathrm{d}(E + 0.015) = 0.000\ 591\ 4 - 0.086\ 767E^* - 0.278\ 074\ 7(E^*)^{1.5} + 1.410\ 202\ 9(E^*)^{1.75} + 4.017\ 298(E^*)^{2.0} - 7.488\ 007\ 6(E^*)^{2.25} \quad (21)$$

where the numerical coefficients were obtained from a least-squares analysis of the emfs of McLeod and Gordon excluding the one experiment with the discrepant reference solution molality. In principle, it should be possible to estimate E^* once an accurate thermodynamic model has been obtained for $\mathrm{CaCl_2(aq)}$ and thus to refine the approximation used in obtaining and evaluating eq 20. Given the very small size of these corrections and the large amount of activity data in the critically assessed database, this refinement would have an insignificant effect on the final recommended results and was therefore neglected. However, slightly lower weights were assigned to the data of McLeod and Gordon because of the approximations used.

Three emf studies have been reported at 298.15 K using a calcium-ion responsive liquid ion-exchange electrode [67-ros, 70-sha, 74-bri/lil]. This electrode consists of a solution of calcium didecylphosphate in di-*n*-octylphenylphosphonate; both substances are nearly insoluble in water. The cells used by Ross [67-ros] and by Shatkay [70-sha] were of the type

$$\mathrm{Ca(II)\ ISE|CaCl_2(aq,}m\mathrm{)|AgCl(cr)|Ag(cr)} \quad \text{(cell I)} \quad (22)$$

where Ca(II) ISE denotes the calcium ion "selective" electrode. A more complicated double-cell arrangement was used by Briggs and Lilley [74-bri/lil]

$$\mathrm{Ag(cr)|AgCl(cr)|CaCl_2(aq,}m_r\mathrm{)|Ca(II)\ ISE|CaCl_2(aq,}m\mathrm{)|AgCl(cr)|Ag(cr)} \quad \text{(cell J)} \quad (23)$$

which amounts to a concentration cell without transference. This double-cell arrangement, along with pairing of solutions close in concentration, allowed Briggs and Lilley to eliminate the asymmetry potential of the Ca(II) ISE. This asymmetry potential was present but not corrected for in the earlier two studies. The emf of cell I is given by

$$E = \text{“}E^\circ\text{”} - (RT/2F)\ln\{a(\mathrm{CaCl_2}, m)\} \quad (24)$$

where "E°" does not have the same meaning as the standard potential of a more traditional electrode system. (It depends on the molality of the $\mathrm{CaCl_2(aq)}$ solution used to "fill" the electrode and on the asymmetry potential, it slowly changes with time, etc.) In contrast, for cell J

$$\Delta E = (RT/2F)\ln\{a(\mathrm{CaCl_2}, m_r)/a(\mathrm{CaCl_2}, m)\} \quad (25)$$

Briggs and Lilley referred to ΔE as a transfer potential, and it has the advantage that "E°" has been eliminated.

This approach used by Briggs and Lilley thus eliminates one of the major uncertainties introduced by using a Ca(II) ISE.

The emf measurements of Ross [67-ros] extend from (8.8×10^{-6} to 4.488) mol·kg^{-1}, of Shatkay [70-sha] from (1.00×10^{-5} to 3.11) mol·kg^{-1}, and Briggs and Lilley [74-bri/lil] from (0.001 027 5 to 0.295 890) mol·kg^{-1}. Shatkay's analysis of his own emfs indicates general agreement with other published studies for $\mathrm{CaCl_2(aq)}$ for molalities at and above 5.00×10^{-4} mol·kg^{-1}, but systematic deviations occurred at lower molalities which Shatkay attributed to some kind of electrode failure. Thus emfs for solutions with molalities $\le 5.00 \times 10^{-4}$ mol·kg^{-1} were not reanalyzed. We made a comparison of these emfs with the better-quality emfs from other cell types, which indicated that the emfs of Ross were very imprecise and inaccurate; they were consequently given weights of zero in the least-squares fits. Ross's emfs for molalities of (0.000 885 6 to 0.8856) mol·kg^{-1} were scattered by about ± 1.5 mV and at the two higher molalities were discrepant by (14 to 36) mV with one point being high and the other low. The emfs of Shatkay show a systematic skewing of about 1.5 mV between high and low molalities and were rather scattered, and thus were given a low weight. In contrast, the emfs of Briggs and Lilley are of very high quality.

The remaining sets of emfs were measured with cells with salt bridges containing solutions of either KCl at various concentrations or 1.0 mol·dm^{-3} $\mathrm{KNO_3}$ [26-dru/luf, 32-has/jel, 70-sha]. A comparison of emfs for two different cells with these two different salt bridge electrolytes [70-sha] indicated good agreement between emfs in some cases, whereas for other solutions of $\mathrm{CaCl_2(aq)}$ the emfs differed by (3.0 to 5.3) mV. The uncertainty in the emfs introduced by using salt bridges yields unacceptably large errors and uncertainties, and these data were thus not included in the final database. For completeness, the cells of this type were

$$\mathrm{Ca}_x\mathrm{Hg(l)|CaCl_2(aq,}m\mathrm{)|KCl\ SB|KCl(aq)|Hg_2Cl_2(cr)|Hg(l)} \quad \text{(cell K)} \tag{26}$$

where the KCl(aq) concentration was 1.0 mol·dm^{-3} [26-dru/luf] and SB denotes a salt bridge

$$\mathrm{Ag(cr)|AgCl(cr)|CaCl_2(aq,}m\mathrm{)|KCl\ SB|KCl(aq)|Hg_2Cl_2(cr)|Hg(l)} \quad \text{(cell L.a)} \tag{27}$$

where the KCl(aq) concentration was 0.1 mol·dm^{-3} [32-has/jel] or saturated KCl [70-sha]

$$\mathrm{Ag(cr)|AgCl(cr)|CaCl_2(aq,}m\mathrm{)|KNO_3\ SB|KCl(aq)|Hg_2Cl_2(cr)|Hg(l)} \quad \text{(cell L.b)} \tag{28}$$

where the $\mathrm{KNO_3(aq)}$ concentration was 1.0 mol·dm^{-3} and the silver chloride plus silver electrode was presumably in a saturated KCl(aq) solution [70-sha]

$$\mathrm{Ca(II)\ ISE(l)|CaCl_2(aq,}m\mathrm{)|KCl\ SB|KCl(aq)|AgCl(cr)|Ag(cr)} \quad \text{(cell M.a)} \tag{29}$$

where saturated KCl(aq) was used [70-sha], and

$$\mathrm{Ca(II)\ ISE(l)|CaCl_2(aq,}m\mathrm{)|KNO_3\ SB|KCl(aq)?|AgCl(cr)|Ag(cr)} \quad \text{(cell M.b)} \tag{30}$$

where the silver chloride plus silver electrode was presumably in a saturated KCl(aq) solution [70-sha].

Table 7 contains the critically assessed emfs for concentration cells with and without transference for all of the data sets at 298.15 K that were assigned nonzero weights. These emfs correspond to those given by eq 25, where results for concentration cells with transference were converted to emfs for the equivalent concentration cell without transference. The emfs for nonconcentration cells are not listed here since they can be obtained from the original publications with little or no recalculation.

Table 7. Values of the Emf for Concentration Cells with and without Transference Containing Aqueous $\mathrm{CaCl_2}$ Solutions of Molality *m* and Reference Solutions of Molality m_r at 298.15 K

$m(\mathrm{CaCl_2})$/(mol·kg^{-1})	ΔE ^{a}/V	relative weight	ref
Concentration Cells without Transference			
0.001 027 5	0.192 14	1.0	74-bri/lil
0.003 251 9	0.151 05	1.0	74-bri/lil
0.010 165	0.111 69	1.0	74-bri/lil
0.033 081	0.072 64	1.0	74-bri/lil
0.099 104	0.036 96	1.0	74-bri/lil
0.295 890^b	0.0	1.0	74-bri/lil
Concentration Cells with Transference			
0.010 00	0.068 81$_5$	0.2	25-luc
0.015 47	0.054 54	0.2	25-luc
0.020 06	0.045 63	0.2	25-luc
0.039 55	0.023 29$_5$	0.2	25-luc
0.049 66	0.015 95	0.2	25-luc
0.080 53^c	0.0	0.2	25-luc
0.001 820 7	0.134 136	1.0	37-she/mac
0.006 110 0	0.091 486	1.0	37-she/mac
0.009 613 4	0.076 014	1.0	37-she/mac
0.024 248	0.045 146	1.0	37-she/mac
0.037 662	0.030 783$_5$	1.0	37-she/mac
0.050 193	0.021 441	1.0	37-she/mac
0.097 003^d	0.0	1.0	37-she/mac
0.003 315 5	0.068 620	0.4	46-mcl/gor
0.005 859 5	0.048 664	0.4	46-mcl/gor
0.006 369 5	0.045 883	0.4	46-mcl/gor
0.009 482	0.032 352	0.4	46-mcl/gor
0.011 342	0.025 993	0.4	46-mcl/gor
0.014 883	0.016 885	0.4	46-mcl/gor
0.025^e	0.0	0.4	46-mcl/gor
0.034 804	−0.010 969	0.4	46-mcl/gor
0.047 946	−0.021 370	0.4	46-mcl/gor
0.060 084	−0.023 888	0.0	46-mcl/gor
0.064 530	−0.031 025	0.4	46-mcl/gor
0.074 929	−0.035 706	0.4	46-mcl/gor

^{a} $\Delta E = (RT/2F)\ \ln\{a(\mathrm{CaCl_2},m_\mathrm{r})/a(\mathrm{CaCl_2},m)\}$ where m_r is the molality of the reference solution. This is the emf that would be observed for a concentration cell without transference containing solutions of $\mathrm{CaCl_2(aq)}$ at these two molalities in the electrode compartments. For a concentration cell with transference, this is the emf for an equivalent concentration cell without transference as calculated from the observed emfs for cells with transference and the transference numbers of $\mathrm{CaCl_2(aq)}$. ^{b} Briggs and Lilley [74-bri/lil] generally determined the emfs for the various solutions relative to the two solutions whose molalities were next closest (both higher and lower) to the one being investigated. Thus all but the lowest molality solution served as a reference solution at least once. The experimental emfs were combined together by us in "piggy back" fashion to reference all emfs to the highest molality solution. ^{c} Lucasse [25-luc] measured emfs for a concentration cell with transference relative to the 0.01 mol·kg^{-1} reference solution. Although these measurements extend from (0.01 to 2.586) mol·kg^{-1}, the high-molality results were not analyzed because of the lack of reliable transference numbers. The experimental emfs were combined together to yield results for an equivalent cell with a reference solution molality of 0.080 53 mol·kg^{-1}. ^{d} Shedlovsky and MacInnes [37-she/mac] measured emfs for a concentration cell with transference relative to the 0.050 193 mol·kg^{-1} reference solution. They were combined together to make all emfs relative to the highest molality solution. ^{e} McLeod and Gordon [46-mcl/gor] used reference solutions with molalities that varied from (0.024 802 to 0.025 025) mol·kg^{-1}, with one reported reference solution molality of 0.028 786 mol·kg^{-1} (possibly a misprint for 0.024 786 mol·kg^{-1}). The tabulated values of emfs correspond to an equivalent concentration cell without transference with a fixed reference solution molality of 0.025 mol·kg^{-1}.

3.5. Stability Constants for the Ion Pair $CaCl^+(aq)$. There are several reports that the following three association equilibria occur in $CaCl_2(aq)$ solutions:

$$Ca^{2+}(aq) + Cl^-(aq) \rightleftarrows CaCl^+(aq) \tag{31}$$

$$CaCl^+(aq) + Cl^-(aq) \rightleftarrows CaCl_2^0(aq) \tag{32}$$

and

$$CaCl_2^0(aq) + Cl^-(aq) \rightleftarrows CaCl_3^-(aq) \tag{33}$$

The corresponding thermodynamic association constants, respectively, are given by the activity products:

$$K(CaCl^+) = a(CaCl^+)/a(Ca^{2+})\cdot a(Cl^-) \tag{34}$$

$$K(CaCl_2^0) = a(CaCl_2^0)/a(CaCl^+)\cdot a(Cl^-) \tag{35}$$

and

$$K(CaCl_3^-) = a(CaCl_3^-)/a(CaCl_2^0)\cdot a(Cl^-) \tag{36}$$

The equivalent concentration products (i.e., without the activity coefficient factors) are denoted here as $K'(CaCl^+)$, $K'(CaCl_2^0)$, and $K'(CaCl_3^-)$.

Roselle and Baumgartner [95-ros/bau] reported evidence for the formation of the $CaCl_3^-(aq)$ complex from mineral dissolution studies under supercritical conditions. Similarly, Gunter and Eugster [78-gun/eug] and Popp and Frantz [79-pop/fra] evaluated the Gibbs energy of formation of $CaCl_2^0(aq)$ at supercritical conditions from the dissolution of wollastonite $\{CaSiO_3(cr)\}$ in acidic chloride solutions. Luce et al. [85-luc/cyg] derived values of $K^*(CaCl_2^0) = 1/\{K'(CaCl^+)\cdot K'(CaCl_2^0)\}$ from equilibria studies of various mineral pairs in chloride solutions at temperatures from (773 to 973) K and pressure of 200 MPa. Inasmuch as the temperature and pressure range of these studies considerably exceed those being analyzed in the present review, they will not be reanalyzed.

Elgquist and Wedborg [75-elq/wed] studied the variation of the solubility of gypsum $\{CaSO_4\cdot 2H_2O(cr)\}$ in electrolyte solutions of various compositions at an ionic strength of 0.7 $mol\cdot dm^{-3}$ at 298.15 K, Ramette [86-ram] the variation of the solubility of calcium iodate $\{Ca(IO_3)_2\cdot 6H_2O(s)\}$ in mixtures of NaCl and $NaClO_4$ at an ionic strength of 5.0 $mol\cdot dm^{-3}$ at 298.15 K, and Williams-Jones and Seward [89-wil/sew] the solubility of AgCl(cr) in aqueous mixtures of $CaCl_2$ and HCl at an ionic strength of (0.30 to 3.00) $mol\cdot dm^{-3}$ at (373 to 633) K. Values of $K'(CaCl^+)$ were determined in all three studies, of $K'(CaCl_2^0)$ in two studies [86-ram, 89-wil/sew], and $K'(CaCl_3^-)$ in one [86-ram]. However, as acknowledged by Ramette, at the high ionic strength of 5.0 $mol\cdot dm^{-3}$ it is not possible to unambiguously distinguish medium effects (changes in activity coefficients with changes in the ionic media at constant ionic strength) from the effects of complex formation. Thus the derived values for the three formation constants from that study may not be meaningful.

Values of $K'(CaCl^+)$ have also been determined using potentiometric measurements, with an "ion-selective" electrode being used in each case [75-suc/cad, 78-jon/pyt, 82-maj/stu]. The various types of "ion-selective" electrodes respond not only to a single target ion but also respond in lesser degrees to other ions present in a solution, and consequently may require corrections for the presence of other electrolytes. Thus the term ion-responsive electrode may be a better description. These potentiometric determinations of $K'(CaCl^+)$ were made with electrolyte mixtures at ionic strengths ≤ 1 $mol\cdot kg^{-1}$, which are low enough that a lack of complete selectivity is not likely to produce a serious error in the measurement.

Šůcha et al. [75-suc/cad] reported $K'(CaCl^+)$ from (288.15 to 333.15) K at (10 to 15) K intervals. According to the heading of their data table the measurements were done at $I = 0.1$ $mol\cdot kg^{-1}$, but in the abstract and experimental section it was given as $I = 1$ $mol\cdot kg^{-1}$, which is presumably correct. Majer and Štulík [82-maj/stu] reported $K'(CaCl^+)$ at $I = 1$ $mol\cdot kg^{-1}$ from (288.15 to 358.15) K at (10 to 20) K intervals. In both studies $NaNO_3$ was used to adjust the ionic strength. The values of $K'(CaCl^+)$ were found to increase with increasing temperature. However, Šůcha et al. derived an enthalpy of association of $-(1.719 \pm 1.004)(4.184) = -(7.192 \pm 4.201)$ $kJ\cdot mol^{-1}$ whereas Majer and Štulík obtained $(1.16)(4.184) = 4.85$ $kJ\cdot mol^{-1}$. These two enthalpies of association differ in sign, and the value of Šůcha et al. is obviously incorrect. A slightly larger enthalpy of association of (7 ± 5) $kJ\cdot mol^{-1}$ was reported by de Robertis et al. [87-der/rig] from the analysis of the temperature dependence of published values of $\ln K'(CaCl^+)$. This value and that of Majer and Štulík do agree within their large uncertainty limits. Majer and Štulík described the concentrations of the stock solutions of $Ca(NO_3)_2(aq)$ and $NaNO_3(aq)$ used to prepare the mixtures as being "1*M*" and "2*M*" but then described the ionic strength as being adjusted to "1*m*" with $NaNO_3$. It is thus not clear if their reported ionic strengths are in molarity or molality units.

The emf measurements for mixtures of $CaCl_2$ and HCl reported by Johnson and Pytkowicz [78-joh/pyt] were referenced as being from an "in preparation" report by Plath, Johnson, and Pytkowicz, which has apparently never been published. Fortunately, reference 78-joh/pyt reported the detailed solution compositions (total chloride ion, total hydrogen ion, and $CaCl^+$ ion concentrations), and from charge balance considerations the initial concentrations of $CaCl_2$ can be deduced. Although this study was restricted to 298.15 K, it was done with 12 different "effective" ionic strengths ranging from (0.3676 to 0.7403) $mol\cdot dm^{-3}$. Their molar concentrations were converted to molalities using the density equations given by Söhnel and Novotný [85-soh/nov] for the binary solutions, assuming that Young's rule [95-mil] was valid for the mixtures.

Values of $K(CaCl^+)$ have also been derived from measured activity coefficients and from calorimetric measurements. Allakhverdov [85-all] obtained $K(CaCl^+) = 1.04 \pm 0.08$ at 298.15 K by fitting available activity coefficients for $CaCl_2(aq)$ from (0.0064 to 0.5) $mol\cdot kg^{-1}$ to a modified Debye−Hückel type of model and assuming that all deviations from this model were due to association to form $CaCl^+(aq)$, and de Robertis et al. [87-der/rig] reanalyzed various published values of $K'(CaCl^+)$ to obtain $K(CaCl^+) = 2.5 \pm 0.6$ at 298.15 K.

Gillespie et al. [92-gil/osc] derived values of $K(CaCl^+)$ from (523 to 598) K from measurements of the enthalpy of mixing of HCl(aq) with mixtures of $CaCl_2$ and HCl using titration calorimetry. Values of the enthalpy of reaction $\Delta_r H_m^\circ$ and the equilibrium constant K for the reaction are evaluated simultaneously from titration calorimetry information, by nonlinear least-squares analysis. However, unless the values of the equilibrium constant are relatively large, of the order of 10^2 or larger (which is not the case for $CaCl_2(aq)$ solutions), the derived reaction enthalpy and equilibrium constant are highly covariant and usually quite sensitive to the errors in the calorimetric measurements. The resulting least-squares values $\Delta_r H_m^\circ$ and K then depend

Table 8. Summary of the Published Studies Yielding Values of the Formation Constants for the Aqueous Monochloro and Dichloro Complexes of Ca(II), $K'(\mathrm{CaCl}^+)$ and $K'(\mathrm{CaCl}_2^0)$, as Functions of Temperature and Ionic Strength[a]

method	I(m) or I(c)	T/K	p/MPa	$K'(\mathrm{CaCl}^+)$[b]	ref
solub[c]	0.7 (c)	298.15	0.1	1.20 (c)	75-elg/wed
ISE	1.0 (m)	288.15−333.15	0.1	0.76_5 (m)	75-suc/cad
solub[c]	variable	995−1115	100−200		78-gun/eug
ISE	0.368−0.740 (c)	298.15	0.1	2.24 (c)	78-joh/pyt
solub[c]	variable	698−875	100−200		79-pop/fra
cond	0.003−0.015 (m)	298.15−873	0.1−400	5.6×10^{-4} (m)[d]	82-fra/mar
ISE	1.0 (m?)	288.15−358.15	0.1	0.68 (m?)	82-maj/stu
activ	0.0192−1.5 (m)	298.15	0.1	1.04 (m)	85-all
phase	variable	773−973	200		85-luc/cyg
calor	0.0017−0.1 (m)	523	20		85-sim/bus
solub[c]	5.0 (c)	298.15	0.1	0.68 (c)	86-ram
lit	0−1.0 (c)	283.15−318.15	0.1	0.40 (c)	87-der/rig
solub[c]	0.30−3.00 (m)	373−633	sat vp		89-wil/sew
calor	≈0.7−2.8 (m)	523−598	10.3−13.2		92-gil/osc
solub[c]	0.006−6.84 (m)[e]	673−873	200		95-ros/bau

[a] For the methods of determination of $K'(\mathrm{CaCl}^+)$ or $K'(\mathrm{CaCl}_2^0)$: "activ" denotes that it was calculated from activity coefficients, "lit" from reanalysis of literature values, "solub" from the variation of solubility of a sparingly soluble electrolyte with added calcium or chloride ions, "cond" from electrical conductivity measurements, "calor" from calorimetric measurements, "ISE" from potentiometric measurements with an ion-selective electrode, and "phase" from determination of the composition of a solution in contact with various calcium-containing minerals in phase equilibrium. Ionic strengths were reported in either units of molality (denoted by m), $\mathrm{mol{\cdot}kg^{-1}}$, or molarity (denoted by c), $\mathrm{mol{\cdot}dm^{-3}}$. [b] The reported values of $K'(\mathrm{CaCl}^+)$ in this column are for 298.15 K and 0.101 325 MPa only. Units of $K'(\mathrm{CaCl}^+)$ for the molal concentration scale (m) are $\mathrm{kg{\cdot}mol^{-1}}$ and for the molar scale (c) are $\mathrm{dm^3{\cdot}mol^{-1}}$. The value from Johnson and Pytkowicz [78-jon/pyt] refers to an effective ionic strength of 0.6 $\mathrm{mol{\cdot}dm^{-3}}$, whereas the value from the study of de Robertis et al. [87-der/rig] was extrapolated by them to infinite dilution and is thus a thermodynamic constant. [c] Elgquist and Wedborg [75-elg/wed] studied the solubility of gypsum ($\mathrm{CaSO_4{\cdot}2H_2O}$) in aqueous solutions of chloride, perchlorate, and sulfate salts; Gunter and Eugster [78-gun/eug] and Popp and Frantz [79-pop/fra] studied the solubility of wollastonite ($\mathrm{CaSiO_3}$) in $\mathrm{CaCl_2}$; Ramette [86-ram] analyzed published solubilities of calcium iodate in mixtures of NaCl and $\mathrm{NaClO_4}$; Williams-Jones and Seward [89-wil/sew] studied the solubility of AgCl in mixtures of $\mathrm{CaCl_2}$ and HCl; Roselle and Baumgartner [95-ros/bau] studied the solubility of synthetic anorthite ($\mathrm{CaAl_2Si_2O_8}$) in HCl solutions. In many of the higher-temperature mineral-dissolution studies, it was not possible to extract a unique value of $K'(\mathrm{CaCl}_2^0)$ or $K^*(\mathrm{CaCl}_2^0)$, but only a solubility product that depended on the activity ratio $a(\mathrm{CaCl}_2^0)/a(\mathrm{HCl}^0)^2$. Although Williams-Jones and Seward performed solubility experiments from (373 to 633) K, they were unable to derive values of $K(\mathrm{CaCl}^+)$ except at 423 K because of the small degree of association at 373 K and because of the predominance of CaCl_2^0(aq) above 473 K. [d] This value of $K(\mathrm{CaCl}^+) = 5.6 \times 10^{-4}$ at 298.15 K was calculated using eq 43 of Holmes et al. [94-hol/bus], which, in turn, was based on the electrical conductivity measurements of Frantz and Marshall [82-fra/mar]. However, eq 25 of Frantz and Marshall yields $K(\mathrm{CaCl}^+) = 4.3 \times 10^{-6}$ at 298.15 K and 0.1 MPa pressure, which is smaller by 2 orders of magnitude. [e] Total molality of chloride in the solutions at equilibrium.

strongly on the initial estimates, and different estimates may yield significantly different final results [85-mul/ype, 97-arc]. Thus the $K(\mathrm{CaCl}^+)$ values derived by Gillespie et al. [92-gil/osc] are not unique.

Simonson et al. [85-sim/bus] studied the enthalpies of dilution of (0.0100, 0.0500, and 0.1000) $\mathrm{mol{\cdot}kg^{-1}}$ $\mathrm{CaCl_2}$(aq) at 573 K and 20 MPa and derived a value of $K(\mathrm{CaCl}^+)$ from these results.

Frantz and Marshall [82-fra/mar] performed electrical conductivity measurements for $\mathrm{CaCl_2}$(aq) solutions from (298 to 873) K at various pressures, including the conductivity at 298.15 K and 0.1 MPa. From these results they derived equations for $K(\mathrm{CaCl}^+)$ and $K(\mathrm{CaCl}_2^0)$ valid from (673 to 873) K for a wide range of solvent densities. Formation constants were not reported at lower temperatures, presumably because the small extent of ion association present under this condition makes this method unreliable. Extrapolation of one of their equations to 298.15 K and 0.1 MPa gives $K(\mathrm{CaCl}^+) = 4.3 \times 10^{-6}$, which is about 5−6 orders of magnitude smaller that the reported values of $K(\mathrm{CaCl}^+)$ at 298.15 K from low-temperature measurements as listed in Table 8 and as discussed above. Holmes et al. [94-hol/bus] have refitted the $K(\mathrm{CaCl}^+)$ of Frantz and Marshall to a different temperature dependent equation that yields $K(\mathrm{CaCl}^+) = 5.6 \times 10^{-4}$ at 298.15 K and 0.1 MPa, which is larger than the value reported by Frantz and Marshall by 2 orders of magnitude. The difference arises because a rather long temperature extrapolation is required to calculate these values from the high-temperature experiments.

Values of $K(\mathrm{CaCl}^+)$ and/or $K(\mathrm{CaCl}_2^0)$ have been reported in several other high-temperature/high-pressure studies. Reported values of $K(\mathrm{CaCl}_2^0)$ agree to about 1 order of magnitude with the values of Frantz and Marshall [82-fra/mar] under comparable temperature and pressure conditions [85-luc/cyg]. Other values determined at somewhat lower [89-wil/sew] temperatures of (423 to 633) K extrapolate smoothly into the Frantz and Marshall results. Gillespie et al.'s [92-gil/osc] flow calorimetry measurements yield values of $\log_{10} K(\mathrm{CaCl}^+)$ from (523 to 598) K that agree to about 0.6 to 1.3 with values obtained from extrapolation using Frantz and Marshall's equation, with the difference increasing as the temperature decreases. However, a linear extrapolation of the experimental $\log_{10} K(\mathrm{CaCl}^+)$ values of Gillespie et al. to 298.15 K yields a value within 1.5 of that calculated with the equation of Holmes et al. [94-hol/bus], which was based on refitting the $K(\mathrm{CaCl}^+)$ values of Frantz and Marshall to a different temperature dependent equation. It is likely that this approximate consistency is accidental, however, because of the large uncertainties in equilibrium constants derived from enthalpy titration experiments as discussed above. Values of $K(\mathrm{CaCl}^+)$ and $K(\mathrm{CaCl}_2^0)$ from the studies cited in this paragraph only agree within 2 orders of magnitude, probably because of uncertainties affecting their derivation and measurement errors.

There is obviously a considerable inconsistency between the lower temperature determinations of $K(\mathrm{CaCl}^+)$, Table 8, and the higher temperature measurements described in the previous two paragraphs. The conductivity study of Frantz and Marshall [82-fra/mar] involved solutions of $\mathrm{CaCl_2}$(aq), whereas most of the other studies involved mixed electrolyte solutions. Most of the lower temperature studies were done in mixed electrolyte solutions at one value of the stoichiometric ionic strength, and activity coefficients were assumed to be independent of the ratio of the electrolytes present. Given the relatively small amount of ionic association present in these solutions at lower temperatures, it is quite possible that the resulting values of $K(\mathrm{CaCl}^+)$ include contributions from the misinterpretation of "ionic medium effects" and not ionic association. This is described briefly above.

The extraction of values of the thermodynamic association constant $K(\mathrm{CaCl}^+)$ from Gibbs energy measurements (e.g., solubility or potentiometry) or other techniques requires the use of estimated activity coefficients for the various ionic species assumed to be present. A particular kind of nonideal behavior is then assumed to apply to the various ions, and differences between the observed value of the measured property and the prediction are attributed to ionic association. When ionic association is fairly weak, as is the case for $\mathrm{CaCl_2(aq)}$ solutions at lower temperatures, derived values of the association constant are highly dependent on the assumed functional form of the nonideal behavior for activity coefficients. That is, derived $K(\mathrm{CaCl}^+)$ values depend strongly on whether the ionic activity coefficients are calculated with the Debye−Hückel limiting law, the Debye−Hückel equation, an extended Debye−Hückel function, the Pitzer equation, etc. The $K(\mathrm{CaCl}^+)$ values will also depend, within the same model, on the value chosen for the ion size parameter. Consequently, values of $K(\mathrm{CaCl}^+)$ obtained from measurements at lower temperatures including 298.15 K are ambiguous, model dependent, and probably not meaningful. Ionic association becomes greater at higher temperatures, and consequently values of $K(\mathrm{CaCl}^+)$ do not depend as strongly on the assumed nonideal behavior.

In view of the above considerations, we consider values of $K(\mathrm{CaCl}^+)$ from measurements on binary solutions of $\mathrm{CaCl_2(aq)}$ to be less ambiguous than those for mixed electrolytes, since it is impossible to separate the effects of complex formation from ionic medium effects when the extent of complex formation is small. In addition, values of $K(\mathrm{CaCl}^+)$ determined from measurements of properties of binary solutions of $\mathrm{CaCl_2(aq)}$ at high temperatures should be more reliable than values obtained for $T < 373$ K since they are less sensitive to the model used for calculating ionic activity coefficients. The best present estimate for $K(\mathrm{CaCl}^+)$ appears to be from the equation of Holmes et al. [94-hol/bus], although the value obtained at 298.15 K is uncertain by at least 2 orders of magnitude, partly because of uncertainties resulting from the long extrapolation from higher-temperature data.

3.6. Direct Structural Information. Direct structural information about the interaction between the $\mathrm{Ca^{2+}(aq)}$ ion, the $\mathrm{Cl^-(aq)}$ ion, and water have been obtained using X-ray diffraction and neutron diffraction methods. Enderby et al. [87-end/cum] have reviewed the neutron diffraction method, and Ohtaki and Radnai [93-oht/rad] have reviewed various diffraction methods in detail and compared these results to various types of computer simulations. None of these measurements provide any evidence for contact (inner sphere) interactions between the calcium and chloride ions in solutions of $\mathrm{CaCl_2(aq)}$ at any of the concentrations studied, (1 to 14) $\mathrm{mol\cdot kg^{-1}}$, although these methods are not sensitive enough to detect the presence of a few percent of such complexes.

Primary (inner sphere) hydration numbers for the $\mathrm{Cl^-(aq)}$ ion from neutron and X-ray diffraction are fairly consistent at about 6 [87-end/cum, 93-oht/rad]. We note that smaller $\mathrm{Cl^-(aq)}$ primary hydration numbers were obtained for some salts at very high molalities where water sharing may be present and for some associated electrolytes such as $\mathrm{CuCl_2(aq)}$, $\mathrm{ZnCl_2(aq)}$, and $\mathrm{FeCl_3(aq)}$. In addition, there are a few studies that report larger primary hydration numbers of 8 to 9 for $\mathrm{Cl^-(aq)}$ at lower molalities of HCl(aq), LiCl(aq), or alkaline earth metal chlorides. Similar diffraction measurements for the hydration number of the $\mathrm{Ca^{2+}(aq)}$ ion in solutions of $\mathrm{CaCl_2(aq)}$ yield primary hydration numbers of about 10 at 1.0 $\mathrm{mol\cdot kg^{-1}}$, of about 7 at 2.8 $\mathrm{mol\cdot kg^{-1}}$, of 6.0 ± 0.5 from (4.5 to 9.2) $\mathrm{mol\cdot kg^{-1}}$, with a decrease to about 3.9 at 13.9 $\mathrm{mol\cdot kg^{-1}}$. This hydration number decrease with molality presumably is partially due to the onset of water sharing between ions when there is insufficient water present to independently fulfill the hydration requirements of the individual ions, and it implies that the calcium ion does not have a stable or well-defined hydration number.

Assuming primary hydration numbers for the chloride ion of ≈6 and of ≈10 for the calcium ion, then the ions in solutions of stoichiometric $\mathrm{CaCl_2(aq)}$ will start sharing their inner sphere hydration waters when the molality of $\mathrm{CaCl_2(aq)}$ exceeds $\approx\{1000\ \mathrm{g\cdot kg^{-1}}/18.0153\ \mathrm{g\cdot mol^{-1}}\}/\{2(6) + 10\} = 2.5\ \mathrm{mol\cdot kg^{-1}}$. A similar calculation using the lower primary hydration number of 6 for the calcium ion yields a molality of $\approx\{1000\ \mathrm{g\cdot kg^{-1}}/18.0153\ \mathrm{g\cdot mol^{-1}}\}/\{2(6) + 6\} = 3.1\ \mathrm{mol\cdot kg^{-1}}$. These molalities correspond to a concentration region where the "forced" onset of formation of outer sphere $\mathrm{CaCl^+(aq)}$ ion pairs will occur, even if they were not present in significant amounts at lower molalities.

Phutela and Pitzer [83-phu/pit] suggested that inner sphere calcium chloride complexes form above 5 $\mathrm{mol\cdot kg^{-1}}$ and, in analogy to the three structurally characterized forms of $\mathrm{CaCl_2\cdot 4H_2O(cr)}$, may exist with variable amounts of inner sphere waters of hydration. The formation of both outer and inner sphere chloride complexes may thus be contributing to the difficulties of representing the available activity data for $\mathrm{CaCl_2(aq)}$ with Pitzer's equation [73-pit/may], where complete dissociation of the electrolyte is assumed.

4. Representation of the Critically-Assessed $\mathrm{CaCl_2(aq)}$ Data at 298.15 K

4.1. Assignment of Weights. Relative weights w_r were assigned to each set of osmotic coefficients and emfs at 298.15 K as described in detail in the preceding sections. Values of $w_r = 0$ were assigned to a few outlying points from otherwise good data sets. Assignment of these weights was based on the internal consistency of each data set, on agreement between measurements of the same property from different laboratories, and on the types and sizes of errors expected for each experimental method. Tables 2−5 and 7 give a complete listing of these data sets along with the assigned values of w_r.

The precision to which the higher-quality osmotic coefficients of $\mathrm{CaCl_2(aq)}$ were determined by the isopiestic and direct vapor-pressure measurements is typically 0.001 to 0.003, whereas for the higher-quality emfs it is typically (0.0001 to 0.0004) V. Weights assigned to different data sets in the least-squares fits to thermodynamic models should also reflect the greater precision of the emf measurements. Consequently, the actual weight assigned to a particular data point was the product of its relative weight w_r times its property weight w_p. For $\phi(\mathrm{CaCl_2})$ at 298.15 K we assigned $w_p = 1$ for all fits and for emfs $w_p = 500$ for fits to larger molality ranges. However, for fits to more restricted molality ranges a value of $w_p = 100$ was generally used for emfs to avoid giving too much of the total weight to data below 0.1 $\mathrm{mol\cdot kg^{-1}}$. These values of w_p were chosen so that the contributions of $\phi(\mathrm{CaCl_2})$ and of emfs to the sum of the squares of the deviations, for the least-squares fits to various models, would be approximately proportional to the number of observations of each property given nonzero weights.

A variety of different equations, all of which are based on Pitzer's equation [91-pit], were used to model the osmotic and activity coefficients of $CaCl_2(aq)$ at 298.15 K and 0.1 MPa. Only one equation was found that could represent all of these critically-assessed data essentially to within experimental accuracy to high molalities. That equation is fairly complicated and is based on the use of Archer's extension of Pitzer's equation as generalized to include association equilibria [94-cle/rar]. However, it was also necessary to include additional terms containing various powers of the ionic molalities in order to accurately represent the experimental data above ca. 8 $mol \cdot kg^{-1}$. We refer to this equation as Archer's extension of Pitzer's equation with additional higher-order virial terms, and which we abbreviate as the AEPEWHOVT equation.

We present these equations in order of increasing complexity, starting with the original equation of Pitzer. To simplify the graphical presentation of the fits to the less complex equations and to give the results of several different fits on a single plot, we generally present those results as differences from the AEPEWHOVT equation rather than showing deviations of the individual data points.

4.2. Application of Pitzer's Binary Solution Equation and Its Extensions. Pitzer's equation [73-pit/may, 83-phu/pit, 91-pit], Archer's extension of Pitzer's equation [92-arc], and empirically extended versions of these equations can be written in the general form for the osmotic coefficient of $CaCl_2(aq)$

$$\phi - 1 = -|z_{Ca}z_{Cl}|A_\phi I_s^{1/2}/(1 + bI_s^{1/2}) + 2m(\nu_{Ca}\nu_{Cl}/\nu)B^{\phi}_{Ca,Cl} + 4m^2(\nu_{Ca}^{2}\nu_{Cl}z_{Ca}/\nu)C^{T\phi}_{Ca,Cl} + \sum_{i\geq 3} m^i D_i \qquad (37)$$

where ν_i denotes the number of ions of type i formed by dissociation of one molecule of $CaCl_2$, z_i their valence, and m the stoichiometric molality. For $CaCl_2(aq)$, $\nu_{Ca} = 1$, $\nu_{Cl} = 2$, $\nu = \nu_{Ca} + \nu_{Cl} = 3$, $z_{Ca} = +2$, $z_{Cl} = -1$, $b = 1.2$ $kg^{1/2} \cdot mol^{-1/2}$, and the ionic strength has the stoichiometric value $I_s = 3m$. The summation in powers of the molality represents the empirical extensions of Pitzer's equation. At 298.15 K, $A_\phi = 0.391\ 475$ $kg^{1/2} \cdot mol^{-1/2}$ was calculated from the Chebychev series of Clegg et al. [94-cle/rar], which was based on the critical evaluation by Archer and Wang [90-arc/wan]. The quantities $B^{\phi}_{Ca,Cl}$ and $C^{T\phi}_{Ca,Cl}$ are defined by

$$B^{\phi}_{Ca,Cl} = \beta^{(0)}_{Ca,Cl} + \beta^{(1)}_{Ca,Cl} \exp(-\alpha_{Ca,Cl} I_s^{1/2}) \qquad (38)$$

and

$$C^{T\phi}_{Ca,Cl} = C^{(0)}_{Ca,Cl} + C^{(1)}_{Ca,Cl} \exp(-\omega_{Ca,Cl} I_s^{1/2}) \qquad (39)$$

where α is usually assigned a value of 2.0 $kg^{1/2} \cdot mol^{-1/2}$ except for the divalent metal sulfates [91-pit]. Mean activity coefficients $\gamma_\pm$ of the electrolyte are then given by

$$\ln \gamma_\pm = -|z_{Ca}z_{Cl}|A_\phi\{I_s^{1/2}/(1 + bI_s^{1/2}) + (2/b)\ln(1 + bI_s^{1/2})\} + 2m(\nu_{Ca}\nu_{Cl}/\nu)[2\beta^{(0)}_{Ca,Cl} + 2(\beta^{(1)}_{Ca,Cl}/\alpha_{Ca,Cl}^{2}I_s)\{1 - (1 + \alpha_{Ca,Cl}I_s^{1/2} - \alpha_{Ca,Cl}^{2}I_s/2)\exp(-\alpha_{Ca,Cl}I_s^{1/2}) + 2m^2(\nu_{Ca}^{2}\nu_{Cl}z_{Ca}/\nu)\{3C^{(0)}_{Ca,Cl} + 4C^{(1)}_{Ca,Cl}[6 - (6 + 6\omega_{Ca,Cl}I_s^{1/2} + 3\omega_{Ca,Cl}^{2}I_s + \omega_{Ca,Cl}^{3}I_s^{3/2} - \omega_{Ca,Cl}^{4}I_s^{2}/2)\exp(-\omega_{Ca,Cl}I_s^{1/2})]/(\omega_{Ca,Cl}^{4}I_s^{2})\} + \sum_{i\geq 3}\{(i + 1)/i\}m^i D_i \qquad (40)$$

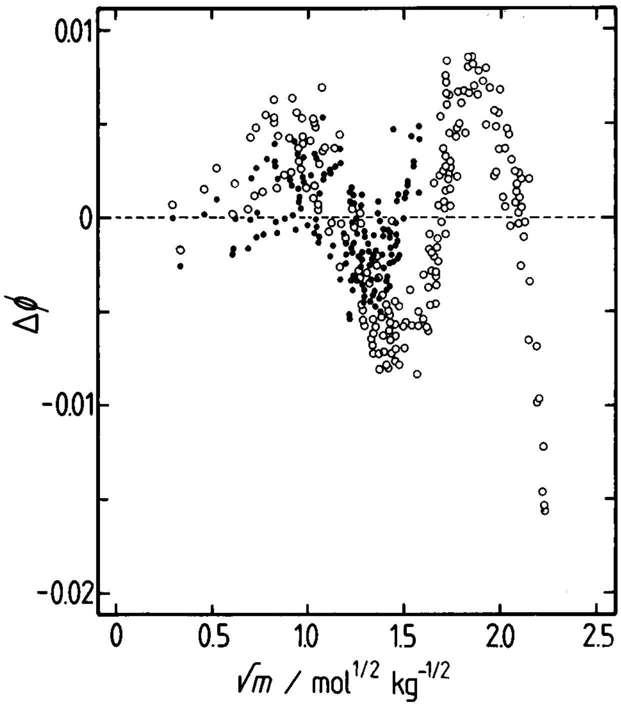

Figure 1. Deviations of the critically-assessed osmotic coefficients from the standard Pitzer model using the parameters $\beta^{(0)}_{Ca,Cl}$, $\beta^{(1)}_{Ca,Cl}$, and $C^{(0)}_{Ca,Cl}$ treating $CaCl_2(aq)$ as a fully dissociated electrolyte. Symbols: ●, model fit to 2.5 $mol \cdot kg^{-1}$; ○, model fit to 5.0 $mol \cdot kg^{-1}$.

The standard forms of Pitzer's equations for the osmotic and activity coefficients [73-pit/may, 83-phu/pit, 91-pit] are obtained by setting the parameters $C^{(1)}_{Ca,Cl}$ and the D_i of eqs 37, 39, and 40 equal to zero. Figure 1 is a plot of the deviations of our critically-assessed osmotic coefficients from two separate least-squares fits of the parameters of Pitzer's equation to data for the molality ranges $0 < m \leq 2.5$ $mol \cdot kg^{-1}$ and $0 < m \leq 5.0$ $mol \cdot kg^{-1}$. It can readily be seen that (1) this equation does not represent ϕ to experimental accuracy even when restricted to these molality ranges, (2) smoothed values of ϕ calculated from the resulting least-squares parameters cycle about the input data, and (3) these fits are unreliable for extrapolations to higher molalities. These conclusions confirm those reported in previous studies [83-phu/pit, 80-har/wea, 82-ana/atk].

As noted in the Introduction, there are several published studies in which higher-order virial terms in powers of the stoichiometric molality were added to the standard forms of Pitzer's equations for osmotic and activity coefficients [82-rog, 85-ana/atk, 87-smi/gar]. These equations do not contain the $C^{(1)}_{Ca,Cl}$ parameter.

Figure 2 is a plot of the differences between the osmotic coefficient equations of Rard et al. [77-rar/hab], of Ananthaswamy and Atkinson [85-ana/atk], and of Staples and Nuttall [77-sta/nut] relative to the AEPEWHOVT equation. Ananthaswamy and Atkinson [85-ana/atk] fitted the parameters of their equation to smoothed values of ϕ at 298.15 K as calculated from the expression of Rard et al. [77-rar/hab] along with other thermodynamic data at various temperatures. However, Figure 2 indicates that the equation of Ananthaswamy and Atkinson agrees well with the input osmotic coefficients at 298.15 K only up to about 5 $mol \cdot kg^{-1}$ but exhibits systematic cyclic deviations of up to 0.005−0.006 at higher molalities. Thus, the equation of Ananthaswamy and Atkinson, even though it contains three additional virial terms through m^5, does not

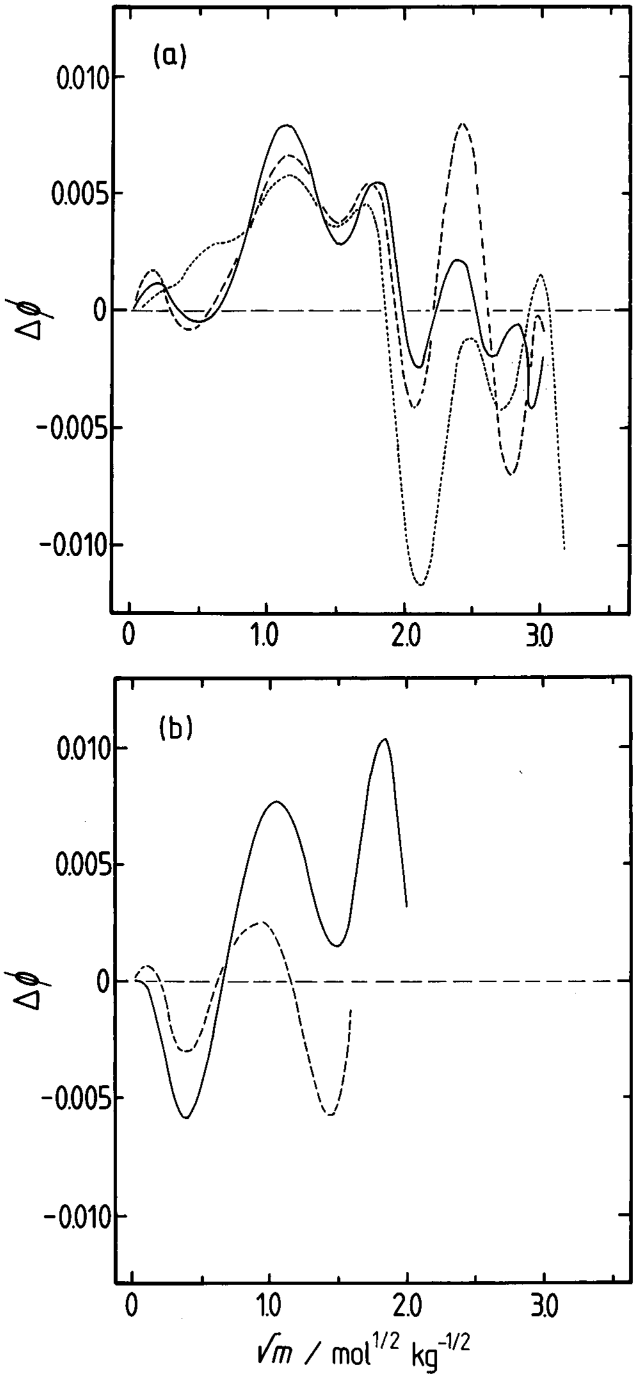

Figure 2. Differences between several previous evaluations for the osmotic coefficients of $CaCl_2$(aq) and our best-fit model (the AEPEWHOVT equation). (a) Solid curve, Rard et al. [77-rar/hab]; dashed curve, Ananthaswamy and Atkinson [85-ana/atk]; dotted curve, Staples and Nuttall [77-sta/nut]. (b) Solid curve, Phutela and Pitzer [83-phu/pit]; dashed curve, Pitzer and Mayorga [73-pit/may].

represent the higher molality osmotic coefficients within experimental error. A similar comparison between the smoothed results at 298.15 K from the extended Pitzer equation of Smith-Magowan et al. [87-smi/gar] and the evaluated osmotic and activity coefficients upon which it was based [77-sta/nut] yields better agreement, but five additional virial terms through m^7 were required. It thus appears that simply adding additional terms to the standard form of Pitzer's equation will not represent the available thermodynamic data without systematic cyclic deviations unless very high powers of the stoichiometric molality are used.

All of these equations exhibit very similar systematic positive deviations from the AEPEWHOVT equation between roughly (0.5 and 3) mol·kg^{-1}. Differences in this molality region result largely from revisions in the osmotic coefficient of the NaCl(aq) and KCl(aq) isopiestic reference standards.

Archer [92-arc] has proposed a modification of Pitzer's equation for the osmotic coefficient in which the third virial coefficient is given an ionic strength dependence similar to that of the second virial coefficient. This modified equation was shown to represent the available thermodynamic data for NaCl(aq) and NaBr(aq) to high accuracy over very wide ranges of temperature, pressure, and molality [92-arc, 95-rar/arc]. Archer's equations for the osmotic and activity coefficients can be obtained by setting the parameters D_i of eqs 37 and 40 equal to zero. Test calculations indicated that Archer's equation was able to represent the ϕ values for $CaCl_2$(aq) significantly better than the standard version of Pitzer's equation. However, it was still incapable of representing more that a fraction of the available molality region without excessive deviations. For example, when the fitted molality range was restricted to $m < 4$ mol·kg^{-1}, systematic cyclic deviations of up to 0.006 in ϕ were present, and increasing the molality range resulted in even larger errors.

Pitzer's equation can be further extended by the addition of higher-order virial terms to Archer's equation, as given by eqs 37 and 40. Figure 3 is a plot of the differences between values of ϕ calculated from four fits to the extended equation, compared to the more accurate AEPEWHOVT equation. In all cases, systematic cyclic deviations are present whose amplitudes depend on the molality range being fitted and on the number of higher-order virial terms. Adding further virial terms is unlikely to produce a quantitative model fit until very high powers of the molality are included. However, the use of terms containing powers of the molality of m^6 and above is undesirable because of the very large magnitude of m^i at high molalities, which results in numerous terms of similar magnitude but alternating sign in the expressions for ϕ and ln $\gamma_\pm$.

None of the model fits to Pitzer's equations and extended versions of Pitzer's equations that were described in this section give a quantitative agreement with the experimental thermodynamic data for $CaCl_2$(aq), and systematic cyclic deviations are always present. Since we do not consider these fits to be reliable, we do not report values of the resulting parameters. It appears likely that these fitting difficulties result from the effects of ion-pair formation at intermediate and higher molalities, and two models that include such speciation are described in the next section.

4.3. Modeling of Solutions as Mixtures Containing $CaCl^+$(aq). Clegg et al. [94-cle/rar] have generalized the extended Pitzer equation of Archer [92-arc], for binary solutions, to include arbitrary mixtures of electrolytes including those with self-association equilibria. They also showed that their generalized equations for the osmotic and activity coefficients were capable of representing the available experimental thermodynamic data for H_2SO_4(aq) up to 6.1 mol·kg^{-1}, virtually to within experimental error. That model required a value for the thermodynamic association constant for formation of HSO_4^-.

The extended Pitzer equation of Archer, as generalized here to include self-association to form $CaCl^+$(aq) ion pairs, was found capable of representing the available values of ϕ and the emfs to high accuracy over wide ranges of molality. We denote this equation as the AEP equation. The AEPEWHOVT equation, which also contains higher-order terms, was able to represent our critically-accessed database to essentially experimental accuracy over the entire molality range of (0 to 10.771) mol·kg^{-1}.

The higher-order virial terms used with the extended Pitzer equations given above, eqs 37 to 40, involved formally treating the $CaCl_2$(aq) solutions as being completely dissociated, and thus these terms were expressed in powers of the stoichiometric molality. However, because isopiestic data for $CaCl_2$(aq) at 298.15 K extend up to 10.771 mol·kg^{-1}, these values of m^i with $i \geq 3$ can become very large, which results in a series that converges rather slowly. Once speciation to form $CaCl^+$(aq) is introduced into the Pitzer-based models, it becomes more realistic to do this expansion in terms of combinations of powers of the ionic molalities of Ca^{2+}(aq), $CaCl^+$(aq), and Cl^-(aq), whose molality products do not reach such large values. A simplified expansion of this type has been used by Filippov and co-workers [87-fil/cha] for self-associated electrolytes such as cadmium chloride, although these authors still used a binary-solution form of Pitzer's equation rather than a full mixed-electrolyte treatment.

The expressions for the osmotic coefficient and the ionic activity coefficients from the extended Pitzer equation of Archer as generalized to include self-association to form $CaCl^+$(aq) ion pairs were derived from the expressions given in Appendix I of Clegg et al. [94-cle/rar]. Higher-order virial terms of the type used by Filippov et al. [87-fil/cha] were added onto these expressions. The higher-order terms were formulated as separate interactions of the cations Ca^{2+}(aq) and $CaCl^+$(aq) with variable numbers of Cl^-(aq) ions, and as simultaneous interactions of Ca^{2+}(aq) and $CaCl^+$(aq) with variable numbers of Cl^-(aq) ions. The AEPEWHOVT expressions are thus

$$\begin{aligned}\phi_e - 1 = (2/\textstyle\sum_i m_i)[-A_\phi I_e^{3/2}/(1 + bI_e^{1/2}) +{}& \\ m_{Ca}m_{Cl}(B^\phi_{Ca,Cl} + ZC^{T\phi}_{Ca,Cl}) + m_{CaCl}m_{Cl}(B^\phi_{CaCl,Cl} +{}& \\ ZC^{T\phi}_{CaCl,Cl}) + m_{Ca}m_{CaCl}(\Phi^\phi_{Ca,CaCl} + m_{Cl}\Psi_{Ca,CaCl,Cl}) +{}& \\ 0.5m_{Ca}\sum_{i\geq 3} i m_{Cl}{}^i D_{Ca,iCl} + 0.5m_{CaCl}\sum_{i\geq 3} i m_{Cl}{}^i D_{CaCl,iCl} +{}& \\ 0.5m_{Ca}m_{CaCl}\sum_{i\geq 2}(i+1)m_{Cl}{}^i D_{Ca,CaCl,iCl}]& \end{aligned} \tag{41}$$

$$\begin{aligned}\ln \gamma_{Ca} = 4F + m_{Cl}(2B_{Ca,Cl} + ZC^T_{Ca,Cl}) +{}& \\ 2(m_{Ca}m_{Cl}C^T_{Ca,Cl} + m_{CaCl}m_{Cl}C^T_{CaCl,Cl}) + m_{CaCl}(2\Phi_{Ca,CaCl} +{}& \\ m_{Cl}\Psi_{Ca,CaCl,Cl}) + \sum_{i\geq 3} m_{Cl}{}^i D_{Ca,iCl} + m_{CaCl}\sum_{i\geq 2} m_{Cl}{}^i D_{Ca,CaCl,iCl}& \end{aligned} \tag{42}$$

$$\begin{aligned}\ln \gamma_{CaCl} = F + m_{Cl}(2B_{CaCl,Cl} + ZC^T_{CaCl,Cl}) +{}& \\ (m_{Ca}m_{Cl}C^T_{Ca,Cl} + m_{CaCl}m_{Cl}C^T_{CaCl,Cl}) + m_{Ca}(2\Phi_{Ca,CaCl} +{}& \\ m_{Cl}\Psi_{Ca,CaCl,Cl}) + \sum_{i\geq 3} m_{Cl}{}^i D_{CaCl,iCl} + m_{Ca}\sum_{i\geq 2} m_{Cl}{}^i D_{Ca,CaCl,iCl}& \end{aligned} \tag{43}$$

$$\begin{aligned}\ln \gamma_{Cl} = F + m_{Ca}(2B_{Ca,Cl} + ZC^T_{Ca,Cl}) + m_{CaCl}(2B_{CaCl,Cl} +{}& \\ ZC^T_{CaCl,Cl}) + (m_{Ca}m_{Cl}C^T_{Ca,Cl} + m_{CaCl}m_{Cl}C^T_{CaCl,Cl}) +{}& \\ m_{Ca}m_{CaCl}\Psi_{Ca,CaCl,Cl} + m_{Ca}\sum_{i\geq 3} i m_{Cl}{}^{i-1} D_{Ca,iCl} +{}& \\ m_{CaCl}\sum_{i\geq 3} i m_{Cl}{}^{i-1} D_{CaCl,iCl} + m_{Ca}m_{CaCl}\sum_{i\geq 2} i m_{Cl}{}^{i-1} D_{Ca,CaCl,iCl}& \end{aligned} \tag{44}$$

where $B^\phi_{Ca,Cl}$ and $C^{T\phi}_{Ca,Cl}$ were defined above. Following Pitzer [91-pit] and Clegg et al. [94-cle/rar] a number of auxiliary functions are defined below.

$$\begin{aligned}F = -A_\phi[I_e^{1/2}/(1 + bI_e^{1/2}) + (2/b)\ln(1 + bI_e^{1/2})] +{}& \\ m_{Ca}m_{Cl}(B'_{Ca,Cl} + ZC^{T\prime}_{Ca,Cl}/2) + m_{CaCl}m_{Cl}(B'_{CaCl,Cl} +{}& \\ ZC^{T\prime}_{CaCl,Cl}/2) + m_{Ca}m_{CaCl}\Phi'_{Ca,CaCl}& \end{aligned} \tag{45}$$

$$Z = \textstyle\sum_i m_i|z_i| = 2m_{Ca} + m_{CaCl} + m_{Cl} \tag{46}$$

$$I_e = (1/2)\textstyle\sum_i m_i(z_i)^2 = (1/2)\{4m_{Ca} + m_{CaCl} + m_{Cl}\} \tag{47}$$

$$B_{Ca,Cl} = \beta^{(0)}_{Ca,Cl} + \beta^{(1)}_{Ca,Cl}g(\alpha_{Ca,Cl}I_e^{1/2}) \tag{48}$$

$$B_{CaCl,Cl} = \beta^{(0)}_{CaCl,Cl} + \beta^{(1)}_{CaCl,Cl}g(\alpha_{CaCl,Cl}I_e^{1/2}) \tag{49}$$

$$B^\phi_{CaCl,Cl} = \beta^{(0)}_{CaCl,Cl} + \beta^{(1)}_{CaCl,Cl}\exp(-\alpha_{CaCl,Cl}I_e^{1/2}) \tag{50}$$

$$B'_{Ca,Cl} = \beta^{(1)}_{Ca,Cl}g'(\alpha_{Ca,Cl}I_e^{1/2})/I_e \tag{51}$$

$$B'_{CaCl,Cl} = \beta^{(1)}_{CaCl,Cl}g'(\alpha_{CaCl,Cl}I_e^{1/2})/I_e \tag{52}$$

$$C^{T\phi}_{CaCl,Cl} = C^{(0)}_{CaCl,Cl} + C^{(1)}_{CaCl,Cl}\exp(-\omega_{CaCl,Cl}I_e^{1/2}) \tag{53}$$

$$C^T_{Ca,Cl} = C^{(0)}_{Ca,Cl} + 4C^{(1)}_{Ca,Cl}h(\omega_{Ca,Cl}I_e^{1/2}) \tag{54}$$

$$C^T_{CaCl,Cl} = C^{(0)}_{CaCl,Cl} + 4C^{(1)}_{CaCl,Cl}h(\omega_{CaCl,Cl}I_e^{1/2}) \tag{55}$$

$$C^{T\prime}_{Ca,Cl} = 4C^{(1)}_{Ca,Cl}h'(\omega_{Ca,Cl}I_e^{1/2})/I_e \tag{56}$$

$$C^{T\prime}_{CaCl,Cl} = 4C^{(1)}_{CaCl,Cl}h'(\omega_{CaCl,Cl}I_e^{1/2})/I_e \tag{57}$$

$$g(x) = 2[1 - (1 + x)\exp(-x)]/x^2 \tag{58}$$

$$g'(x) = \exp(-x) - g(x) \tag{59}$$

$$h(x) = \{6 - [6 + x(6 + 3x + x^2)]\exp(-x)\}/x^4 \tag{60}$$

$$h'(x) = [\exp(-x)]/2 - 2h(x) \tag{61}$$

$$\Phi_{Ca,CaCl} = \theta_{Ca,CaCl} + \theta^E_{Ca,CaCl}(I_e) \tag{62}$$

$$\Phi'_{Ca,CaCl} = \theta^{E\prime}_{Ca,CaCl}(I_e) \tag{63}$$

$$\Phi^\phi_{Ca,CaCl} = \theta_{Ca,CaCl} + \theta^E_{Ca,CaCl}(I_e) + I_e\theta^{E\prime}_{Ca,CaCl}(I_e) \tag{64}$$

where $B^\phi_{Ca,Cl}$ and $C^{T\phi}_{Ca,Cl}$ were defined by eqs 38 and 39. The mean molal activity coefficient of $CaCl_2$(aq) is related to the above ionic activity coefficients by

$$\gamma_\pm{}^3 = \gamma_{Ca}\gamma_{Cl}{}^2(m_{Ca}m_{Cl}{}^2/4m^3) \tag{65}$$

where $m = m_{Ca} + m_{CaCl} = (1/2)(m_{CaCl} + m_{Cl})$ is the stoichiometric molality of $CaCl_2$(aq). The osmotic coefficient based upon the derived equilibrium ionic molalities, ϕ_e, is related to the value based upon stoichiometric molalities, ϕ, by

$$\phi_e = 3m\phi/(\textstyle\sum_i m_i) \tag{66}$$

The speciation of $CaCl_2$(aq) among Ca^{2+}(aq), $CaCl^+$(aq), and Cl^-(aq) ions depends on the molality of the solution, the selected value of $K(CaCl^+)$, and the ionic activity

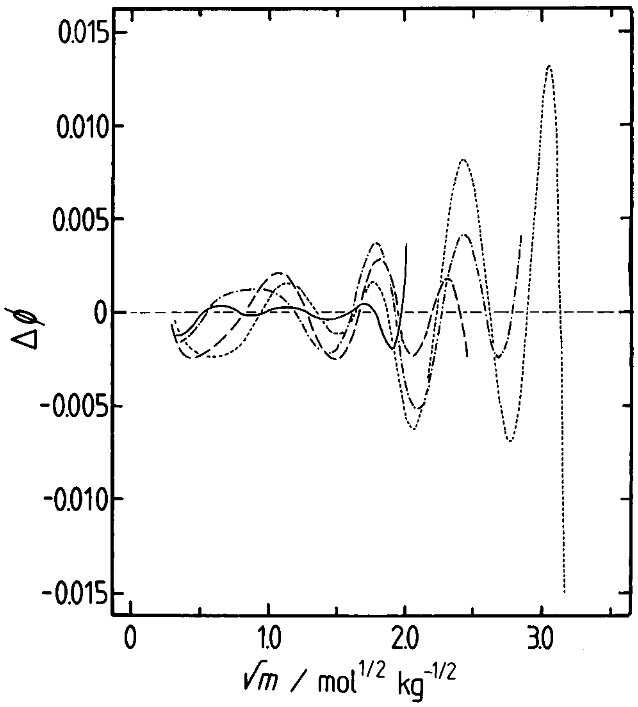

Figure 3. Comparison of various model fits using the extended Pitzer equation of Archer, eq 37, treating $CaCl_2(aq)$ as a fully dissociated electrolyte, using the parameters $\beta^{(0)}_{Ca,Cl}$, $\beta^{(1)}_{Ca,Cl}$, $C^{(0)}_{Ca,Cl}$, and $C^{(1)}_{Ca,Cl}$ with two or three higher-order virial terms, all relative to our best-fit model (the AEPEWHOVT equation). Solid curve, fit to 4.0 mol·kg^{-1} with D_3 and D_4 parameters; dashed curve, fit to 6.0 mol·kg^{-1} with D_3 and D_4 parameters; dotted−dashed curve, fit to 8.0 mol·kg^{-1} with D_3, D_4, and D_5 parameters; dotted curve, fit to 10.0 mol·kg^{-1} with D_3, D_4, and D_5 parameters.

Table 9. Model Parameter Values of Archer's Extended Pitzer Equation for Aqueous $CaCl_2$ at 298.15 K and 0.1 MPa, for $0 \le m(CaCl_2) \le 8$ mol·kg^{-1}, Treating the Solution as Mixtures of Ca^{2+}, Cl^-, and $CaCl^+$ Ions (AEP Equation)[a]

parameter	parameter value	standard error	parameter units
$\beta^{(0)}_{Ca,Cl}$	−0.298 649 948	0.014 80	kg·mol^{-1}
$\beta^{(1)}_{Ca,Cl}$	2.178 671 47	0.026 36	kg·mol^{-1}
$C^{(0)}_{Ca,Cl}$	0.022 524 497	0.000 453	kg^2·mol^{-2}
$C^{(1)}_{Ca,Cl}$	0.540 824 906	0.014 98	kg^2·mol^{-2}
$\alpha_{Ca,Cl}$	1.4		kg$^{1/2}$·mol$^{-1/2}$
$\omega_{Ca,Cl}$	1.0		kg$^{1/2}$·mol$^{-1/2}$
$\beta^{(0)}_{CaCl,Cl}$	−1.013 304 02	0.016 30	kg·mol^{-1}
$\beta^{(1)}_{CaCl,Cl}$	7.274 563 68	0.129 5	kg·mol^{-1}
$C^{(0)}_{CaCl,Cl}$	0.064 161 134	0.000 738 7	kg^2·mol^{-2}
$C^{(1)}_{CaCl,Cl}$	−3.695 676 54	0.067 72	kg^2·mol^{-2}
$\alpha_{CaCl,Cl}$	1.4		kg$^{1/2}$·mol$^{-1/2}$
$\omega_{CaCl,Cl}$	2.5		kg$^{1/2}$·mol$^{-1/2}$

[a] Mixing parameters $\theta_{Ca,CaCl}$ and $\Psi_{Ca,CaCl,Cl}$ were not necessary for an accurate model fit and were therefore set equal to zero. The selected value of ln $K(CaCl^+) = -7.488$ at 298.15 K was computed from the equation of Holmes et al. [94-hol/bus]. Standard potentials were fixed at the values obtained from the AEPEWHOVT equation (next table). The weighted standard errors for this model fit are $\sigma(\phi) = 0.0023$ and $\sigma(E) = 0.141$ mV.

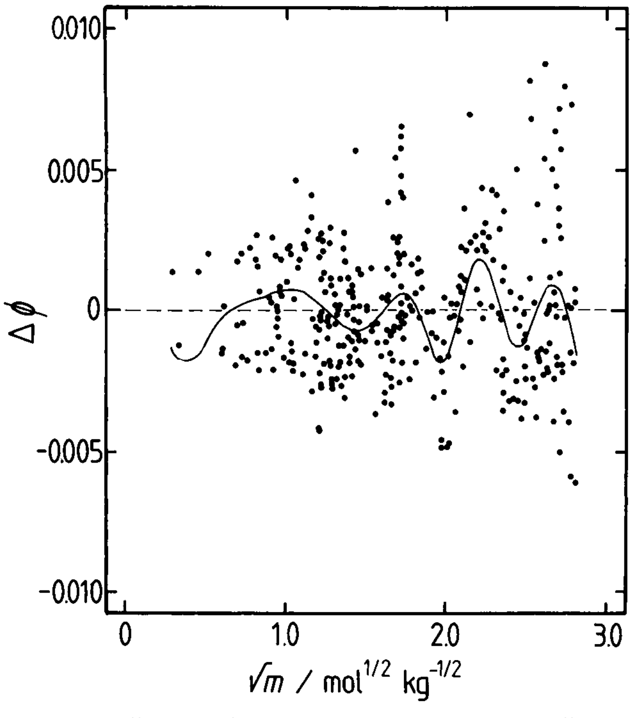

Figure 4. Differences of the critically-assessed osmotic coefficients from the extended Pitzer model fit to 8.0 mol·kg^{-1}, eq 41 without the higher-order virial coefficients and coefficients from Table 9 (the AEP equation), treating $CaCl_2(aq)$ as a mixture containing $CaCl^+(aq)$ ion pairs and using the parameters $\beta^{(0)}_{Ca,Cl}$, $\beta^{(1)}_{Ca,Cl}$, $C^{(0)}_{Ca,Cl}$, $C^{(1)}_{Ca,Cl}$, $\beta^{(0)}_{CaCl,Cl}$, $\beta^{(1)}_{CaCl,Cl}$, $C^{(0)}_{CaCl,Cl}$, and $C^{(1)}_{CaCl,Cl}$ from Table 9. The critically-assessed emfs of Table 5 were also included in this fit. Symbols: ●, experimental isopiestic and other vapor-pressure values; solid curve, differences from our best-fit model (the AEPEWHOVT equation).

coefficients which are initially unknown. We chose the value of ln $K(CaCl^+) = -7.488$ at 298.15 K from the equation of Holmes et al. [94-hol/bus] as being the best available estimate. Ionic activity coefficients were then obtained by successive approximations. These iterations were continued until self-consistency was obtained for the following expression:

$$m - m_{Ca}[1 + m_{Cl}K'(CaCl^+)] = 0 \qquad (67)$$

This equation describes the stoichiometric molality in terms of speciation of the calcium between free $Ca^{2+}(aq)$, m_{Ca}, and $CaCl^+(aq)$ ion pairs, m_{CaCl}. The apparent association constant (concentration product) $K'(CaCl^+)$ is defined by $K(CaCl^+)\cdot(\gamma_{Ca}\gamma_{Cl}/\gamma_{CaCl})$. Test calculations indicated that good quality model fits could be obtained with $\alpha_{Ca,Cl} = 1.4$ kg$^{1/2}$·mol$^{-1/2}$, $\alpha_{CaCl,Cl} = 1.4$ kg$^{1/2}$·mol$^{-1/2}$, $\omega_{Ca,Cl} = 1.0$ kg$^{1/2}$·mol$^{-1/2}$, and $\omega_{CaCl,Cl} = 2.5$ kg$^{1/2}$·mol$^{-1/2}$.

Least-squares model fits to eqs 41−44 without the higher-order virial terms were performed over various molality regions. When the fits were restricted to data with $m = (0$ to $6)$ mol·kg^{-1} or smaller molality ranges, the fits were of excellent quality with essentially no cycling of the model equation about the input data. The corresponding model fits with data for $m = (0$ to $8)$ mol·kg^{-1} showed a small amount of cycling about the experimental data, whereas fits to even higher molalities gave larger systematic cyclic deviations. Parameters for the fit to the range $m = (0$ to $8)$ mol·kg^{-1} are presented in Table 9 along with the standard errors of these coefficients. Including the mixing parameters $\theta_{Ca,CaCl}$ and $\Psi_{Ca,CaCl,Cl}$ resulted in little improvement in the model fits and were thus set equal to zero. However, the theoretically-based term $\theta^{E}_{Ca,CaCl}(I_e)$ for mixing of ions with different electrical charges of like sign [91-pit] was included. See eq AI24 of Clegg et al. [91-cle/rar] for the mathematical approximation used.

Figure 4 shows the deviations of this equation from the critically-assessed values of ϕ; also shown on this plot as a solid curve are the differences between this model fit and the fit to the AEPEWHOVT equation to the full molality range of $m = (0$ to $10.771)$ mol·kg^{-1}. It can be seen that

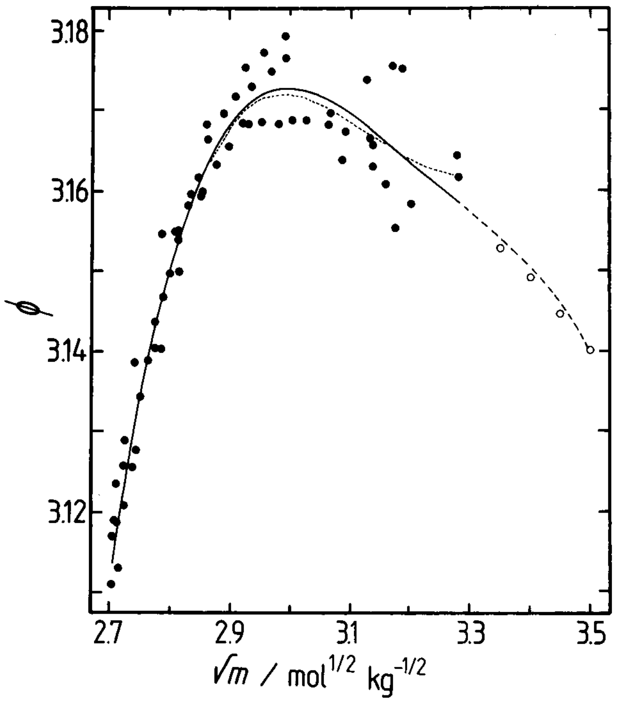

Figure 5. Osmotic coefficients of $CaCl_2$(aq) in the supersaturated molality region as a function of the square root of the molality. Symbols: ●, experimental isopiestic results; ○, estimated values at higher molalities; solid curve (with a dashed extension), fit to the AEPEWHOVT equation, eq 41, including the four estimated values; dotted curve, fit to the AEPEWHOVT equation without the four estimated values. Note that the latter fit exhibits a spurious upturn above 9.5 mol·kg^{-1}.

for values of $m \leq$ (0 to 8) mol·kg^{-1}, eq 41 without the higher-order terms (the AEP equation) represents the available ϕ values to within $\Delta\phi \leq 0.0018$ of a smoothed curve drawn through these data and agrees equally well with the complete AEPEWHOVT equation. The more accurate AEPEWHOVT equation should be used when values of ϕ or $\gamma_\pm$ of the highest accuracy are required, such as when $CaCl_2$(aq) is being used as an isopiestic reference standard. However, since the parameters of Table 9 are valid to 8 mol·kg^{-1}, which is above the solubility of (7.4 ± 0.1) mol·kg^{-1} for $CaCl_2 \cdot 6H_2O$(cr), it could be used for analysis of solubility data for ternary solutions involving $CaCl_2$(aq). Slightly more accurate solubility calculations would result from use of the complete AEPEWHOVT equation, but it contains higher-order terms which make the mathematical analysis somewhat more complicated.

Model fits, using the AEPEWHOVT equation, to the data over the entire molality range generally predicted a spurious upturn in ϕ beginning around 9.6 mol·kg^{-1}, even though this feature was not present in the individual isopiestic data sets. This can be seen in a plot of the isopiestic values of ϕ at supersaturated molalities, Figure 5. This is caused, apparently, by the large scatter in ϕ above about 8.5 mol·kg^{-1}, since the available ϕ values are not precise enough to completely constrain the model equations near their upper molality limit. This upturn was eliminated by adding to the database four values of ϕ at higher molalities which were estimated by graphical extrapolation of the experimental results. These values are $\phi = 3.1545$, 3.1510, 3.1465, and 3.1420 at $m =$ (11.22, 11.56, 11.90, and 12.25) mol·kg^{-1}, respectively. Fits with and without these estimated values are compared in Figure 5, which shows that including the additional ϕ values has essentially no effect on the model results below about 8.5 mol·kg^{-1} and has relatively little influence at higher molalities.

Final model fits were done with the complete AEPEWHOVT equation using data for the full molality range, including the coefficients of the higher-order virial terms $D_{Ca,iCl}$ with $i = 3, 4, 5$, $D_{CaCl,iCl}$ with $i = 3, 4, 5$, and $D_{Ca,CaCl,iCl}$ with $i = 2, 3$. All three of the $D_{Ca,iCl}$ were found to be statistically significant in these fits. However, two of the $D_{CaCl,iCl}$ and one of the $D_{Ca,CaCl,iCl}$ had very large uncertainties, were found to be redundant to other model parameters, and were consequently set equal to zero. On intuitive grounds this appears to be reasonable. Since the molality of Ca^{2+}(aq) is always greater than that of $CaCl^+$(aq) in these solutions, the $D_{Ca,iCl}$ terms should be the most important. As before, the mixing parameters $\theta_{Ca,CaCl}$ and $\Psi_{Ca,CaCl,Cl}$ were set to zero, although the theoretically-based term $\theta^E_{Ca,CaCl}(I_e)$ for mixing of ions with different electrical charges of like sign was retained. The parameter $\beta^{(0)}_{CaCl,Cl}$ was also redundant to the other parameters and was set equal to zero.

The least-squares fitting routine used was "E04FDF"; see ref 111 of Clegg et al. [94-cle/rar]. Because of the considerable numerical difficulties with performing nonlinear least-squares fits to complicated multiparameter equations (as the AEP and AEPEWHOVT equations), the calculations were done in stages. Initial fits were used to evaluate the parameters of simpler Pitzer-based models over more restricted molality ranges, and the resulting parameter values were used as the initial estimates. Additional fits were then performed in which the molality range and number of parameters were gradually increased, with the parameter values from each cycle being used as the starting "guesses" for the next cycle of calculations, until the final model parameters were obtained. Some parameters were eliminated as not being statistically significant, based on the ratio of the standard error of that parameter to its value.

Table 10 contains the values of the least-squares parameters and their standard errors for the AEPEWHOVT equation based on a fit of the parameters to the critically-assessed database to the full molality range of $m =$ (0 to 10.771) mol·kg^{-1}. Table 11 contains values of ϕ, a_w, $\gamma_\pm$, and the degree of dissociation a at rounded values of the molality. Given the complexity of eqs 41 through 44, we give these results at numerous molalities to aid graphical interpolation. As noted following the references, copies of a computer code will also be made available by the authors.

Figure 6 shows the deviations of all of the osmotic coefficients from the AEPEWHOVT equation. This equation gives an excellent representation of the experimental data to the highest molalities, and there is no region where any systematic deviations are obviously present except for minor differences for the four points below 0.27 mol·kg^{-1}. However, at low molalities, the fits are dominated by emf data for cells H and J and those results are represented accurately (see below). It is also obvious that deviations of the experimental ϕ values are spread essentially randomly about the least-squares lines. The increasing scatter with increasing molality corresponds approximately to a constant percentage of ± 0.3% in ϕ.

A more detailed presentation of the deviations of the critically-assessed osmotic coefficient database from the AEPEWHOVT equation is given in Figure 7. Results for each isopiestic reference standard (NaCl, KCl, H_2SO_4) are given separately as plots a, b, and c, and the nonisopiestic vapor pressures as plot d. Individual data sets are plotted with separate symbols. There is a slight tendency for values of ϕ determined with NaCl(aq) as reference standard to be higher than those with KCl(aq) as reference standard, but the differences are not large. In the overlapping

Table 10. Model Parameter Values of the Extended Pitzer Equation for Aqueous $CaCl_2$ at 298.15 K and 0.1 MPa for the Molality Range $0 \leq m(CaCl_2) \leq 10.771$ $mol \cdot kg^{-1}$, Treating the Solution as a Mixture of Ca^{2+}, Cl^-, and $CaCl^+$ Ions (AEPEWHOVT Equation)

parameter	parameter value	standard error	parameter units
$\beta^{(0)}_{Ca,Cl}$	−0.951 245 617	0.029 36	$kg \cdot mol^{-1}$
$\beta^{(1)}_{Ca,Cl}$	3.066 988 27	0.049 24	$kg \cdot mol^{-1}$
$C^{(0)}_{Ca,Cl}$	−0.062 276 316	0.002 867	$kg^2 \cdot mol^{-2}$
$C^{(1)}_{Ca,Cl}$	1.688 402 14	0.034 05	$kg^2 \cdot mol^{-2}$
$\alpha_{Ca,Cl}$	1.4		$kg^{1/2} \cdot mol^{-1/2}$
$\omega_{Ca,Cl}$	1.0		$kg^{1/2} \cdot mol^{-1/2}$
$\beta^{(0)}_{CaCl,Cl}$	0^a		$kg \cdot mol^{-1}$
$\beta^{(1)}_{CaCl,Cl}$	−14.730 640 8	0.131 6	$kg \cdot mol^{-1}$
$C^{(0)}_{CaCl,Cl}$	0.059 275 582	0.000 770 0	$kg^2 \cdot mol^{-2}$
$C^{(1)}_{CaCl,Cl}$	21.222 685 3	0.267 6	$kg^2 \cdot mol^{-2}$
$\alpha_{CaCl,Cl}$	1.4		$kg^{1/2} \cdot mol^{-1/2}$
$\omega_{CaCl,Cl}$	2.5		$kg^{1/2} \cdot mol^{-1/2}$
$D_{Ca,3Cl}$	0.030 364 061 2	0.000 755 3	$kg^3 \cdot mol^{-3}$
$D_{Ca,4Cl}$	−0.001 959 330 4	0.000 041 01	$kg^4 \cdot mol^{-4}$
$D_{Ca,5Cl}$	0.000 047 100 87	0.000 000 751	$kg^5 \cdot mol^{-5}$
$D_{CaCl,3Cl}$	0^a		$kg^3 \cdot mol^{-3}$
$D_{CaCl,4Cl}$	−0.000 134 898 0	0.000 001 450	$kg^4 \cdot mol^{-4}$
$D_{CaCl,5Cl}$	0^a		$kg^5 \cdot mol^{-5}$
$D_{Ca,CaCl,2Cl}$	−0.010 534 914 0	0.000 269 7	$kg^3 \cdot mol^{-3}$
$D_{Ca,CaCl,3Cl}$	0^a		$kg^4 \cdot mol^{-4}$
$E°$ (cell E)	2.145 90	0.000 31	V
"$E°$" (cell J)[b]	−0.180 00	0.000 51	V

[a] These parameters were redundant to the others and were therefore set equal to zero for the final least-squares fit. Mixing parameters $\theta_{Ca,CaCl}$ and $\Psi_{Ca,CaCl,Cl}$ were not necessary for an accurate model fit and were therefore set equal to zero. The selected value of $\ln K(CaCl^+) = -7.488$ at 298.15 K was computed from the equation of Holmes et al. [94-hol/bus]. The weighted standard errors for this model fit are $\sigma(\phi) = 0.0024$ and $\sigma(E) = 0.141$ mV. [b] Cell J contains a Ca(II) ISE, so this not a well-defined thermodynamic standard potential.

molality region, values of ϕ with H_2SO_4(aq) as reference standard fall in the middle range of values determined with the other two reference standards and thus are highly consistent.

Figure 8 is a plot of the deviations of all of the more reliable emfs from the AEPEWHOVT equation. Results for each type of electrochemical cell are plotted with different symbols. These emf values are represented well, except for the cell I results of Shatkay [70-sha] which are both slightly skewed and fairly scattered and which were given low weight in the fits. Deviations for the three sets of emfs for the electrochemical concentration cells with transference, cell H, are given in Figure 9 and are essentially random.

Figure 10a gives a plot of the recommended values of ϕ and $\log_{10} \gamma_{\pm}$ as a function of the square root of the stoichiometric molality. The presence of the broad flat maximum at high molalities is a feature that makes it difficult to develop model equations that represent the thermodynamic properties of $CaCl_2$(aq) within experimental accuracy, since the ϕ values initially vary rapidly with molality but then become nearly constant. The saturation molality of $CaCl_2 \cdot 6H_2O$(cr) is indicated on this plot, and the $\log_{10} \gamma_{\pm}$ curve has a distinct change in slope around this molality, the significance of which is unclear.

A few other highly soluble inorganic electrolytes have a maximum in ϕ as a function of molality, e.g., H_2SO_4(aq) at ca. 30 $mol \cdot kg^{-1}$ and LiCl(aq) at 19 $mol \cdot kg^{-1}$ [65-rob/sto]. Unique features of the maximum for ϕ of $CaCl_2$(aq) are its broadness and the relatively low molalities at which it occurs: although alkali metal trifluoroacetate salts exhibit similar qualitative behavior, their values of ϕ are much smaller [95-gam/lib].

Table 11. Smoothed Values of Osmotic Coefficients ϕ, Water Activities a_w, Mean Molal Activity Coefficients $\gamma_{\pm}$, and Degree of Dissociation α of Aqueous $CaCl_2$ Solutions at 298.15 K and 0.1 MPa at Various Round Molalities[a]

$m(CaCl_2)$/ $(mol \cdot kg^{-1})$	ϕ	a_w	$\gamma_{\pm}$	α[b]
0.001	0.9623	0.999 948	0.8886	0.999 999
0.002	0.9493	0.999 897	0.8508	0.999 998
0.005	0.9275	0.999 749	0.7871	0.999 995
0.01	0.9078	0.999 509	0.7290	0.999 990
0.02	0.8871	0.999 042	0.6651	0.999 975
0.05	0.8628	0.997 671	0.5786	0.999 87
0.10	0.8527	0.995 402	0.5187	0.999 32
0.20	0.8588	0.990 760	0.4716	0.995 42
0.30	0.8748	0.985 92	0.4538	0.986 14
0.40	0.8944	0.980 85	0.4476	0.971 63
0.50	0.9163	0.975 54	0.4479	0.953 47
0.60	0.9401	0.969 98	0.4527	0.933 41
0.70	0.9655	0.964 13	0.4609	0.912 82
0.80	0.9924	0.958 00	0.4721	0.892 65
0.90	1.0205	0.951 57	0.4859	0.873 50
1.00	1.0495	0.944 86	0.5021	0.855 71
1.20	1.1100	0.930 54	0.5411	0.824 81
1.40	1.1733	0.915 05	0.5891	0.800 22
1.60	1.2393	0.898 4	0.6467	0.781 45
1.80	1.3079	0.880 5	0.7153	0.767 81
2.00	1.3793	0.861 5	0.7965	0.758 65
2.25	1.4725	0.836 1	0.9191	0.752 79
2.50	1.5699	0.808 9	1.0702	0.752 64
2.75	1.6705	0.780 1	1.2554	0.758 00
3.00	1.7731	0.750 1	1.4811	0.768 77
3.25	1.8759	0.719 3	1.7534	0.784 39
3.50	1.9778	0.687 9	2.0795	0.803 11
3.75	2.0788	0.656 2	2.4695	0.822 02
4.00	2.1796	0.624 3	2.9377	0.838 37
4.25	2.2805	0.592 3	3.5010	0.850 66
4.50	2.3808	0.560 4	4.1762	0.858 64
4.75	2.4792	0.529 2	4.9786	0.862 56
5.00	2.5743	0.498 8	5.9208	0.862 89
5.25	2.6643	0.469 6	7.0112	0.860 06
5.50	2.7479	0.441 8	8.2526	0.854 52
5.75	2.8241	0.415 8	9.6418	0.846 71
6.00	2.8920	0.391 5	11.169	0.837 05
6.25	2.9514	0.369 0	12.820	0.825 93
6.50	3.0022	0.348 3	14.575	0.813 71
6.75	3.0447	0.329 3	16.416	0.800 69
7.00	3.0796	0.311 9	18.322	0.787 11
7.25	3.1074	0.295 9	20.276	0.773 15
7.50	3.1291	0.281 3	22.263	0.758 94
7.75	3.1453	0.267 8	24.270	0.744 61
8.00	3.1570	0.255 4	26.291	0.730 22
8.25	3.1649	0.243 9	28.321	0.715 83
8.50	3.1697	0.233 1	30.360	0.701 50
8.75	3.1721	0.223 1	32.411	0.687 26
9.00	3.1727	0.213 7	34.477	0.673 14
9.25	3.1720	0.204 8	36.566	0.659 16
9.50	3.1704	0.196 4	38.685	0.645 34
9.75	3.1683	0.188 3	40.841	0.631 70
10.00	3.1659	0.180 7	43.042	0.618 24
10.25	3.1635	0.173 3	45.292	0.604 99
10.50	3.1610	0.166 3	47.598	0.591 93
10.75	3.1586	0.159 6	49.960	0.579 09
(11.00)[c]	(3.1563)[c]	(0.153 1)[c]	(52.377)[c]	(0.566 46)[c]

[a] These thermodynamic quantities were calculated using the parameters of Table 10. [b] Fraction of $CaCl_2$(aq) present as completely dissociated Ca^{2+}(aq) according to the final model. Values of α are reported to five or six decimal places to allow for accurate conversion between stoichiometric mean activity coefficients and the activity coefficients of the "free ions" at their calculated molalities. [c] Values of these quantities at 11.0 $mol \cdot kg^{-1}$ are extrapolated slightly above the range of experimental data.

Figure 10b is a plot of the predicted degree of dissociation α of $CaCl_2$(aq) as a function of the square root of the stoichiometric molality, both for the AEPEWHOVT equation (Table 10 parameters) and for the analogous AEP equation without the higher-order virial terms (Table 9 parameters). Although the model equations are identical except for the higher-order virial terms and the same value of $K(CaCl^+)$ was used, the predicted molality dependencies of α differ considerably. Values of α calculated from eqs

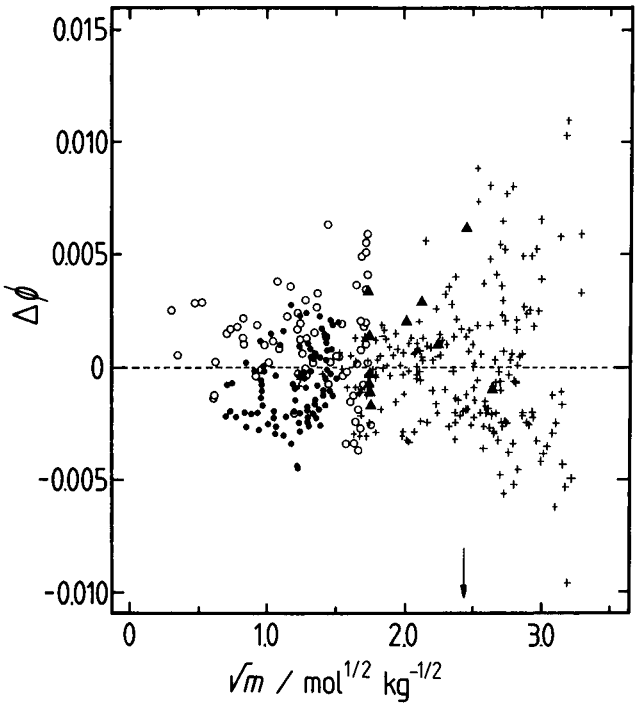

Figure 6. Differences of the critically-assessed osmotic coefficients from the AEPEWHOVT equation, eq 41 with the coefficients from Table 10, treating $CaCl_2$(aq) as a mixture containing $CaCl^+$(aq) ion pairs. The critically-assessed emfs of Table 5 were also included in the fit. Symbols: ●, isopiestic results with KCl(aq) reference standard; ○, isopiestic results with NaCl(aq) reference standard; +, isopiestic results with H_2SO_4(aq) reference standard; ▲, nonisopiestic vapor pressures. The arrow indicates the transition molality between the Clegg et al. [94-cle/rar] and Rard et al. [76-rar/hab] equations for the reference standard ϕ values of H_2SO_4(aq).

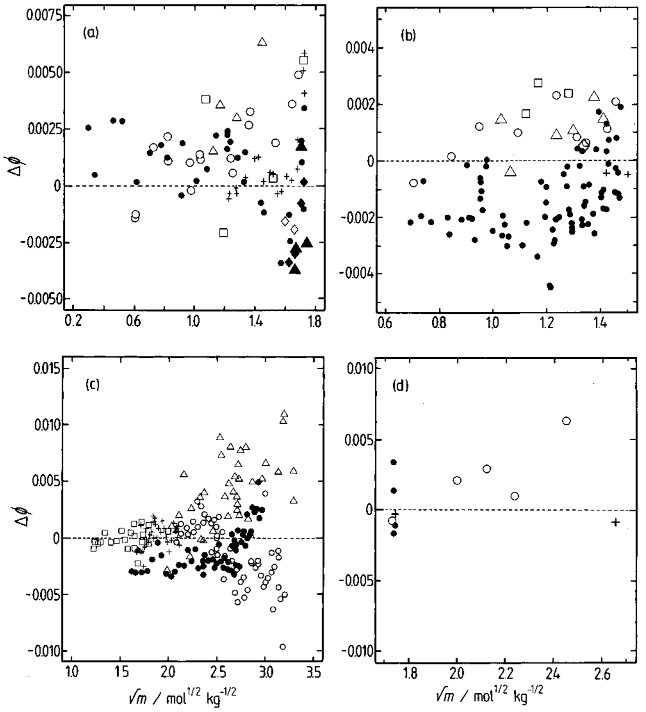

Figure 7. Detailed differences of the critically-assessed osmotic coefficients from the AEPEWHOVT equation, eq 41 with the coefficients from Table 10, treating $CaCl_2$(aq) as a mixture containing $CaCl^+$(aq) ion pairs, with individual data sets shown. The critically-assessed emfs of Table 5 were also included in the fit. (a) Isopiestic results with NaCl(aq) reference standard: ●, ref 45-sto; ○, ref 66-rob/bow; △, ref 67-kir/luk; □, ref 75-pla; +, ref 81-rar/mil; ♦, ref 83-mac/bat; ◇, ref 86-mac/bat; ▲, ref 95-rar/arc. (b) Isopiestic results with KCl(aq) reference standard: ◇, ref 60-sae/spe; △, ref 66-kir/luk; □, ref 67-kir/luk; ○, ref 68-rob/cov; ●, ref 76-spe/web; +, ref 81-rar/mil. (c) Isopiestic results with H_2SO_4(aq) reference standard: △, ref 45-sto; ●, ref 77-rar/spe; □, ref 81-rar/mil; +, ref 95-rar/arc; ○, present study Table 1. (d) Nonisopiestic vapor pressure measurements: +, ref 40-bec/new; ●, ref 47-sto; ○, ref 65-pet.

41 to 44 without the higher-order virial terms decrease regularly with increasing molality, whereas those predicted with the higher-order virial terms have a minimum and maximum. Reversals in α of this type are known as "redissociation" and have been directly observed for a few systems such as H_2SO_4(aq) [94-cle/rar].

One or both of these α curves are unrealistic. We note that it is possible to fit the thermodynamic data for $CaCl_2$(aq) with eqs 41 to 44 equally well using a variety of different values of $K(\mathrm{CaCl}^+)$, although using values of $K(\mathrm{CaCl}^+)$ around unity, as reported in some of the studies summarized in Table 8, leads to predictions of unrealistically large amounts of $CaCl^+$(aq) at very low molalities where available evidence suggests that $CaCl_2$(aq) is essentially completely dissociated. Test calculations indicated that values of $\ln K(\mathrm{CaCl}^+) \le \approx -1$, i.e., $K(\mathrm{CaCl}^+) \le \approx 0.4$, were necessary to produce the correct low-molality behavior. However, the value of $K(\mathrm{CaCl}^+)$ could be varied over many orders of magnitude within this constraint without adversely affecting the quality of the least-squares representation of the experimental data. Although it would be possible to determine $K(\mathrm{CaCl}^+)$ as an additional least-squares parameter from the fits to eqs 41 to 44, the value so obtained would likely depend strongly on the details of the calculation such as the molality range being fitted and the presence or absence of higher-order virial coefficients. Our choice of $\ln K(\mathrm{CaCl}^+) = -7.488$ at 298.15 K from the equation of Holmes et al. [94-hol/bus], although somewhat arbitrary, is consistent with the above upper bound for $K(\mathrm{CaCl}^+)$.

The nonlinear least-squares fitting routine locates local minima in the sum of the squares of the deviations, and other local minima may possibly occur where the same model form yields different parameters and different α values. Unfortunately, there are no direct experimental values of α to compare with these model predictions.

Predicted values of α from the AEP equation are probably more "realistic" than those from the AEPEWHOVT equation, both on grounds of simplicity and because the AEP equation contains fewer parameters. However, since the provisional value of $K(\mathrm{CaCl}^+)$ is uncertain by at least 2 orders of magnitude, values of α are highly uncertain.

At high molalities, solutions of $CaCl_2$(aq) will contain both $CaCl^+$(aq) and the dichloride complex $CaCl_2^0$(aq) since there is insufficient water present to separately satisfy the hydration needs of the unassociated ions. These neutral complexes were neglected in the model calculations since $K(\mathrm{CaCl}_2^0)$ is unknown at 298.15 K. The higher-order virial terms account for this complex in an indirect manner, along with other factors not incorporated into Pitzer-equation-based models.

Parameter values given in Tables 9 and 10 are similar to each other in some cases, but in others, especially for the "binary" electrolyte formed from $CaCl^+$ and Cl^- ions, there are certain parameters that differ by an order of magnitude for the two fits. These dissimilar parameter values and different degrees of dissociation (α) imply that ionic activity coefficients from eqs 42 to 44 will be significantly different for the two models. However, from a macroscopic thermodynamic viewpoint values of γ_{Ca}, γ_{CaCl}, and γ_{Cl} are not meaningful. The thermodynamically

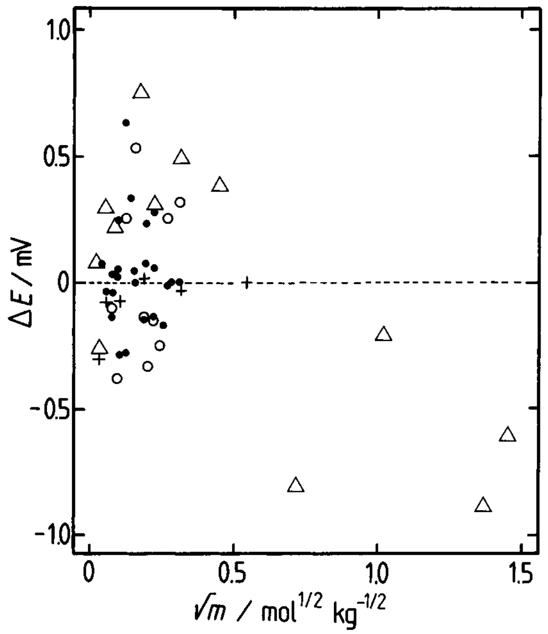

Figure 8. Differences of the critically-assessed emfs for four different electrochemical cells from the AEPEWHOVT equation, eqs 41 through 44 with the coefficients from Table 10, treating $CaCl_2(aq)$ as a mixture containing $CaCl^+(aq)$ ion pairs. Symbols: ○, cell E; ●, cell H; △, cell I; +, cell J. The skewing of the emfs of Shatkay [70-sha], cell I, can be seen clearly.

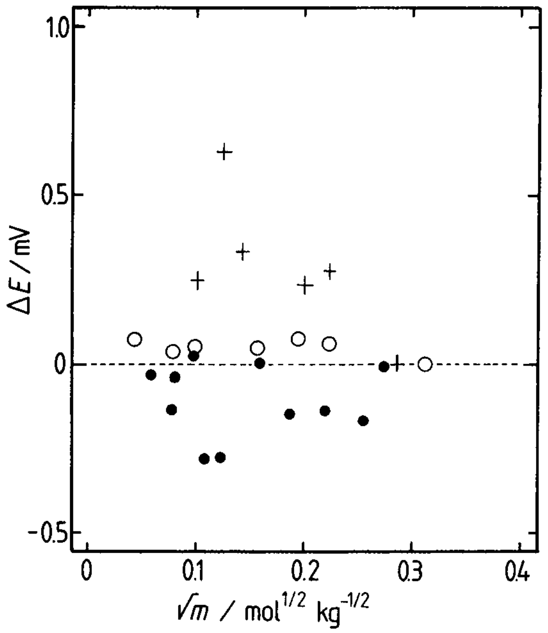

Figure 9. Differences of the critically-assessed emfs for electrochemical cell H from the AEPEWHOVT equation, eqs 41 through 44 with the coefficients from Table 10, treating $CaCl_2(aq)$ as a mixture containing $CaCl^+(aq)$ ion pairs, with individual data sets shown. Symbols: +, ref 25-luc; ○, ref 37-she/mac; ●, ref 46-mcl/gor.

significant quantities are those for the solvent and for the total electrolyte: ϕ, a_w, and $\gamma_\pm$. Values of these three quantities for the two models are in very good agreement, $\Delta\phi \leq 0.0018$ and $10^2(\Delta\gamma_\pm/\gamma_\pm) \leq 0.5\%$, and reliably reproduce the critically-assessed input data.

Osmotic coefficients and mean molal activity coefficients for $CaCl_2(aq)$ were reported by Robinson and Stokes [65-rob/sto] at 298.15 K on the basis of graphical smoothing of the best data available at that time. Since then many new experimental studies have been reported and there have been significant revisions in the other isopiestic reference standards NaCl(aq), KCl(aq), and $H_2SO_4(aq)$. In spite of this, there is fairly good agreement between Robinson and Stokes's values and ours. There is a maximum difference in ϕ of 0.006 with $\Delta\phi$ usually ≤ 0.004 and of $10^2(\Delta\gamma_\pm/\gamma_\pm) \leq 1\%$. Examination of the deviation curves given in Figure 2 indicates that several of the evaluations done after that of Robinson and Stokes were less accurate.

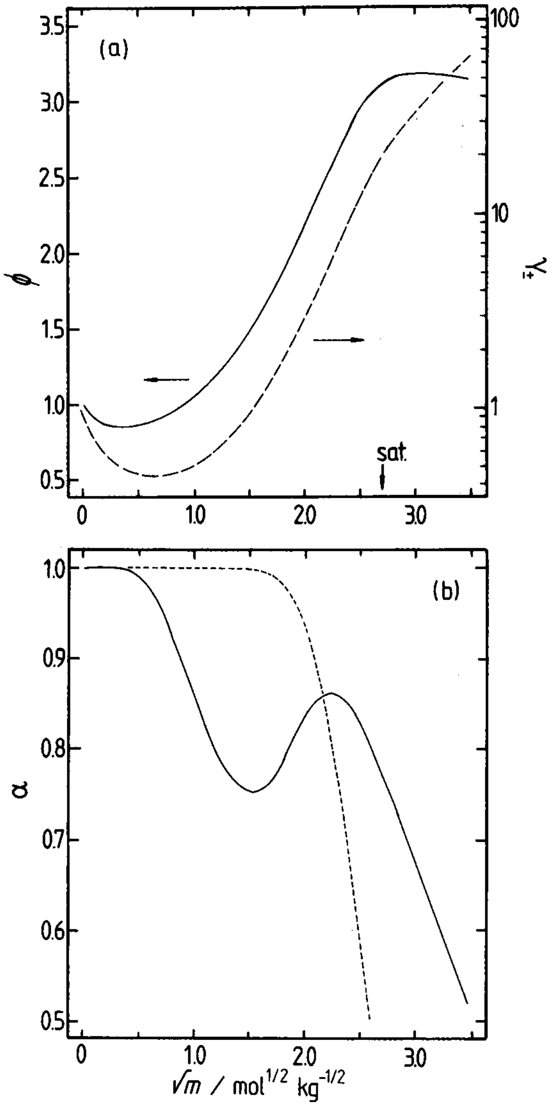

Figure 10. (a) Fitted osmotic coefficients (solid curve) and activity coefficients (dashed curve) of $CaCl_2(aq)$ at 298.15 K from the AEPEWHOVT equation, eqs 41 through 44 with the coefficients from Table 10, treating $CaCl_2(aq)$ as a mixture containing $CaCl^+(aq)$ ion pairs. (b) The calculated degree of dissociation of $CaCl^+(aq)$ from the AEPEWHOVT equation using coefficients from Table 10 (solid curve), and without higher-order virial coefficients and using coefficients from Table 9 (dashed curve).

Table 10 contains the standard potential for cell E evaluated from the emfs of Mussini and Pagella [71-mus/pag] with activity coefficients from the AEPEWHOVT equation using parameters given in that table, $E°(\text{cell E}) = (2.145\,90 \pm 0.000\,31)$ V. On the basis of the cell configuration and electrode compositions, eq 11, the emf will be given by

$$E = E°(\text{cell } E) - (RT/2F)\ln\{a(\text{CaCl}_2,m)\}$$
$$= E°(\text{Ag/AgCl}) - E°(\text{Ca,Hg}) + (RT/2F)\ln\{a(\text{Ca,Hg})\} - (RT/2F)\ln\{a(\text{CaCl}_2,m)\} \quad (68)$$

where $E°(\mathrm{Ag/AgCl})$ is the standard potential of the silver–silver chloride half-cell and $E°(\mathrm{Ca,Hg})$ is the standard potential of the calcium amalgam half-cell. Following Mussini and Pagella, we define the standard potential and activity coefficients of calcium in the amalgam in terms of Henry's law on the mole fraction scale and similarly assume that the amalgam solution was dilute enough ($x_{\mathrm{Ca}} = 0.003\,21$) that the activity coefficient of calcium can be assumed to be unity. Thus,

$$E°(\mathrm{Ca,Hg}) = E°(\mathrm{Ag/AgCl}) - E°(\text{cell E}) + (RT/2F)\ln(0.003\,21) \quad (69)$$

Experimental values of the standard potential of the silver–silver chloride half-cell are slightly variable and typically range between about (0.2223 and 0.2227) V [78-bat/mac, 87-dic]. This variability does not appear to correlate with the method of preparing the electrode, the cell design, or exposure to light [78-bat/mac]. Wu et al. [84-wu/koc] reported that exposure of the electrode or electrolyte solution to atmospheric air tended to yield slightly larger values of $E°(\mathrm{Ag/AgCl})$. We selected $E°(\mathrm{Ag/AgCl}) = (0.222\,49 \pm 0.000\,13)$ V from the report by Bates and Macaskill [78-bat/mac], which is an average of 35 values from 14 different laboratories. The derived value of the standard potential of the calcium amalgam half-cell is $E°(\mathrm{Ca,Hg}) = -(1.997\,17 \pm 0.000\,35)$ V, where the assumption that the activity coefficient of calcium in the amalgam is unity was assumed to introduce an uncertainty of 0.1 mV. This value agrees well with the value of $E°(\mathrm{Ca,Hg}) = -(1.9974 \pm 0.0004)$ V reported by Mussini and Pagella [71-mus/pag] from analysis of their own emfs.

5. Summary

Available literature data for the determination of isopiestic vapor pressures and direct vapor pressures of water above solutions of $\mathrm{CaCl_2(aq)}$, of the emfs of electrochemical cells containing $\mathrm{CaCl_2(aq)}$, and of the stability constants of $\mathrm{CaCl^+(aq)}$ have been critically reviewed and recalculated in a consistent manner.

This critically-assessed database at 298.15 K was then modeled with the Pitzer equation and various extended versions. It was found that both the standard Pitzer and empirically-extended expansions were incapable of accurately representing the available database over more than a very limited molality region if $\mathrm{CaCl_2(aq)}$ was considered to be a completely dissociated electrolyte. However, if its solutions were assumed to undergo association to form $\mathrm{CaCl^+(aq)}$, and the solutions then treated as equilibrium mixtures of $\mathrm{Ca^{2+}(aq)}$, $\mathrm{Cl^-(aq)}$, and $\mathrm{CaCl^+(aq)}$ ions, extended Pitzer models were obtained that were capable of representing the data accurately. Two such models are presented, one which is valid to 8.0 $\mathrm{mol{\cdot}kg^{-1}}$ and the other to the maximum molality of 10.77 $\mathrm{mol{\cdot}kg^{-1}}$.

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