A Review of the Osmotic Coefficients of Aqueous $CaCl_2$ at 25 °C

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New data have become available since Robinson and Stokes' review of the use of $CaCl_2$ solutions as isopiestic standards. Electrolyte activity coefficient and water activity determinations for aqueous $CaCl_2$ solutions from vapor pressure, isopiestic, freezing point depression, emf, and diffusion coefficient measurements are reviewed here. These activities have been updated to presently accepted values of the physical constants, and vapor pressure measurements have been corrected for the nonideal behavior of the solvent vapor. A semiempirical equation is given which represents the osmotic coefficients of aqueous $CaCl_2$ solutions at 25 °C from 0 to 9 *m*, to within the experimental uncertainty of the data. This equation is recommended for all isopiestic measurements using a $CaCl_2$ standard at 25 °C.

One of the most important methods for the determination of the water activities of electrolyte solutions is the isopiestic method, in which samples of various different solutions are allowed to reach thermodynamic equilibrium, through the vapor phase, with standard solutions. If these measurements are performed as a function of concentration, then application of the Gibbs-Duhem equation to these data yields the solute activity coefficients. This method is a relative method so standard solutions are used for which accurate water activity data are needed.

For isopiestic experiments, KCl and NaCl solutions have been widely used as standards. Hamer and Wu (*7*) have reviewed the data for KCl and NaCl solutions and have obtained equations which reliably represent the osmotic coefficients for these salts to saturation at 25 °C. The use of KCl solutions as isopiestic standards is restricted to water activities above 0.84 and NaCl solutions are restricted to water activities above 0.75.

H_2SO_4 can be used as an isopiestic standard to much lower water activities and an equation is available (*27*) which represents the osmotic coefficients up to concentrations which correspond to water activities as low as 0.026. H_2SO_4 is rather corrosive so tantalum, platinum, or gold-plated metal cups are generally used for the isopiestic measurements. To avoid the use of these specialized containers many workers have used $CaCl_2$ solutions for isopiestic standards. $CaCl_2$ solutions readily supersaturate (the solubility is about 7.3 *m* at 25 °C) and water activities as low as 0.18 can easily be obtained. The purpose of this review is to evaluate the available activity data for $CaCl_2$ and to obtain a least-squares representation of the osmotic coefficient data at 25 °C. Most of the available data are from isopiestic measurements, but data from other methods are also included.

Discussion

The largest amount of activity data for aqueous $CaCl_2$ solutions at 25 °C has been determined using the isopiestic method. Any isopiestic measurement involving $CaCl_2$ solutions can be used to yield osmotic coefficients for $CaCl_2$ provided these measurements are done relative to a solution whose osmotic coefficients are accurately known as a function of concentration. KCl, NaCl, and H_2SO_4 appear to be the most reliable standards for this purpose.

Robinson (*29*) has determined the KCl-$CaCl_2$ isopiestic ratio for 29 concentrations corresponding to 0.09-2.20 *m* $CaCl_2$. Stokes (*38*) has determined the NaCl-$CaCl_2$ isopiestic ratio for 29 concentrations from 0.09 to 2.98 *m* in $CaCl_2$ and the H_2SO_4-$CaCl_2$ ratio for 42 solutions with $CaCl_2$ concentrations between 2.95 and 10.77 *m*. In the course of studying phosphoric acid, Platford (*26*) determined the NaCl-$CaCl_2$ ratio for four $CaCl_2$ solutions between 1.15 and 2.95 *m*. In their study of rare earth chloride solutions, Spedding et al. (*37*) determined the KCl-$CaCl_2$ isopiestic ratio for 78 solutions with $CaCl_2$ concentrations between 0.48 and 2.17 *m*. Rard and Spedding (*28*) have determined the H_2SO_4-$CaCl_2$ ratio for 60 solutions between 2.63 and 8.83 *m* in $CaCl_2$. Nearly all of these isopiestic measurements are in good agreement with each other.

Consider an electrolyte solution of molality *m*, with a water activity a_1 and each molecule of electrolyte dissociating into ν ions. The osmotic coefficient of this solution is given by

$$\phi = -\frac{1000 \ln a_1}{\nu m M_1} \tag{1}$$

where $M_1 = 18.0154$ g mol^{-1} is the molecular weight of water. If this solution is in isopiestic equilibrium with a standard solution,

$$\phi = \frac{\nu^* \phi^* m^*}{\nu m} \tag{2}$$

where the asterisk refers to the standard solution.

Values for the osmotic coefficients of H_2SO_4 were taken from Rard, Habenschuss, and Spedding (*27*). The osmotic coefficients of KCl and NaCl solutions were taken from Hamer and Wu (*7*), with a small correction applied to their data for the nonideal behavior of the solvent vapor (*27*). These standard solution osmotic coefficients were used with eq 2 and available isopiestic data (*26, 28, 29, 37, 38*) to generate $CaCl_2$ osmotic coefficients and the resulting values are listed in Table I. It is not necessary to convert activity data to the International Practice Temperature Scale of 1968 (IPTS-68) from older temperature scales since this correction amounts to only about 0.0001 or less for ϕ.

The H_2SO_4-$CaCl_2$ isopiestic data of Platford (*25*) at 0 °C were not included in this review. To convert these data to $CaCl_2$ osmotic coefficients at 25 °C would require two separate 25 °C temperature conversions. This process would result in a loss of much of the accuracy of the original data, especially since the necessary $CaCl_2$ enthalpy and heat capacity data are lacking at high concentrations.

The solvent activities of $CaCl_2$ solutions have also been studied by vapor pressure methods including direct pressure measurements (*2, 11, 24*), bithermal isopiestic measurements (*39*) and dew point measurements (*10*). In terms of vapor pressure, the osmotic coefficient of a solution is given by

$$\phi = \frac{1000}{\nu m M_1} \ln\left(\frac{p_0}{p}\right) + \frac{1000B(p_0 - p)}{\nu m M_1 RT} \tag{3}$$

where *p* is the vapor pressure above the solution, p_0 is the vapor pressure of the pure solvent at the same temperature *T*, *R* is the universal gas constant, and *B* is the second virial coefficient of water vapor. From McCullough et al. (*19*), $B = -1194$ cm^3 mol^{-1} at 25 °C (the value of McCullough et al. was misprinted as -1994 in ref 27). This value is in good agreement with Keyes'

Table I. $CaCl_2$ Osmotic Coefficients from Isopiestic Data

m, ref	m, $CaCl_2$	ϕ, $CaCl_2$	m, ref	m, $CaCl_2$	ϕ, $CaCl_2$	m, ref	m, $CaCl_2$	ϕ, $CaCl_2$	m, ref	m, $CaCl_2$	ϕ, $CaCl_2$
Robinson-KCl Reference Electrolyte (*29*)											
0.1234	0.0887	0.8548	2.167	1.202	1.0995	0.8476	0.5481	0.9246	3.580	1.765	1.2865
0.2127	0.1512	0.8547	2.523	1.355	1.1456	1.361	0.8242	0.9916	4.014	1.921	1.3436
0.2304	0.1628	0.8585	2.616	1.391	1.1599	1.417	0.8512	1.0004	4.021	1.933	1.3379^a
0.2780	0.1963	0.8562	2.843	1.485	1.1881	1.554	0.9194	1.0180	4.534	2.107	1.4071^a
0.4534	0.3117	0.8730	2.934	1.519	1.2018	1.781	1.027	1.0488	4.747	2.178	1.4352
0.5453	0.3692	0.8847	3.098	1.583	1.2234	1.958	1.105	1.0756	4.810	2.202	1.4414^a
0.7667	0.5009	0.9151	3.224	1.631	1.2403	2.010	1.133	1.0781			
0.7890	0.5159	0.9144	3.532	1.752	1.2768^a						
Spedding et al.—KCl Reference Electrolyte (*37*)											
0.7292	0.4798	0.9088	3.1969	1.6179	1.2388	1.8967	1.0777	1.0669	4.0066	1.9152	1.3448
0.8245	0.5349	0.9216	3.2179	1.6253	1.2420	1.9239	1.0903	1.0703	4.0835	1.9411	1.3557
0.8521	0.5500	0.9263	3.2655	1.6449	1.2472	1.9589	1.1067	1.0744	4.1503	1.9674	1.3624
0.9252	0.5919	0.9348	3.2955	1.6565	1.2509	1.9835	1.1175	1.0780	4.1512	1.9675	1.3626
1.1069	0.6907	0.9595	3.3345	1.6716	1.2558	2.2513	1.2356	1.1134	4.2051	1.9863	1.3697
1.1279	0.7022	0.9618	3.3405	1.6741	1.2564	2.3347	1.2707	1.1250	4.2460	2.0011	1.3746
1.2691	0.7754	0.9816	3.3450	1.6757	1.2570	2.5585	1.3657	1.1537	4.3007	2.0201	1.3816
1.3553	0.8179	0.9949	3.3559	1.6800	1.2583	2.6203	1.3889	1.1637	4.3152	2.0222	1.3855
1.3733	0.8282	0.9959	3.4950	1.7294	1.2785	2.7064	1.4252	1.1741	4.3211	2.0251	1.3857
1.4121	0.8476	1.0011	3.5388	1.7462	1.2837	2.7249	1.4318	1.1772	4.3637	2.0402	1.3909
1.4553	0.8695	1.0065	3.5927	1.7679	1.2894	2.7361	1.4368	1.1783	4.3793	2.0447	1.3935
1.5284	0.9037	1.0181	3.6171	1.7747	1.2942	2.8209	1.4735	1.1873	4.5782	2.1141	1.4181
1.5333	0.9062	1.0187	3.6264	1.7805	1.2937	2.8393	1.4809	1.1897	4.6072	2.1231	1.4224
1.5367	0.9083	1.0186	3.6401	1.7843	1.2964	2.8724	1.4924	1.1954	4.6202	2.1264	1.4248
1.5560	0.9174	1.0215	3.6532	1.7897	1.2976	2.9017	1.5044	1.1990	4.6660	2.1429	1.4300
1.5728	0.9260	1.0233	3.6851	1.8013	1.3018	2.9195	1.5114	1.2014	4.6789	2.1473	1.4316
1.6297	0.9521	1.0323	3.7661	1.8315	1.3118	2.9443	1.5206	1.2051	4.6893	2.1515	1.4325
1.6321	0.9531	1.0328	3.7829	1.8363	1.3149	3.0206	1.5505	1.2151	4.7195	2.1616	1.4364
1.7145	0.9939	1.0419	3.9116	1.8835	1.3310	3.1406	1.5958	1.2318	4.7520	2.1694	1.4426
1.8751	1.0684	1.0635	3.9483	1.8973	1.3353						
Stokes—NaCl Reference Electrolyte (*38*)											
0.1255	0.0908	0.8557	2.622	1.487	1.1989	1.325	0.8382	0.9994	5.342	2.658	1.6309
0.1586	0.1148	0.8524	2.724	1.535	1.2142	1.350	0.8503	1.0050	5.384	2.676	1.6371
0.3034	0.2156	0.8630	2.988	1.657	1.2545	1.683	1.028	1.0541	6.008	2.921	1.7409
0.3901	0.2742	0.8720	3.241	1.772	1.2932	1.963	1.170	1.0970	6.028	2.928	1.7447
0.5617	0.3875	0.8905	3.302	1.798	1.3037	2.244	1.307	1.1410	6.147	2.978	1.7621
0.7366	0.4968	0.9151	3.937	2.077	1.4027	2.611	1.482	1.1970	6.166	2.981	1.7679^a
0.9232	0.6090	0.9418	4.084	2.140	1.4260	2.612	1.483	1.1968			
1.046	0.6808	0.9593	4.865	2.467	1.5514						
Platford—NaCl Reference Electrolyte (*26*)											
1.918	1.145	1.0925	4.404	2.273	1.4787	2.476	1.422	1.1733	6.085	2.947	1.7561^a
Stokes—H_2SO_4 Reference Electrolyte (*38*)											
4.329	2.951	1.7593^a	10.813	6.874	3.0709	8.381	5.366	2.7074	12.199	7.914	3.1551
4.520	3.072	1.8077^a	11.115	7.092	3.0946	8.557	5.473	2.7390	12.331	8.023	3.1582
4.985	3.362	1.9255^a	11.315	7.233	3.1111	8.622	5.511	2.7512	12.552	8.193	3.1682
5.561	3.715	2.0695	11.383	7.286	3.1145	8.801	5.611	2.7866	13.209	8.749	3.1772
5.899	3.929	2.1471	11.434	7.326	3.1168	9.547	6.064	2.9087	13.458	8.963	3.1793
6.237	4.126	2.2314	11.456	7.341	3.1188	10.091	6.394	2.9904	14.371	9.785^a	3.1737
6.742	4.422	2.3515	11.483	7.354	3.1235	10.136	6.425	2.9952	14.701	10.071^a	3.1754
6.916	4.525	2.3910	11.582	7.430	3.1287	10.456	6.640	3.0307	14.800	10.159^a	3.1752
7.116	4.635	2.4398	11.575	7.431	3.1257	10.786	6.861	3.0659	15.429	10.750^a	3.1644
7.611	4.928	2.5456	11.715	7.525	3.1385	10.780	6.862	3.0630	15.442	10.771^a	3.1617
7.687	4.967	2.5644	12.041	7.775	3.1547						
Rard and Spedding—H_2SO_4 Reference Electrolyte (*28*)											
3.8135	2.6341	1.6206	10.482	6.6662	3.0295	8.3817	5.3739	2.7038	11.763	7.5779	3.1343
4.0329	2.7748	1.6766	10.588	6.7375	3.0408	8.7002	5.5592	2.7645	11.844	7.6387	3.1389
4.3210	2.9581	1.7501	10.714	6.8246	3.0530	8.7043	5.5630	2.7646	11.939	7.7117	3.1436
4.6645	3.1746	1.8374	10.819	6.8956	3.0637	8.7166	5.5703	2.7668	12.036	7.7902	3.1467
4.9087	3.3263	1.8996	10.923	6.9692	3.0727	8.7390	5.5826	2.7713	12.111	7.8496	3.1496
5.2915	3.5613	1.9965	11.056	7.0570	3.0867	8.8855	5.6677	2.7984	12.185	7.9019	3.1549
5.5427	3.7152	2.0587	11.074	7.0717	3.0874	9.0406	5.7609	2.8250	12.206	7.9234	3.1538
5.8672	3.9105	2.1390	11.192	7.1606	3.0948	9.1765	5.8422	2.8480	12.376	8.0596	3.1595
6.1892	4.1022	2.2175	11.237	7.1874	3.1007	9.3449	5.9438	2.8756	12.450	8.1196	3.1617
6.4495	4.2558	2.2799	11.301	7.2344	3.1051	9.5049	6.0416	2.9006	12.567	8.2107	3.1665
6.7945	4.4573	2.3613	11.349	7.2701	3.1083	9.6885	6.1563	2.9274	12.740	8.3557	3.1695
7.1360	4.6554	2.4397	11.348	7.2720	3.1071	9.8271	6.2426	2.9474	12.880	8.4736	3.1717
7.4182	4.8164	2.5038	11.480	7.3631	3.1185	10.030	6.3690	2.9759	12.992	8.5626	3.1754
7.7500	5.0084	2.5752	11.556	7.4258	3.1207	10.203	6.4828	2.9968	13.052	8.6225	3.1728
8.1238	5.2225	2.6536	11.638	7.4876	3.1255	10.369	6.5926	3.0161	13.288	8.8254	3.1748

[a] This value given a weight of zero in the least-squares fit to eq 14.

Table II. $CaCl_2$ Osmotic Coefficients from Vapor Pressure Data

m	p/p_0	ϕ	m	p/p_0	ϕ
		Bechtold and Newton—Direct Vapor Pressure (*2*)			
0.3043	0.986 32	0.8364[a]	7.0310	0.309 64	3.0825
3.0335	0.745 81	1.7866			
		Petit—Direct Vapor Pressure (*24*)			
0.250	0.988 38	0.8636[a]	3.000	0.749 92	1.7727
0.500	0.976 76	0.8687[a]	3.500	0.685 17	1.9963[a]
0.750	0.959 38	1.0216[a]	4.000	0.623 59	2.1820
1.000	0.941 95	1.1049[a]	4.500	0.559 65	2.3840
1.500	0.903 35	1.2520[a]	5.000	0.498 23	2.5754
2.000	0.860 71	1.3857[a]	6.000	0.390 3	2.8985
2.500	0.807 50	1.5803[a]			
		Stokes—Bithermal Equilibration (*39*)			
3.019	0.747 15	1.7842[a]	3.024	0.747 15	1.7813
3.021	0.747 15	1.7830	3.036	0.745 58	1.7869

[a] This value given a weight of zero in the least-squares fit to eq 14.

Table III. $CaCl_2$ Osmotic Coefficients from Freezing Point Depression Measurements

m	ϕ_f[a]	ϕ_{25}	m	ϕ_f[a]	ϕ_{25}
0.027 55	0.8861	0.8820[b]	0.291 90	0.8770	0.8710
0.049 30	0.8705	0.8660	0.364 65	0.8903	0.8841
0.112 90	0.8585	0.8535	0.448 30	0.9075	0.9011
0.144 45	0.8581	0.8529	0.529 00	0.9270	0.9205
0.173 85	0.8604	0.8550	0.727 35	0.9762	0.9694

[a] The osmotic coefficient of the solution at its freezing temperature. The number to the right is the corresponding osmotic coefficient converted to 25 °C. [b] This value given a weight of zero in the least-squares fit to eq 14.

value (*13*) of $-1162\ \mathrm{cm^3\ mol^{-1}}$. Inserting numerical values into eq 3 yields

$$\phi = \frac{55.508}{\nu m} \ln\left(\frac{p_0}{p}\right) - (3.564 \times 10^{-3})\left(\frac{p_0 - p}{\nu m}\right) \tag{4}$$

where p and p_0 are in millimeters of mercury. The second term in eq 4 is the correction for the nonideal behavior of the solvent vapor and is about 0.1% of ϕ. The change in ϕ with concentration, due to the change in the water activity of the liquid phase with pressure, can be neglected at 25 °C.

At low concentrations ϕ is a very sensitive function of the vapor pressure. Vapor pressure measurements are almost never more reliable than 0.003 mmHg and are frequently less accurate. For $CaCl_2$ at 25 °C, an error of 0.003 mmHg in p would result in errors for ϕ of 0.01 at 0.25 m, 0.005 at 0.5 m, 0.003 at 0.75 m, and 0.002 at 1.0 m. Since the vapor pressure of pure water also has some uncertainty, it is clear that values of ϕ from vapor pressure measurements are not very reliable at low concentrations. Emf and isopiestic measurements frequently give much better accuracy at these low concentrations, so dilute solution vapor pressure data were assigned zero weights in the least-squares representation of the osmotic coefficients.

Hepburn (10) measured the vapor pressures of $CaCl_2$ solutions from 0.20 to 7.28 m using the dew point method. The measurement consists of isolating a sample of the vapor from the solution, and cooling it until condensation occurs. Measurements of this type are difficult and seldom highly accurate. Below 1.0 m Hepburn's osmotic coefficients are about 10–15% low (experimental vapor pressures are too high). Above this concentration the osmotic coefficients differ by 0.5–2.5% from the isopiestic data and also exhibit a large amount of scatter. These osmotic coefficients are not of sufficient accuracy to include here. Similar considerations hold for earlier vapor pressure measurements referenced by Hepburn.

Bechtold and Newton (*2*) measured vapor pressures above 0.30, 3.03, and 7.03 m $CaCl_2$ solutions. Stokes (*39*) determined the vapor pressure of four solutions between 3.02 and 3.04 m bithermally, relative to pure water. Stokes' relative vapor pressures were recalculated using his temperature differences and recent values for the vapor pressure of water at various temperatures (*42*). These two series of measurements were made using temperature scales nearly equivalent to IPTS-48 so p_0 = 23.754 mmHg (*42*) was used in calculating osmotic coefficients for these solutions from eq 4. These osmotic coefficients are listed in Table II.

Petit (*24*) measured the vapor pressure of $CaCl_2$ solutions from 0.25 to 6 m. Most of Petit's data above 3 m appear to be moderately reliable, but between 0.75 and 2.5 m these osmotic coefficients are rather high (experimental vapor pressures are too low). Petit also measured the vapor pressure of pure water and this value was used in calculating the osmotic coefficients reported in Table II. Jakli and Van Hook (*11*) studied three concentrations of $CaCl_2$ as a function of temperature. Their experimental vapor pressures were somewhat different than expected from the isopiestic data, and they attributed this to the presence of water in the $CaCl_2$ crystals used to prepare their stock solution. Since they found it necessary to adjust their solution concentrations using Robinson and Stokes' osmotic coefficients at 25 °C (*30*), their three points are not included here.

Gibbard and Fong (*6*) have recently measured the freezing point depressions of 0.028–0.727 m $CaCl_2$ solutions. Osmotic coefficients at the freezing points of the solutions were calculated using the constants of Scatchard et al. (*34*). These osmotic coefficients were converted to 25 °C using the equation given on page 187 of Robinson and Stokes (*30*), and available heat of dilution (*22*) and heat capacity (*14, 23*) data. The resulting osmotic coefficients are listed in Table III. Earlier freezing point depression measurements are not included here. References to most of these early studies can be found in the Landolt-Bornstein "Tabellen".

Amdur (*1*) has determined the water activity of 0.051 and 0.061 m $CaCl_2$ using an "osmometric" method. The measurements consist of determining the rate of water vapor absorption by a drop of solution in a solvent atmosphere. While this method may possibly be more accurate than vapor pressure measurements in the dilute concentration region, it is probably less accurate than most emf and freezing point depression measurements at low concentrations. The osmotic coefficients calculated from these data differ from the best emf results by about 1.5–2.0% so they will not be considered further.

The activity coefficients of aqueous $CaCl_2$ solutions at 25 °C have been measured using calcium amalgam electrodes (*5, 16, 18, 21, 33*), silver–silver chloride concentration cells with transference (*16, 18, 20, 36*), ion sensitive membrane electrodes (*3, 31, 35*), and a lead–lead oxalate electrode (*32*). Shatkay (*35*) used a calomel electrode for his second electrode while all of the other studies used silver–silver chloride. Although a few of these studies report emf data at high concentrations, in no case were the data above 0.3 m spaced at close enough intervals to allow an accurate Gibbs–Duhem integration to yield osmotic coefficients at these high concentrations.

If the activity coefficients of $CaCl_2$ solutions are known as a function of concentration, the osmotic coefficients of these solutions can be calculated from

$$\phi = 1 + 1/m \int_0^m m \,\mathrm{d} \ln \gamma_\pm \tag{5}$$

where $\gamma_\pm$ is the mean molal activity coefficient of $CaCl_2$. Some of the emf studies report the emf as a function of the molarity whereas the molalities are needed to perform the integration in eq 5. Conversion of molarities to molalities was made using the

IUPAC-1969 molecular weight of 110.986 g mol^{-1} for $CaCl_2$ and the density data of Dunn (*4*). These density data are accurately represented by

$$d = 0.997075 + 0.09290489c - 0.005702555c^{3/2} \quad (6)$$

where c is the molarity of the solution.

The activity coefficients reported by the various authors from emf studies had been calculated by various different methods. To put all of the emf calculations on a consistent basis, all of these data were recalculated to give the activity coefficients relative to some fixed experimental concentration (this avoids the necessity of knowing E^0 for the cell or the activity coefficient of Ca metal in the amalgam). For cells without transference, the relative activity coefficients are given by

$$\frac{\gamma_\pm}{\gamma_\pm'} = \frac{m'}{m} \exp\left(\frac{-2F\Delta E}{3RT}\right) \quad (7)$$

where the prime refers to the reference solution, $2F/3RT = 2\cdot(96\,487.0)/3(8.3143)(298.15) = 25.9488$ V^{-1} and $\Delta E = E - E'$ is the difference in the emf's between the two solutions of interest. This equation was used for calcium amalgam (*5, 16, 21, 33*), ion sensitive membrane (*3, 35*), and lead oxalate (*32*) electrode systems. Older emf measurements were converted from international to absolute volts. If necessary, each set of emf data was coupled so that activity coefficients were always obtained relative to the highest usable concentration. These molalities and relative activity coefficients are given in Table IV.

Shatkay (*35*) found that membrane electrode systems fail at low concentrations so data below 0.001 m were not included in our calculations for these systems (*3, 35*). Ross (*31*) and Masaki (*18*) did not measure enough data to include their results here. Sahay's lead oxalate system (*32*) was not reproducible above 0.05 m so his two highest concentrations were not used. In addition, calcium amalgam based activity coefficients frequently have large systematic errors (*29*).

Each set of relative activity coefficients, obtained from emf studies, was separately fitted to the extended Debye-Hückel equation

$$\ln \gamma_\pm = \ln\left(\frac{\gamma_\pm}{\gamma_\pm'}\right) + \ln \gamma_\pm' = \frac{-Am^{1/2}}{1 + Bm^{1/2}} + Dm \quad (8)$$

where $A = (0.510\,82)(2)(3^{1/2})(2.302\,585) = 4.0744$, $B = (0.328\,66)(3^{1/2})\mathring{a} = 0.569\,26\mathring{a}$ and $\mathring{a}$ is the Debye-Hückel ion-size parameter in Ångstroms. The prime refers to the reference concentration. Optimum values of $\gamma_\pm'$, $\mathring{a}$, and D were obtained by a nonlinear least-squares procedure. Since the usable emf data are restricted to 0.3 m and lower, eq 8 has enough parameters to accurately represent each data set. Substitution of eq 8 into eq 5 and integrating yields

$$\phi = 1 - \left(\frac{A}{B^3 m}\right)[1 + Bm^{1/2} - 1/(1 + Bm^{1/2}) - 2\ln(1 + Bm^{1/2})] + (D/2)m \quad (9)$$

and the osmotic coefficients can be calculated from the least-squares parameters. The values of $\mathring{a}$ and D for each data set are listed in Table V while values of the molalities, relative activity coefficients, and osmotic coefficients appear in Table IV.

It was necessary to treat Scatchard and Tefft's emf data (*33*) in a slightly different manner. These authors used a two-fluid cell and obtained relative activity coefficients directly, but they allowed their "reference" concentration to vary from 0.0998 to 0.1004 m. Their data were first calculated by the procedure described above using 0.1000 m as the reference for all solutions. Least-squares parameters were obtained for eq 8 and used to calculate mean molal activity coefficients at each "reference" concentration. These $\gamma_\pm$ values were substituted into eq 7 and the emf differences between the actual reference concentrations

Table IV. $CaCl_2$ Osmotic Coefficients from EMF and Diffusion Coefficient Measurements [a]

m	$\gamma_\pm/\gamma_\pm'$	ϕ	m	$\gamma_\pm/\gamma_\pm'$	ϕ
Lucasse[b]—Calcium Amalgam Electrode (*16*)					
0.010 0[c]	1.5060	—	0.103 2	1.0817	0.8629
0.035 04	1.2478	0.8728	0.206 6	1.0124	0.8841
0.062 94	1.1542	0.8631	0.371 3	1.0000	0.9344
Fosbinder[b]—Calcium Amalgam Electrode (*5*)					
0.009 9[c]	1.4738	—	0.089 7[d]	0.9223	—
0.043 5	1.1875	0.8723	0.141 1	1.0529	0.8771
0.062 8	1.1230	0.8682	0.306 9	1.0000	0.9278
0.078 1	1.1157	0.8677			
Scatchard and Tefft[b]—Calcium Amalgam Electrode (*33*)					
0.009 921	1.4385	0.9111	0.027 58[d]	1.2799	—
0.010 51	1.4254	0.9095	0.041 13	1.1809	0.8729
0.025 94	1.2750	0.8844	0.126 34	1.0000	0.8559
Mussini and Pagella—Calcium Amalgam Electrode (*21*)					
0.005 828	1.5025	0.9226	0.038 83	1.1746	0.8674
0.009 197	1.4383	0.9093	0.048 30	1.1295	0.8626
0.014 72	1.3332	0.8950	0.058 48	1.0985	0.8592
0.019 32	1.2534	0.8867	0.072 36	1.0482	0.8563
0.024 36	1.2330	0.8799	0.096 80	1.0000	0.8547
0.034 03	1.1926	0.8707			
Lucasse—Silver–Silver Chloride Concentration Cells (*16*)					
0.010 0[c]	1.3504	—	0.039 55	1.1125	0.8692
0.015 47	1.2641	0.8937	0.049 66	1.0720	0.8653
0.020 06	1.2287	0.8862	0.080 53	1.0000	0.8620[e]
Shedlovsky and MacInnes—Silver–Silver Chloride Concentration Cells (*36*)					
0.001 820 7	1.6391	0.9513	0.037 649	1.1581	0.8697
0.006 109 7	1.4772	0.9220	0.050 170[c]	1.1075	—
0.009 612 6	1.4026	0.9090	0.096 916	1.0000	0.8544
0.024 243	1.2390	0.8815			
McLeod and Gordon—Silver–Silver Chloride Concentration Cells (*20*)					
0.003 315 5	1.5101	0.9378	0.025 000[f]	1.1861	—
0.005 859 5	1.4310	0.9229	0.034 804	1.1288	0.8705
0.006 369 5	1.4168	0.9206	0.047 946	1.0732	0.8625
0.009 482	1.3556	0.9090	0.060 084	1.0345	0.8579
0.011 342	1.3268	0.9036	0.064 530	1.0235	0.8566
0.014 883	1.2811	0.8953	0.074 929	1.0000	0.8542
Shatkay—Ion Sensitive Membrane Electrodes (*35*)					
0.003 00[g]	1.7533	0.9397	0.050 2	1.2295	0.8601
0.007 15	1.6148	0.9164	0.101	1.0957	0.8515
0.011 7	1.5221	0.9015	0.201	1.0000	0.8612
0.030 0	1.3167	0.8729			
Briggs and Lilley—Ion Sensitive membrane Electrodes (*3*)					
0.001 027 5	1.9676	0.9617	0.033 081	1.3578	0.8708
0.003 251 9	1.8057	0.9379	0.099 104	1.1443	0.8515
0.010 165	1.6041	0.9062	0.295 89	1.0000	0.8753
Sahay[b]—Lead–Lead Oxalate Electrodes (*32*)					
0.001 00[c]	1.5650	—	0.010 0	1.2737	0.9043
0.002 00	1.4931	0.9483	0.020 0	1.1567	0.8820
0.005 00	1.3808	0.9253	0.050 0	1.0000	0.8568
Harned and Levy—Diffusion Coefficient Measurements (*8*)					
0.001 05	1.1316	0.9608	0.002 31	1.0733	0.9448
0.001 74	1.0963	0.9511	0.003 10	1.0473	0.9376
0.001 84	1.0919	0.9499	0.004 30	1.0158	0.9289
0.001 94	1.0877	0.9487	0.005 03	1.0000	0.9244

[a] Data exist at higher concentrations but were not used in the calculations for some of the data sets (*5, 16, 33, 35*). [b] This set of data not included in the least-squares fit to eq 14. [c] This solution used as the reference solution for the experimental measurements. [d] This value given a weight of zero in the least-squares fit to eq 8. [e] This value given a weight of zero in the least-squares fit to eq 14. [f] This was used as a reference concentration in our calculations; the reference concentration was allowed to vary in the original work. [g] Data at lower concentrations were not used because of electrode failure.

Table V. Debye–Hückel Equation Parameters

Investigators	å[a]	D	$\gamma_{\pm}'$	m[b]
Calcium Amalgam Electrodes				
Lucasse (*16*)	4.569	0.65	0.4859	0.371 3
Fosbinder (*5*)	4.737	0.70	0.4987	0.306 9
Scatchard and Tefft (*33*)	5.517	0.10	0.5111	0.126 34
Mussini and Pagella (*21*)	4.556	0.50	0.5168	0.096 80
Silver–Silver Chloride Concentration Cells				
Lucasse (*16*)	4.336	0.80	0.5401	0.080 53
Shedlovsky and MacInnes (*36*)	4.829	0.35	0.5223	0.096 92
McLeod and Gordon (*20*)	4.807	0.30	0.5410	0.074 93
Ion Sensitive Membrane Electrodes				
Shatkay (*35*)	4.531	0.45	0.4690	0.201
Briggs and Lilley (*3*)	4.620	0.40	0.4519	0.295 89
Lead–Lead Oxalate Electrodes				
Sahay (*32*)	4.049	0.70	0.5677	0.050
Diffusion Coefficient Measurements				
Harned and Levy (*8*)	4.297	0.00	0.7819	0.005 03

[a] Given in Ångstroms. [b] Highest concentrations to which eq 8 and 9 apply.

and 0.1000 m were calculated. These values were then used to correct the original emf's to a 0.1000 m reference concentration, the calculations were repeated, and the final results are given in Tables IV and V.

Relative activity coefficients were calculated from emf data for concentration cells with transference using the equation

$$\ln\left(\frac{\gamma_{\pm}}{\gamma_{\pm}'}\right) = \ln\left(\frac{m'}{m}\right) - \frac{2F}{3RT}\left(\frac{E}{t_+'} + \int_0^E \left(\frac{1}{t_+} - \frac{1}{t_+'}\right) \mathrm{d}E\right) \tag{10}$$

where t_+ is the cation transference number of the solution of interest. Transference numbers of $CaCl_2$ solutions have been measured by Keenan et al. (*12*) and Longsworth (*15*). If necessary, molarities were converted to molalities. The cation transference numbers of Keenan et al. and Longsworth were fitted to the equation

$$t_+ = 0.4380 - 0.168\,1173m^{1/2} + 0.194\,193\,2m - 0.274\,492\,2m^{3/2} \tag{11}$$

where $t_+{}^0 = 0.4380$ was fixed using the limiting ionic conductances given by Robinson and Stokes (*30*). The standard deviation of this equation is 0.0005 and the equation applies up to 0.0985 m. The emf data of Lucasse (*16*) and Shedlovsky and MacInnes (*36*) were used with eq 10 and 11 to yield relative activity coefficients and these, in turn, were used to yield osmotic coefficients as described above. Lucasse's high concentration data could not be used because of the absence of reliable transference number data (these high concentration data also appear to have large systematic errors). The results of these calculations are given in Tables IV and V.

McLeod and Gordon (*20*) also studied concentration cells with transference but varied their "reference" concentration from 0.0248 to 0.0250 m with one measurement using a 0.0288 m reference. Approximate relative activity coefficients were calculated using $m' = 0.0250$ in eq 10 except that actual data were used for the integral. These approximate relative activity coefficients were fitted to eq 8. The measurement using the 0.0288 m reference solution was not included in the first cycle of calculations; it was included in the next stage of the calculations. The least-squares parameters from eq 8 were used to correct the approximate relative activity coefficients to the same reference concentration. The least-squares calculations were repeated, using the corrected activity coefficients. The final results are listed in Tables IV and V.

Table VI. Parameters for Equation 14

i	r_i	A_i
1	1.00	6.894 741
2	1.25	−8.602 477
3	1.75	5.991 581
4	2.00	−3.092 098
5	2.50	$2.090\,240 \times 10^{-1}$
6	8.50	$-1.014\,690 \times 10^{-6}$
7	9.00	$6.137\,891 \times 10^{-7}$
8	9.50	$-9.377\,663 \times 10^{-8}$

The Onsager–Fuoss theory for diffusion results in the equation

$$D = \left(1 + \frac{\mathrm{d}\ln y_{\pm}}{\mathrm{d}\ln c}\right)(D^0 + \Delta 1 + \Delta 2 + \ldots) \tag{12}$$

where D is the diffusion coefficient of a solution of molar concentration c, D^0 is the diffusion coefficient at infinite dilution, and $y_{\pm}$ is the mean molar activity coefficient. This equation is applicable only to dilute solutions. The Δ's are small concentration dependent terms, obtained from consideration of the electrophoresis effect. Values of Δ1 through Δ5 have been tabulated by Stokes (*40*) for $CaCl_2$ solutions up to 0.138 m, assuming a Debye–Hückel ion-size of 4.73 Å. Stokes (*40*) and Robinson and Stokes (*30*) have concluded that theory and experiment justify the use of Δ1 and Δ2 for symmetric electrolytes but only Δ1 values for unsymmetric electrolytes like $CaCl_2$. Substituting in the relationship between mean molar and mean molal activity coefficients into eq 12 and rearranging gives

$$\ln\left(\frac{\gamma_{\pm}}{\gamma_{\pm}'}\right) = \ln\left(\frac{m'}{m}\right) + \int_{c'}^{c} \frac{D}{(D^0 + \Delta 1)c}\,\mathrm{d}c \tag{13}$$

which can be used to calculate relative mean molal activity coefficients for $CaCl_2$ solutions.

Diffusion coefficient measurements for dilute $CaCl_2$ solutions (*8, 9*) are not in good agreement with each other, and measurements for more concentrated solutions (*17*) have failed to resolve this discrepancy. The data of Harned and Levy (*8*) and Harned and Parker (*9*) were separately used to calculate relative mean molal activity coefficients. Since Δ1 depends on the Debye–Hückel ion-size parameter, successive approximations were used to obtain its value. As a first approximation, Stokes' (*40*) Δ1 values were used and the resulting relative activity coefficients fitted to eq 8 and a new least-squares ion-size parameter obtained for each data set. These new ion-size parameters were used to generate new Δ1's and the process repeated until å no longer changed. The data of Harned and Parker (*9*) gave an å value twice as large as those obtained from emf data so their results are not included in the tables. The "self-consistent" results for Harned and Levy's data (*8*) are listed in Tables IV and V.

The osmotic coefficients of $CaCl_2$ solutions were fitted to the equation

$$\phi = 1 - (A/3)(m^{1/2}) + \sum_i A_i m^{r_i} \tag{14}$$

where $A = (0.51082)(2)(3^{1/2})(2.302\,585) = 4.0744$. This equation is equivalent to the Debye–Hückel limiting law with a power series added. Three sets of calcium amalgam emf data (*5, 16, 33*) and the lead–lead oxalate emf data (*32*) were not included in the least-squares fit to eq 14 since these measurements apparently have large systematic errors. Because of the temperature correction to 25 °C, the freezing point depression data of Gibbard and Fong (*6*) were assigned weights of 0.75 (9 points). Diffusion coefficient data (*8*) were given weights of 0.5

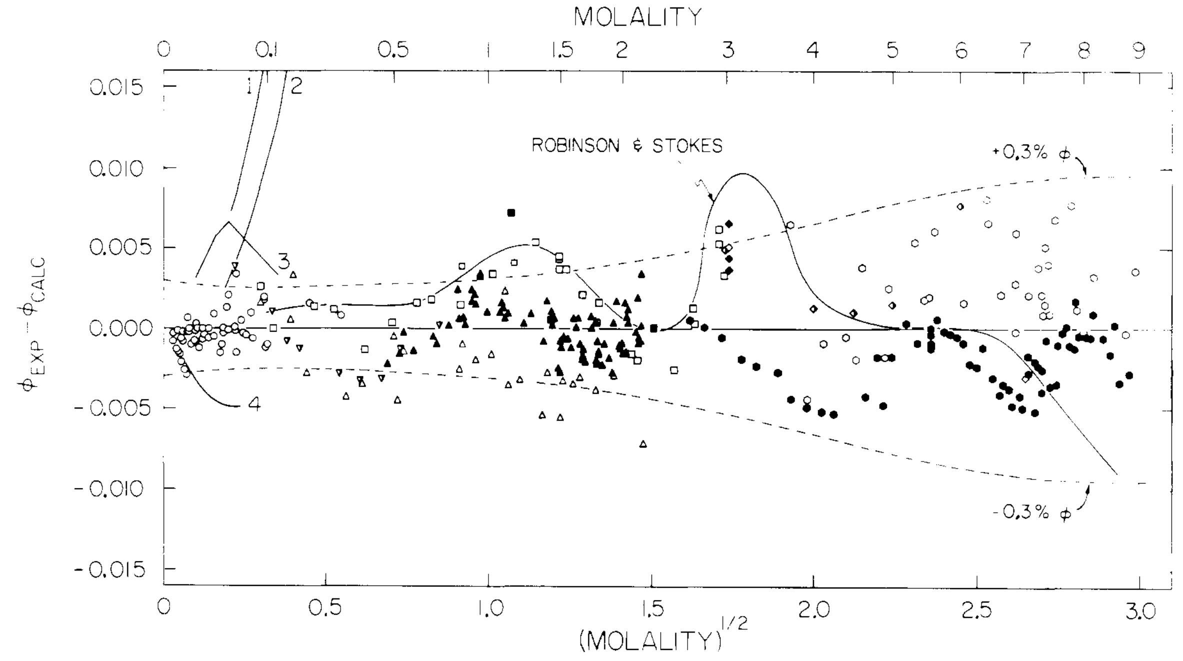

Figure 1. Differences between experimental and calculated osmotic coefficients for aqueous $CaCl_2$ at 25 °C: - -, deviation of ±0.3% ϕ; O, Stokes vs. H_2SO_4 (*38*); ●, Rard and Spedding (*28*); □, Stokes vs. NaCl (*38*); ■, Platford (*26*); △, Robinson (*29*); ▲, Spedding et al. (*37*); ◇, Bechtold and Newton (*2*); ◆, Stokes (*39*); ◇, Petit (*24*); ▽, Gibbard and Fong (*6*); O, emf and diffusion coefficient data (*3, 8, 16, 20, 21, 35, 36*). Data sets not included in least-squares fit: 1, Lucasse Ca amalgam (*16*); 2, Fosbinder (*5*); 3, Scatchard and Tefft (*33*); 4, Sahay (*32*).

(eight points) since it is unclear to what concentration the Onsager–Fuoss theory should be valid. All other data were assigned weights of 1 (283 points, of which 228 are based on isopiestic measurements) or 0 (26 points). The powers and coefficients for the best fit to eq 14 are given in Table VI.

A considerable number of least-squares fits of the osmotic coefficient data to eq 14 were performed, with three to eight terms in the polynomial. Series in m, $m^{1/2}$, $m^{1/4}$, and $m^{1/8}$ were investigated and the r_i were not constrained to form consecutive series. Eight terms were required to reliably fit the data and a number of series in $m^{1/4}$ and $m^{1/8}$ did fairly well. The values of r_i and A_i for the best fit are given in Table VI. The standard deviation of this fit, σ, is 0.0027. The errors of the coefficients range from 0.6 to 5.0%, and increase with the size of the power. These power series are completely empirical but eq 14 has the correct theoretical limiting law behavior at low concentrations. The osmotic coefficients of $CaCl_2$ solutions go through a maximum, in the supersaturated concentration region, around 9.0 m. Since this maximum is rather flat, a large number of terms are required to represent this behavior. The five highest concentrations of Stokes (*38*) occur after this maximum. They were given weights of zero (although they are probably reliable) in the least-squares fit since to include them would have reduced the quality of the fit below 9.0 m. A rejection criteria of three σ was used above 1.0 m. Below 1.0 m, the osmotic coefficients of $CaCl_2$ solutions fall below 1.0 and a two σ rejection criteria was used in this region. On this basis, 21 points were assigned weights of zero, 8 of these from Petit (*24*).

In Figure 1 the differences between the experimental and calculated osmotic coefficients of $CaCl_2$ are shown, as a function of the square root of the molality, for the best fit. The tabulated osmotic coefficients of Robinson and Stokes (*30*) are also compared to the experimental data and eq 14 in Figure 1. The scatter in the data about eq 14 indicates that the osmotic coefficients of $CaCl_2$ are uncertain to about ±0.3% over the entire concentration range. Most of the data above 3.0 m were determined by isopiestic comparison to H_2SO_4, and the osmotic coefficients of H_2SO_4 are also uncertain to about ±0.3% (*27*). The main differences between Robinson and Stokes' results and eq 14 arise from the revision of the H_2SO_4 standard data (*27*) and the incorporation of additional data into this review. The four sets of emf data that were not included in the least-squares fit to eq 14 are also indicated in Figure 1. It can be seen that these data show large systematic differences from the other data sets.

As can be seen from Figure 1, eq 14 falls within the scatter of the experimental data. In addition, differences between this equation and actual trends in the data are small, being 0–0.2% of ϕ. It was found that some of the six- and seven-term polynomial fits did moderately well, with standard deviations being only 12–20% larger than the fit finally chosen to represent these data. However, while these polynomials with fewer terms did fairly well below 2.5 m, they cycled outside the scatter of the data at high concentrations so an eight-term polynomial was felt to be justified. There were a number of other eight-term series that had only slightly larger standard deviations than the series finally chosen. It should also be noted that eq 14 is based on data from dilute solution to 9.0 m and is not reliable for extrapolations beyond this concentration region (it turns down too sharply above 9.0 m).

Application of the Gibbs–Duhem relationship to eq 14 yields

$$\ln \gamma_\pm = -Am^{1/2} + \sum_i A_i \left(\frac{r_i + 1}{r_i}\right) m^{r_i} \qquad (15)$$

for the mean molal activity coefficient of $CaCl_2$. Values of ϕ, a_1, and $\gamma_\pm$ are given in Table VII at various even molalities.

Thermodynamic data at temperatures other than 25 °C are sometimes required for various purposes. For some of these purposes data of lower accuracy or precision, than are required for isopiestic standards, are adequate. A listing of such data for $CaCl_2$ solutions, from the 1800's to 1957 is available (*41*). While data are listed in that work, they are not critically evaluated. Similar data for H_2SO_4 are given in volume IV of that work.

Summary

Osmotic coefficient data for aqueous solutions of $CaCl_2$ at 25 °C have been reviewed and updated. A semiempirical equation is given which represents these data up to 9.0 m, but

Table VII. Thermodynamic Properties of $CaCl_2$ Solutions at 25 °C

m	ϕ	a_1	$\gamma_\pm$
0.005	0.9275	0.999 749	0.7874
0.01	0.9075	0.999 510	0.7291
0.02	0.8863	0.999 042	0.6645
0.03	0.8744	0.998 583	0.6256
0.04	0.8668	0.998 128	0.5981
0.05	0.8617	0.997 674	0.5773
0.06	0.8582	0.997 221	0.5608
0.07	0.8558	0.996 768	0.5472
0.08	0.8541	0.996 314	0.5359
0.09	0.8531	0.995 859	0.5261
0.1	0.8525	0.995 403	0.5178
0.2	0.8594	0.990 753	0.4713
0.3	0.8752	0.985 910	0.4535
0.4	0.8943	0.980 85	0.4471
0.5	0.9154	0.975 57	0.4470
0.6	0.9381	0.970 04	0.4511
0.7	0.9623	0.964 25	0.4586
0.8	0.9878	0.958 19	0.4689
0.9	1.0146	0.951 85	0.4817
1.0	1.0426	0.945 21	0.4968
1.2	1.1021	0.931 02	0.5342
1.4	1.1656	0.915 58	0.5809
1.6	1.2327	0.898 89	0.6379
1.8	1.3028	0.880 96	0.7061
2.0	1.3756	0.861 8	0.7870
2.2	1.4508	0.841 6	0.8824
2.4	1.5278	0.820 2	0.9945
2.6	1.6065	0.797 9	1.126
2.8	1.6866	0.774 7	1.280
3.0	1.7678	0.750 8	1.459
3.2	1.8498	0.726 2	1.669
3.4	1.9324	0.701 1	1.913
3.6	2.0153	0.675 6	2.197
3.8	2.0982	0.649 9	2.527
4.0	2.1807	0.624 1	2.910
4.5	2.3830	0.560 1	4.142
5.0	2.5739	0.498 8	5.858
5.5	2.7457	0.442 1	8.150
6.0	2.8908	0.391 6	11.04
6.5	3.0032	0.348 2	14.44
7.0	3.0816	0.311 7	18.17
7.5	3.1299	0.281 2	22.05
8.0	3.1576	0.255 3	26.04
8.5	3.1739	0.232 7	30.17
9.0	3.1746	0.213 5	34.20

this equation should not be used for extrapolation beyond this concentration region. The scatter of the experimental osmotic coefficients around the least-squares representation of these data is about ±0.3% at all concentrations, but some additional data would be desirable in the 2–4-m concentration range.

Acknowledgments

The authors thank Dr. Bert R. Staples at the NBS Electrolyte Data Center for access to his calculations prior to publication.

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Received for review June 14, 1976. Accepted December 13, 1976. This work was performed for the U.S. Energy Research and Development Administration under Contract No. W-7405-eng-82.