The Activity and Osmotic Coefficients of Trivalent Metal Chlorides in Aqueous Solution from Vapor Pressure Measurements at 25°

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In a previous communication[1] it was shown how the isotonic or isopiestic method of Robinson and Sinclair[2] could be adapted to the measurement of the vapor pressures of the aqueous solutions of the three–one electrolyte, lanthanum chloride. In the present investigation, with revised technique, this method has been extended to the determination of the vapor pressures of six more three–one electrolytes: namely, aluminum chloride, scandium chloride, yttrium chloride, cerous chloride, praseodymium chloride, and neodymium chloride. In the present work the previous data for lanthanum chloride were extended to higher concentrations and more accurate data obtained in the concentration range below 0.4 molal. All the data obtained in each case have been used to compute the osmotic and activity coefficients for the corresponding salt.

Experimental Details

Apparatus.—The apparatus employed was modified from that described by Mason and Gardner.[3] The brass desiccator used was supplemented by an additional one cast of monel metal. This metal was found to be freer of pinholes and easier to make vacuum tight. For this investigation the metal tee tube formerly used was replaced by a brass needle valve to which was soldered the female half of a brass union. The male half of the union was connected by rubber tubing to the vacuum line. Another male half of the union, interchangeable with the first, was soldered shut and served to keep water out of the needle valve during immersion in the thermostat. A diagram of the metal desiccator as used is shown in Fig. 1.
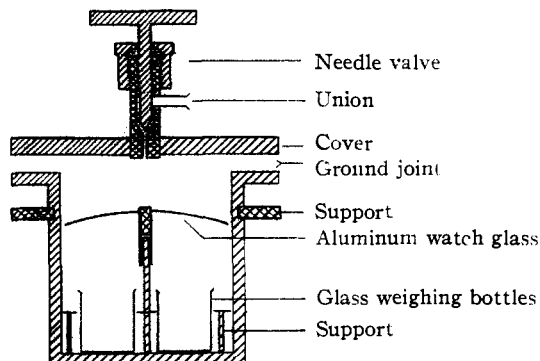

Fig. 1.—Metal desiccator.

With the more concentrated solutions it was found possible to obtain reproducible results using 30-cc. glass-stoppered weighing bottles in the apparatus. The solutions under investigation were weighed in these bottles. In order to ensure more rapid thermal and distillation equilibrium, platinum gauze was placed in the solutions in the glass bottles. This was done in the form of strips of gauze 1 cm. wide by 10 cm. long folded like a bellows and placed edgewise to stand up in the bottom of the weighing bottles. The strips were then about half in and half out of the solution, providing additional surface as well as thermal conduction. The platinum gauze was found to decrease by more than half the minimum time needed to obtain equilibrium. In order to prevent grease and other films from interfering with the wetting of the platinum they were ignited in the Meker burner before each run.

The glass bottles in the desiccator were immersed to a depth of about 0.3 cm. in potassium chloride or sodium chloride solution of the same concentration as that used in the reference bottles. They were held in place by a brass frame which kept them from tipping over and at the same time served as a shield to prevent any of the solution in the bottom from splashing into the bottles themselves. Attached to the frame above the bottles was a watch glass shaped disk of aluminum which acted as a shield to keep any spray from getting into the bottles when air was admitted at the end of a run.

Below 0.5 molal the accuracy obtained with glass bottles decreased rapidly with decreasing concentration. The glass bottles were therefore replaced in this range by similar bottles made of sterling silver and heavily gold plated. Stainless steel was tried but was found not to withstand corrosion. The design of the silver containers is shown in Fig. 2. They were made to fit tightly into
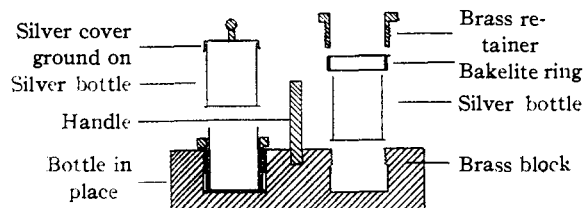
Fig. 2.—Brass block with silver bottles.

recesses in a heavy copper block. A good thermal contact was secured by pressing them firmly against the bottom of the recess with a bakelite collar (to prevent wear) which was in turn forced down by a brass collar screwed into the top of the recess. It was found that equilibrium could be obtained without a contacting solution and so none was used. The air was removed from under the bottles and from under the copper block by putting a drop of water under each silver bottle and several drops under the block in the bottom of the desiccator. This evaporated when the desiccator was evacuated and swept the air out ahead

(1) Mason and Ernst, THIS JOURNAL, **58**, 2032 (1936).
(2) Robinson and Sinclair, *ibid.*, **56**, 1830 (1934).
(3) Mason and Gardner, *J. Chem. Ed.*, **13**, 188 (1936).

of it. No water was ever found in these places when a run was completed. In all cases the desiccator was evacuated slowly to prevent boiling and splashing. allowed to stand for one hour or more. and then reëvacuated to remove the last traces of air.

The concentration of the solution in all of the bottles was determined in the usual manner. namely. by weighing. Care was taken to wipe the bottles with a damp cloth before each weighing and thus the weights could always be reproduced within the error of the balance.

All measurements were carried out in a water thermostat at 25 ± 0.01°. The temperature was determined by thermometers checked against thermometers calibrated by the Bureau of Standards. The thermostat was equipped with a shaking device to rock the metal desiccators back and forth. about forty-five times a minute. thereby keeping the solutions in constant agitation.

Materials. (a) **Aluminum Chloride.**—The best commercial grade of hydrated aluminum chloride was dissolved in water, filtered, and recrystallized four times by shaking out of solution with hydrogen chloride gas at 0°. The hydrated salt so obtained was carefully dried in a current of warm air at 50–70° and then ground in an agate mortar to pass 20 mesh. This material was then placed for several weeks over potassium hydroxide in a vacuum desiccator to remove the last traces of hydrogen chloride. The product was analyzed gravimetrically for chloride ion by the usual methods and for the aluminum present by the method of Willard and Tang.[4] The results of the analysis indicated a purity better than 99.97%.

(b) **Cerous Chloride.**—The cerous chloride used had been prepared from a very pure sample of cerium oxalate by the method of Hönigschmid and Holch[5] and was found to be of high purity by spectroscopic analysis. The salt was recrystallized three times by shaking out of solution with hydrogen chloride gas at 0°. A pure white product was obtained entirely free from any trace of ceric cerium. This product was then purified as follows: The hydrated salt was dried in a current of warm air at 50–70° until all traces of hydrogen chloride appeared to be removed. The dried salt was then dissolved in a minimum amount of conductivity water. a few drops of concentrated hydrochloric acid added to prevent hydrolysis, and evaporated to a thick sirup on the steam-bath. This sirup was chilled to 0°, seeded if possible. and stirred vigorously with a motor stirrer. This action produced a mass of very fine crystals which were easily filtered onto a fritted glass plate. sucked free of mother liquor, and air-dried as before. The final drying was accomplished in a vacuum desiccator.

(c) **Hydrochloric Acid.**—All the hydrochloric acid used was obtained by distilling the best commercial grade of arsenic-free acid in an all-glass still and discarding the first and third portions.

(d) **Lanthanum Chloride.**—The lanthanum material had been prepared carefully by repeated crystallization as the oxalate and the hydroxide. The chloride was prepared by ignition of the oxalate to the oxide in an electric muffle furnace and solution of this oxide in hydrochloric acid. After filtering, the solution was evaporated and the chlo-

ride shaken out at 0° with hydrogen chloride. The product was purified by the same procedure as for cerous chloride.

(e) **Neodymium Chloride.**—This was prepared in a manner similar to that for cerous and lanthanum chloride.

(f) **Potassium and Sodium Chlorides.**—These salts were the best commercial material twice recrystallized from water and dried for twenty-four hours in an electric oven at 120°.

(g) **Praseodymium Chloride.**—Praseodymium oxalate was obtained from the estate of the late Charles James. It was purified by the method of Brauner[6] to remove cerium and lanthanum. The oxide so obtained was converted to the chloride and purified by the same method as that given for lanthanum and cerous chloride.

(h) **Scandium Chloride.**—Scandium oxalate was converted to the chloride and purified in a manner similar to the lanthanum chloride.

(i) **Yttrium Chloride.**—The yttrium oxalate was ignited to the oxide, dissolved in hydrochloric acid, and reprecipitated as the oxalate five times until all trace of the impurity, sodium, was removed. The chloride was then prepared and purified in a manner similar to that for lanthanum chloride.

Procedure.—In all the experimental work the analysis of the solutions under investigation was obtained from the weight of the bottles containing them. To make the standard reference solutions, enough potassium or sodium chloride. whichever was used, was weighed directly into the bottles to make between 1 and 2 cc. of solution of the concentration desired. The requisite amount of water was then added. Below 0.4 molal the weights of these salts became so small as to introduce weighing errors, and solutions of known concentration were weighed into the bottles instead. These were diluted with the proper amount of water before being placed in the desiccator.

It was not practical to weigh out the hydrated salts directly, so concentrated solutions in conductance water were prepared and carefully analyzed for chloride ion by the gravimetric method. These solutions were weighed directly into the bottles and diluted to the approximate concentration before being placed in the apparatus. All solutions were stored in Pyrex brand glass to prevent introduction of any dissolved material.

In several cases the solutions were also analyzed for rare earth content by precipitation of the oxalate and subsequent ignition to the oxide in the muffle furnace according to the standard procedure. The only divergence in the analyses was for cerium where the method outlined by Moore and Bonardi[7] and modified by Hillebrand and Lundell[8] was employed. In every case the concentration of the solutions checked that obtained from the chloride analysis within the known experimental error.

Density Measurements.—In the theoretical treatment it was necessary to know the concentration in moles per liter. which was calculated from the molality by means of the density. The densities of all these salts in aqueous solution were determined in duplicate at 25° using a 25-g.

(4) Willard and Tang. THIS JOURNAL. **59**, 1190 (1937).

(5) Hönigschmid and Holch, Z. anorg. allgem. Chem.. **177**. 91 (1928).

(6) Brauner. Coll. Czech. Chem. Comm.. **5**. 279 (1933).

(7) Moore and Bonardi. Bur. Mines Bull.. **212**, 43 (1923).

(8) Hillebrand and Lundell. "Applied Inorganic Analysis." John Wiley and Sons. Inc.. New York. N. Y.. 1929. p. 434.

TABLE I
ISOTONIC RATIOS AND OSMOTIC COEFFICIENTS OF THE SALT SOLUTIONS

Aluminum Chloride (m_2) against Sodium Chloride (m_1)

m_1	m_2	φ_1	φ_2
6.1440	1.8025	1.2987	2.2132
6.1440	1.8048	1.2987	2.2105
6.1440	1.8065	1.2987	2.2084
5.7681	1.7259	1.2658	2.1151
5.7380	1.7213	1.2630	2.1050
5.5518	1.6819	1.2470	2.0581
5.4913	1.6629	1.2418	2.0504
5.4047	1.6527	1.2346	2.0187
5.3806	1.6442	1.2324	2.0165
5.0535	1.5737	1.2046	1.9341
4.6805	1.4920	1.1725	1.8391
4.6081	1.4735	1.1670	1.8248
4.0092	1.3323	1.1175	1.6814

Aluminum Chloride (m_2) against Potassium Chloride (m_1)

m_1	m_2	φ_1	φ_2
4.6099	1.3350	0.9835	1.6981
4.4577	1.3108	.9785	1.6638
4.2475	1.2650	.9713	1.6307
3.9090	1.2002	.9603	1.5638
3.5684	1.1306	.9500	1.4992
3.4809	1.1167	.9473	1.4765
3.1511	1.0437	.9375	1.4153
2.9196	0.9903	.9308	1.3721
2.7913	.9617	.9272	1.3456
2.7241	.9477	.9254	1.3300
2.3830	.8645	.9165	1.2632
2.0056	.7680	.9082	1.1859
1.8342	.7176	.9053	1.1570
1.3561	.5782	.9004	1.0559
1.3511	.5745	.9004	1.0588
1.3266	.5682	.9002	1.0509
1.0185	.4632	.8985	0.9878
0.9905	.4537	.8984	.9807
.8531	.4039	.8980	.9495
.8150	.3885	.8980	.9419
.6994	.3462	.8980	.9071
.5472	.2792	.8993	.8812
.3916	.2073	.9027	.8526
.3814	.2040	.9029	.8440
.2494	.1370	.9093	.8276
.1851	.1041	.9150	.8134
.1681	.09473	.9169	.8136
.1643	.09230	.9174	.8164
.1488	.08374	.9195	.8170
.1409	.08015	.9208	.8093
.1205	.06811	.9240	.8174
.1034	.05830	.9272	.8222
.09569	.05416	.9287	.8204

Scandium Chloride (m_2) against Sodium Chloride (m_1)

m_1	m_2	φ_1	φ_2
6.1440	1.9549	1.2987	2.0408
6.1440	1.9568	1.2987	2.0388
5.7609	1.8679	1.2663	1.9527
5.7313	1.8596	1.2625	1.9455
5.7247	1.8596	1.2618	1.9422
5.7313	1.8642	1.2625	1.9407
5.4983	1.7993	1.2425	1.8984
5.4047	1.7814	1.2364	1.8756
5.0535	1.6891	1.2046	1.8018
4.6860	1.5960	1.1752	1.7253

Scandium Chloride (m_2) against Potassium Chloride (m_1)

m_1	m_2	φ_1	φ_2
4.8040	1.4599	0.9900	1.6289
4.7704	1.4535	.9887	1.6225
4.4252	1.3790	.9770	1.5676
4.3707	1.3631	.9752	1.5635
4.3618	1.3631	.9750	1.5600
4.3468	1.3596	.9745	1.5578
4.3360	1.3616	.9741	1.5510
3.9044	1.2602	.9602	1.4875
3.8839	1.2653	.9595	1.4726
3.8796	1.2602	.9594	1.4768
3.5077	1.1780	.9483	1.4119
3.3977	1.1493	.9449	1.3970
3.2965	1.1282	.9418	1.3759
3.2788	1.1217	.9413	1.3757
3.1241	1.0845	.9369	1.3495
3.0378	1.0699	.9343	1.3265
2.7903	1.0031	.9272	1.2896
2.7652	0.9980	.9265	1.2835
2.6955	.9812	.9246	1.2700
2.5656	.9471	.9212	1.2477
2.3147	.8834	.9148	1.1985
1.8067	.7387	.9049	1.1066
1.7990	.7339	.9047	1.1088
1.6753	.6978	.9032	1.0842
1.4169	.6160	.9009	1.0361
1.1667	.5313	.8992	0.9873
0.9721	.4602	.8983	.9483
.9359	.4470	.8982	.9403
.7213	.3612	.8980	.8966
.6927	.3483	.8981	.8931
.5634	.2980	.8991	.8499
.5627	.2963	.8991	.8537
.5621	.2919	.8991	.8657
.4849	.2569	.9002	.8496
.4896	.2565	.9002	.8591
.4762	.2598	.9005	.8253
.4345	.2330	.9015	.8406
.4221	.2322	.9018	.8197
.4183	.2322	.9019	.8124
.3916	.2139	.9026	.8262
.3814	.2074	.9030	.8303
.3786	.2113	.9031	.8091
.3587	.1994	.9037	.8128
.2584	.1433	.9087	.8193
.2205	.1270	.9132	.7928
.1626	.09363	.9176	.7966
.1559	.09179	.9185	.7800
.1559	.09140	.9185	.7833

Yttrium Chloride (m_2) against Sodium Chloride (m_1)

m_1	m_2	φ_1	φ_2
6.1440	2.0166	1.2987	1.9784
5.3806	1.8255	1.2324	1.8162
4.6081	1.6235	1.1670	1.6561
4.0092	1.4634	1.1175	1.5531

Yttrium Chloride (m_2) against Potassium Chloride (m_1)

m_1	m_2	φ_1	φ_2
4.8040	1.5118	0.9900	1.5729
4.3663	1.4164	.9752	1.5031
3.8920	1.3051	.9598	1.4311
3.1241	1.1240	.9376	1.3030
2.7652	1.0337	.9265	1.2392
2.3147	0.9114	.9148	1.1617
1.8067	.7617	.9049	1.0732
1.4169	.6337	.9008	1.0071
1.1667	.5449	.8992	0.9627
0.9721	.4715	.8983	.9261
.6927	.3567	.8981	.8720
.6055	.3165	.8989	.8599
.4118	.2266	.9020	.8196
.3494	.1957	.9042	.8072
.2372	.1366	.9102	.7902
.2312	.1347	.9106	.7815
.1974	.1148	.9138	.7856
.1237	.07104	.9235	.8040

Lanthanum Chloride (m_2) against Sodium Chloride (m_1)

m_1	m_2	φ_1	φ_2
6.1440	2.1461	1.2987	1.8629
5.6391	2.0018	1.2544	1.7668
5.3127	1.9103	1.2292	1.7092
5.0510	1.8360	1.2046	1.6569
4.3974	1.6473	1.1493	1.5340

Lanthanum Chloride (m_2) against Potassium Chloride (m_1)

m_1	m_2	φ_1	φ_2
4.2776	1.4573	0.9705	1.4243
4.1533	1.4317	.9679	1.4039
3.8814	1.3663	.9595	1.3629
3.8541	1.3595	.9586	1.3588
3.7674	1.3381	.9559	1.3456
3.5795	1.2908	.9503	1.3176
3.4381	1.2574	.9461	1.2934
3.4075	1.2472	.9450	1.2910
3.2548	1.2071	.9406	1.2681
2.8414	1.0967	.9285	1.2028
2.5870	1.0272	.9217	1.1606
2.4924	0.9985	.9182	1.1460
2.0895	.8767	.9098	1.0842
1.7321	.7618	.9038	1.0274
1.7105	.7548	.9035	1.0238
1.4362	.6603	.9010	0.9798
1.0312	.5069	.8990	.9144
0.7337	.3794	.8980	.8683
.5697	.3063	.8990	.8361
.5440	.2953	.8994	.8284
.3784	.2096	.9031	.8150
.2494	.1439	.9092	.7893
.2003	.1172	.9133	.7811
.1955	.1131	.9138	.7898
.1913	.1103	.9112	.7902
.1698	.09874	.9166	.7880
.1671	.09767	.9170	.7846
.1390	.08117	.9325	.7986
.1385	.08165	.9209	.7820
.1268	.07349	.9230	.7972
.1109	.06424	.9257	.7989

TABLE I (Continued)

Cerium Chloride (m_2) against Sodium Chloride (m_1)

m_1	m_2	φ_1	φ_2
6.1440	2.1202	1.2987	1.8817
6.1440	2.1165	1.2987	1.8850
5.6391	1.9821	1.2544	1.7844
5.4913	1.9303	1.2418	1.7662
5.3127	1.8923	1.2292	1.7256
5.0510	1.8210	1.2046	1.6707
5.0535	1.8172	1.2046	1.6750
4.3974	1.6345	1.1493	1.5460

Cerium Chloride (m_2) against Potassium Chloride (m_1)

m_1	m_2	φ_1	φ_2
4.8040	1.5907	0.9900	1.4949
4.3663	1.4851	.9752	1.4335
3.8920	1.3672	.9598	1.3661
3.1241	1.1734	.9376	1.2481
2.8408	1.0861	.9290	1.2149
2.7652	1.0766	.9265	1.1900
2.4474	0.9862	.9182	1.1393
2.0903	.8676	.9097	1.0967
1.7990	.7801	.9047	1.0432
1.7643	.7667	.9043	1.0408
1.6236	.7165	.9026	1.0226
1.4169	.6513	.9008	0.9798
1.3672	.6303	.9005	.9767
1.2461	.5876	.8997	.9540
1.1667	.5616	.8992	.9340
1.0759	.5210	.8988	.9280
0.9721	.4822	.8983	.9055
.6927	.3625	.8981	.8581
.4082	.2263	.9021	.8136
.3482	.1955	.9042	.8052
.2074	.1203	.9126	.7867
.1436	.08461	.9203	.7810
.1276	.07570	.9227	.7777

Praseodymium Chloride (m_2) against Sodium Chloride (m_1)

m_1	m_2	φ_1	φ_2
6.1440	2.1298	1.2987	1.8732
6.1440	2.1346	1.2987	1.8690
5.9287	2.0712	1.2840	1.8377
5.5518	1.9711	1.2470	1.7562
5.4913	1.9515	1.2418	1.7471
5.3806	1.9225	1.2324	1.7245
5.0535	1.8283	1.2046	1.6648
4.6081	1.7076	1.1670	1.5746
4.0092	1.5307	1.1175	1.4634

Praseodymium Chloride (m_2) against Potassium Chloride (m_1)

m_1	m_2	φ_1	φ_2
4.3663	1.4808	0.9752	1.4377
3.8920	1.3665	.9598	1.3669
3.1241	1.1710	.9376	1.2507
2.7652	1.0767	.9265	1.1897
2.3147	0.9465	.9148	1.1186
1.8067	.7908	.9049	1.0337
1.7990	.7854	.9047	1.0362
1.4169	.6540	.9008	0.9758
1.1667	.5635	.8992	.9309
0.9721	.4844	.8983	.9014
.6927	.3648	.8981	.8527
.6055	.3216	.8989	.8461
.4115	.2296	.9020	.8101
.3494	.1977	.9042	.7990
.2372	.1374	.9102	.7857
.2312	.1338	.9106	.7867
.1974	.1158	.9138	.7783
.1355	.08038	.9215	.7767
.1187	.06985	.9244	.7854

Neodymium Chloride (m_2) against Sodium Chloride (m_1)

m_1	m_2	φ_1	φ_2
5.9376	2.0517	1.2848	1.8591
5.9287	2.0517	1.2840	1.8551
5.5518	1.9491	1.2470	1.7760
5.3806	1.9098	1.2324	1.7369
4.6081	1.6908	1.1670	1.5903
4.0092	1.5183	1.1175	1.4754

Neodymium Chloride (m_2) against Potassium Chloride (m_1)

m_1	m_2	φ_1	φ_2
4.6046	1.5254	0.9832	1.4889
4.4254	1.4840	.9772	1.4570
4.4205	1.4841	.9770	1.4550
4.3747	1.4724	.9775	1.4485
4.3264	1.4622	.9642	1.4264
3.9793	1.3783	.9626	1.3886
3.9739	1.3765	.9623	1.3890
3.7302	1.3196	.9547	1.3494
3.6443	1.2998	.9522	1.3349
3.3946	1.2344	.9447	1.2990
3.0498	1.1453	.9345	1.2442
2.9095	1.1085	.9306	1.2213
2.6249	1.0293	.9227	1.1765
2.2975	0.9346	.9144	1.1239
1.8291	.7905	.9051	1.0471
1.5467	.6945	.9019	1.0043
1.2232	.5791	.8485	.9489
0.8961	.4505	.8980	.8932
.6898	.3608	.8981	.8585
.4924	.2695	.9001	.8224
.4724	.2613	.9005	.8140
.4082	.2282	.9021	.8068
.3482	.1960	.9042	.8032
.2686	.1541	.9080	.7913
.2074	.1207	.9126	.7841
.1436	.08443	.9203	.7826
.1276	.07430	.9227	.7923

Regnault specific gravity bottle. The usual precautions were observed and the results are given in Table IV.

Results and Discussion

In most of the experimental runs three samples of the salt solution were allowed to come to isotonic equilibrium with a like number of the standard reference solution. When the silver bottles were used two samples were in equilibrium with the two samples of standard solutions. In some experiments only two samples of the standard solution were used and these were opposed by two or four different salt solutions as the case might be. Ample time, usually more than forty-eight hours, was allowed in every case for the solutions to reach equilibrium with each other. No experiment was considered satisfactory if the deviation between identical samples was greater than one part per thousand.

Potassium chloride was used as a reference salt up to saturation and sodium chloride was used to extend the range of the three–one electrolytes beyond the concentrations which could be obtained with potassium chloride.

The silver bottles gave good results down to about 0.25 molal but below this concentration, although fair results were obtained down to about 0.06 molal, the results were inclined to be quite erratic and had about ten times the error of the results above 0.25 molal. In general, the results for all the salts are of about the same accuracy. The observed values of φ_2 did not, as a rule, deviate more than one per cent. from a smooth curve such as is shown in Fig. 3. The average deviation was about 0.2% in concentrated solutions and 0.5% in dilute. Scandium chloride was more erratic than the rest and gave larger

TABLE II

SMOOTHED OSMOTIC COEFFICIENTS, φ_2

m_1	μ	AlCl$_3$	ScCl$_3$	YCl$_3$	LaCl$_3$	CeCl$_3$	PrCl$_3$	NdCl$_3$
0.05	0.30	0.826	0.807	0.810	0.800	0.800	0.801	0.797
.1	0.60	.812	.794	.791	.788	.784	.782	.784
.2	1.2	.841	.815	.808	.801	.798	.796	.795
.3	1.8	.890	.858	.847	.831	.832	.828	.828
.4	2.4	.948	.912	.892	.869	.871	.865	.866
.5	3.0	1.009	.970	.940	.910	.914	.906	.909
.6	3.6	1.074	1.028	.990	.952	.958	.950	.954
.7	4.2	1.141	1.088	1.042	.998	1.005	.995	1.003
.8	4.8	1.213	1.150	1.096	1.046	1.055	1.042	1.053
.9	5.4	1.291	1.216	1.155	1.097	1.106	1.094	1.105
1.0	6.0	1.378	1.285	1.217	1.150	1.160	1.148	1.159
1.1	6.6	1.471	1.359	1.283	1.205	1.214	1.206	1.216
1.2	7.2	1.564	1.433	1.351	1.264	1.270	1.267	1.275
1.3	7.8	1.657	1.507	1.420	1.323	1.328	1.327	1.335
1.4	8.4	1.753	1.583	1.491	1.382	1.387	1.388	1.399
1.5	9.0	1.855	1.659	1.564	1.445	1.455	1.447	1.464
1.6	9.6	1.966	1.734	1.639	1.506	1.515	1.508	1.529
1.8	10.8	2.203	1.889	1.796	1.633	1.657	1.638	1.662
2.0	12.0	...	2.040^a	1.965	1.766	1.796	1.777	1.809
2.2	13.2	...	...	...	1.899	1.935^a	1.922^a	1.940^a

^{a} Extrapolated.

deviations. The isotonic data obtained are listed in Table I.
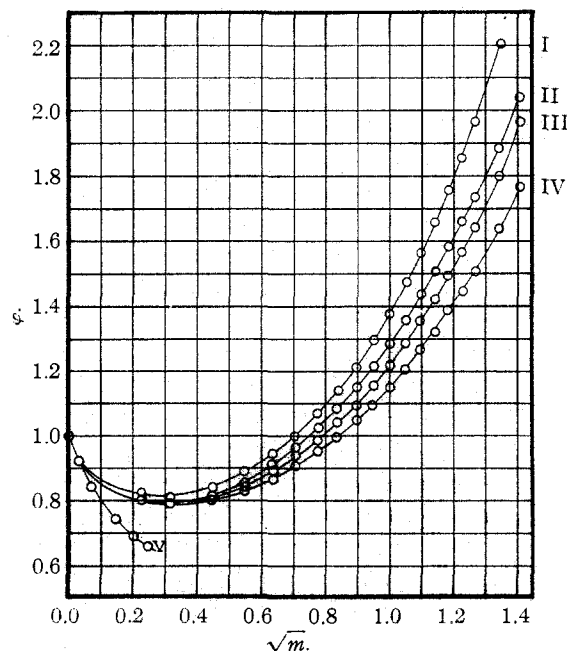
Fig. 3.—Osmotic coefficients of salts: I, AlCl$_3$; II. ScCl$_3$; III. YCl$_3$; IV. LaCl$_3$; V. φ_0. limiting law.

Table I includes the values of φ_1 and φ_2. The values of φ_1 were taken from those of Scatchard and Wood[9] which were given to me prior to publication by Professor Scatchard. These data represent the best possible evaluation of all the

(9) Scatchard and Wood, unpublished.

known data for potassium and sodium chlorides. The values of φ_1 in Table I were read from a large-scale plot of the data described above.

φ_2 is defined by the equation

$$\varphi_2 = (55.51/4 \; m_2) \ln p_0/p \qquad (1)$$

and φ_1 by the equation

$$\varphi_1 = (55.51/2 \; m_1) \ln p_0/p \qquad (2)$$

p_0/p is the same for both salts when at isotonic equilibrium and combining equations (1) and (2) we obtain

$$\varphi_2 = \frac{m_1}{2m_2} \varphi_1 \qquad (3)$$

By means of equation (3) the values of φ_2 in Table I were computed. These values have been smoothed graphically by plotting φ_2 against $m^{1/2}$ on a large scale as shown in Fig. 3. The data which were obtained are listed at round concentrations in Table II.

The activity coefficients have been computed from the osmotic coefficients by a modification of the method of Randall and White[10] using the equation

$$\log \gamma = -\frac{h}{2.303} - \frac{2}{2.303} \int_0^{m^{1/2}} \frac{h}{m^{1/2}} \, dm^{1/2} \qquad (4)$$

From the data of Wyman[11] the intercept on the $h/m^{1/2}$ axis was calculated to be 2.844. When the curve was constructed, as shown in Fig. 4, it was found that a large portion of the area was in the region below 0.25 molal where the data were least

(10) Randall and White, THIS JOURNAL, 48, 2514 (1926).
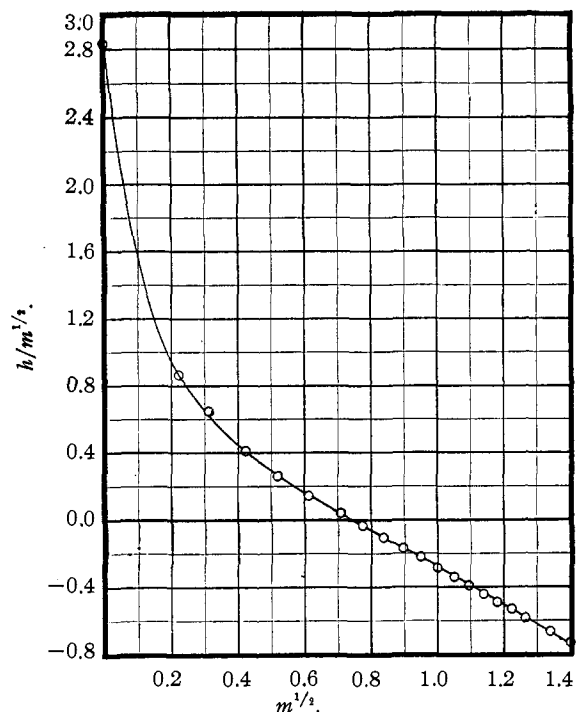(11) Wyman. Phys. Rev.. 35, 623 (1930).

Fig. 4.—Plot of $h/m^{1/2}$ against $m^{1/2}$ for ScCl$_3$ to compute the graphical integration.

accurate and that there was probably a very long error in log γ resulting from this. Furthermore, there was the additional error in drawing this curve that it was impossible to determine how much of a hook or hump should be given to these data in considering their approach to zero concentration. Inasmuch as chlorides are peculiarly sensitive to the formation of complex ions, the area represented by such a hump may be considerable. The following method was adopted to correct this error. Equation (4) was rewritten in the form

$$\log \gamma = - \frac{h}{2.303} - \frac{2}{2.303} Y \qquad (5)$$

where Y represents the correct area under the curve at a given value of m. X was then defined as

$$X = Y + Z \qquad (6)$$

becoming equal to the measured area when Z represents the error introduced.

The right-hand term of equation (5) was then substituted for log γ in the equation of Hückel[12]

$$\log \gamma = - \frac{1.068 \sqrt{12c}}{1 + A \sqrt{12c}} + B(12c) - \log (1 + 0.072 \, m) \qquad (7)$$

where m is the molality and c is the concentration in moles per liter.

The constants A and B and the correction

(12) Hückel, *Physik. Z.*, **26**, 93 (1925).

factor Z were then calculated by substitution of the numerical data for 0.5, 1.0 and 1.5 molal and simultaneous solution of the resulting equations. The numerical values obtained for the correction factors Z were larger than one would expect from an error in the linear extrapolation. This would show that a hook or hump of some sort must exist in the curve shown in Fig. 4 near zero concentration. The values obtained for these quantities are given in Table III.

TABLE III
CONSTANTS IN DEBYE AND HÜCKEL EQUATIONS

Salt	A	B	b	Z
AlCl$_3$	0.32953	0.08623	0.14560	−0.63409
ScCl$_3$	.47040	.06446	.11696	− .41977
YCl$_3$	.43836	.06186	.11067	− .50656
LaCl$_3$	.44919	.05506	.09413	− .43880
CeCl$_3$	.51556	.05115	.09663	− .45158
PrCl$_3$	.45350	.05485	.09500	− .46729
NdCl$_3$	.50930	.05118	.09771	− .40575

The values obtained for Z were used to calculate the correct areas, Y, in the graphical integrations. These values of Y were then used in equation (5) to compute the activity coefficients given as $\gamma_{corr.}$ in Table IV. In this same table $\gamma_{obsd.}$ refers to the values of the activity coefficients obtained directly from the graphical integration of Randall and White.[10] The constants A and B were used in Hückel's equation (7) to compute the values of γ_D recorded in Table IV. In order to compare the corrected activity coefficients with those obtained by equation (7), the values of $\Delta\gamma(\gamma_{corr.} - \gamma_D)$ have also been included in Table IV and one set for aluminum chloride have been

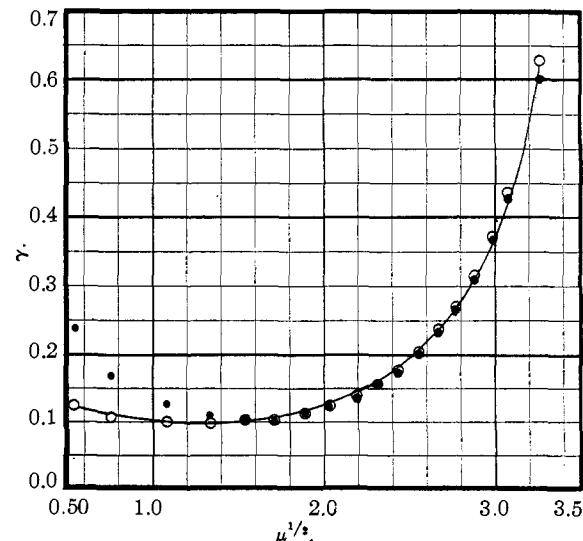Fig. 5.—Activity coefficients of AlCl$_3$: ●, γ_D; ○, γ_{corr}.

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TABLE IV

ACTIVITY AND OSMOTIC COEFFICIENTS OF SALTS

Aluminum Chloride

m	Density	φexptl.	φD	$\Delta\varphi$	γexptl.	γcalc.	γD	$\Delta\gamma$
0.05	1.0030	0.826	0.718	0.108	0.463	0.130	0.247	−0.117
.1	1.0088	.812	.715	.097	.403	.113	.175	— .062
.2	1.0200	.841	.771	.070	.366	.103	.127	— .014
.3	1.0310	.890	.849	.041	.364	.102	.114	— .012
.4	1.0416	.948	.934	.014	.376	.106	.110	— .004
.5	1.0523	1.009	1.022	.013	(.398	.112	.113	— .001
.6	1.0630	1.074	1.112	.038	.428	.120	.120	.000
.7	1.0739	1.141	1.203	.062	.465	.131	.130	.001
.8	1.0845	1.213	1.294	.081	.511	.144	.144	.000
.9	1.0943	1.291	1.384	.093	.569	.161	.161	.000
1.0	1.1048	1.378	1.476	.098	.643)	.181	.183	.002
1.1	1.1147	1.471	1.567	.096	.734	.207	.209	.002
1.2	1.1245	1.564	1.657	.093	.843	.237	.240	.003
1.3	1.1341	1.657	1.749	.092	.971	.273	.277	.004
1.4	1.1437	1.753	1.839	.086	1.126	.317	.321	.004
1.5	1.1532	1.855	1.931	.076	(1.318)	.371	.374	.003
1.6	1.1625	1.966	2.022	.056	1.562	.440	.431	.009
1.8	1.1812	(2.203)	2.205	.000	2.248	.635	.602	.031

Scandium Chloride

m	Density	φexptl.	φD	$\Delta\varphi$	γexptl.	γcalc.	γD	$\Delta\gamma$
0.05	1.0039	0.807	0.709	0.098	0.416	0.180	0.270	−0.090
.1	1.0101	.794	.715	.079	.357	.154	.201	— .047
.2	1.0231	.815	.737	.078	.317	.137	.156	— .019
.3	1.0359	.858	.797	.061	.310	.139	.137	.002
.4	1.0487	.912	.865	.047	.316	.137	.140	.003
.5	1.0613	.970	.936	.034	(.330)	.143	.143	.000
.6	1.0738	1.028	1.009	.019	.350	.151	.150	.001
.7	1.0860	1.088	1.082	.006	.375	.162	.161	.001
.8	1.0980	1.150	1.156	.006	.406	.175	.174	.001
.9	1.1096	1.216	1.230	.014	.443	.191	.191	.000
1.0	1.1209	1.285	1.304	.019	(.487)	.210	.210	.000
1.1	1.1321	1.359	1.378	.019	.541	.234	.235	.001
1.2	1.1433	1.433	1.452	.019	.602	.260	.260	.000
1.3	1.1545	1.507	1.526	.019	.675	.291	.291	.000
1.4	1.1656	1.583	1.600	.017	.757	.327	.327	.000
1.5	1.1763	1.659	1.673	.014	(.852)	.368	.368	.000
1.6	1.1870	1.734	1.747	.013	.961	.415	.415	.000
1.8	1.2088	1.889	1.894	.007	1.234	.533	.529	.004
2.0	1.2280	(2.040)	2.040	.000	1.588	.686	.677	.009

Yttrium Chloride

m	Density	φexptl.	φD	$\Delta\varphi$	γexptl.	γcalc.	γD	$\Delta\gamma$
0.05	1.0056	0.810	0.707	0.103	0.451	0.164	0.262	−0.098
.1	1.0141	.791	.694	.097	.385	.150	.197	— .047
.2	1.0315	.808	.729	.079	.340	.123	.144	— .021
.3	1.0485	.847	.786	.061	.329	.120	.128	— .008
.4	1.0652	.892	.850	.042	.331	.120	.123	— .003
.5	1.0820	.940	.917	.023	(.341)	.124	.124	.000
.6	1.0990	.990	.986	.004	.356	.129	.128	.001
.7	1.1154	1.042	1.056	.006	.376	.135	.135	.002
.8	1.1316	1.096	1.126	.030	.401	.145	.145	.001
.9	1.1472	1.155	1.196	.041	.432	.157	.156	.001
1.0	1.1622	1.217	1.266	.049	(.469)	.170	.170	.000
1.1	1.1765	1.283	1.336	.053	.513	.186	.187	.001
1.2	1.1918	1.351	1.406	.055	.564	.205	.205	.000
1.3	1.2066	1.420	1.476	.056	.623	.226	.227	.001
1.4	1.2211	1.491	1.547	.055	.692	.251	.252	.001
1.5	1.2357	1.564	1.617	.053	.772	.280	.280	.000
1.6	1.2506	1.639	1.686	.047	.866	.315	.313	.002

TABLE IV   (*Continued*)

m	Density	$\varphi_{exptl.}$	φD	$\Delta\varphi$	$\gamma_{exptl.}$	$\gamma_{corr.}$	γD	$\Delta\gamma$
1.8	1.2805	1.796	1.826	−0.030	1.101	0.400	0.403	−0.003
2.0	1.3090	(1.965)	1.965	.000	1.430	.519	.493	+ .026

Lanthanum Chloride

m	Density	$\varphi_{exptl.}$	φD	$\Delta\varphi$	$\gamma_{exptl.}$	$\gamma_{corr.}$	γD	$\Delta\gamma$
0.05	1.0082	0.800	0.702	0.099	0.390	0.162	0.262	−0.100
.1	1.0194	.788	.684	.104	.333	.139	.190	− .051
.2	1.0414	.801	.709	.091	.292	.121	.142	− .021
.3	1.0630	.831	.756	.075	.297	.116	.125	− .009
.4	1.0842	.869	.810	.059	.277	.115	.118	− .003
.5	1.1057	.910	.868	.042	(.282)	.117	.117	.000
.6	1.1265	.952	.927	.025	.290	.121	.119	.002
.7	1.1474	.998	.986	.012	.303	.126	.124	.002
.8	1.1677	1.046	1.047	− .001	.318	.132	.130	.002
.9	1.1877	1.097	1.107	− .010	.338	.140	.139	.001
1.0	1.2075	1.150	1.167	− .017	(.360)	.150	.149	.001
1.1	1.2269	1.205	1.227	− .022	.388	.161	.161	.000
1.2	1.2463	1.264	1.287	− .023	.419	.174	.174	.000
1.3	1.2655	1.323	1.348	− .025	.455	.189	.189	.000
1.4	1.2851	1.382	1.407	− .025	.496	.206	.206	.000
1.5	1.3036	1.445	1.468	− .023	(.543)	.226	.226	.000
1.6	1.3220	1.506	1.528	− .022	.595	.248	.248	.000
1.8	1.3575	1.633	1.647	− .014	.723	.301	.299	.002
2.0	1.3923	(1.766)	1.766	.000	.888	.370	.362	.008
2.2	1.4266	1.899	1.885	.014	1.096	.456	.445	.011

Cerium Chloride

m	Density	$\varphi_{exptl.}$	φD	$\Delta\varphi$	$\gamma_{exptl.}$	$\gamma_{corr.}$	γD	$\Delta\gamma$
0.05	1.0084	0.800	0.703	0.097	0.462	0.187	0.275	−0.088
.1	1.0195	.784	.685	.099	.393	.159	.205	− .046
.2	1.0420	.798	.712	.086	.344	.140	.158	− .018
.3	1.0640	.832	.761	.071	.330	.134	.142	− .008
.4	1.0853	.871	.816	.055	.329	.133	.136	− .003
.5	1.1074	.914	.875	.039	(.335)	.136	.136	.000
.6	1.1275	.958	.936	.022	.346	.140	.140	.000
.7	1.1480	1.005	.997	.008	.362	.147	.146	.001
.8	1.1700	1.055	1.059	− .004	.382	.155	.156	− .001
.9	1.1912	1.106	1.120	− .014	.406	.164	.164	.000
1.0	1.2120	1.160	1.182	− .022	(.434)	.176	.176	.000
1.1	1.2315	1.214	1.243	− .029	.467	.189	.191	− .002
1.2	1.2515	1.270	1.305	− .035	.504	.204	.206	− .002
1.3	1.2715	1.328	1.367	− .039	.547	.222	.223	− .001
1.4	1.2910	1.387	1.429	− .042	.596	.242	.243	− .001
1.5	1.3100	1.455	1.490	− .035	(.658)	.267	.266	.001
1.6	1.3285	1.515	1.552	− .037	.719	.292	.291	.001
1.8	1.3658	1.657	1.674	− .017	.891	.360	.357	.003
2.0	1.4020	(1.796)	1.796	.000	1.103	.447	.420	.027
2.2	1.4380	1.935	1.918	.017	1.376	.558	.508	.050

Praseodymium Chloride

m	Density	$\varphi_{exptl.}$	φD	$\Delta\varphi$	$\gamma_{exptl.}$	$\gamma_{corr.}$	γD	$\Delta\gamma$
0.05	1.0089	0.801	0.702	0.099	0.419	0.165	0.264	−0.099
.1	1.0204	.782	.684	.098	.356	.140	.181	− .041
.2	1.0430	.796	.710	.086	.312	.123	.150	− .023
.3	1.0655	.828	.758	.070	.299	.118	.131	− .013
.4	1.0872	.865	.812	.053	.297	.117	.120	− .003
.5	1.1085	.906	.870	.036	(.302)	.119	.119	.000
.6	1.1290	.950	.930	.020	.310	.122	.121	.001
.7	1.1502	.995	.990	.005	.324	.127	.126	.001
.8	1.1717	1.042	1.051	− .009	.341	.134	.132	.002
.9	1.1925	1.094	1.111	− .017	.362	.142	.141	.001
1.0	1.2129	1.148	1.172	− .024	(.387)	.152	.151	.001
1.1	1.2330	1.206	1.233	− .027	.417	.164	.164	.000
1.2	1.2530	1.267	1.293	− .026	.452	.178	.177	.001

TABLE IV (Concluded)

m	Density	φexptl.	φD	$\Delta\varphi$	γexptl.	γcorr.	γD	$\Delta\gamma$
1.3	1.2727	1.327	1.354	− .027	.492	.193	.192	.001
1.4	1.2925	1.388	1.415	− .027	.537	.211	.210	.001
1.5	1.3115	1.447	1.476	− .029	(.586)	.230	.230	.000
1.6	1.3300	1.508	1.536	− .028	.643	.253	.253	.000
1.8	1.3674	1.638	1.656	− .018	.782	.307	.306	.001
2.0	1.4047	(1.777)	1.777	.000	.968	.380	.368	.012
2.2	1.4407	1.922	1.896	.024	1.214	.477	.454	.023

Neodymium Chloride

m	Density	φexptl.	φD	$\Delta\varphi$	γexptl.	γcorr.	γD	$\Delta\gamma$
0.05	1.0090	0.797	0.703	0.094	0.415	0.184	0.273	−0.089
.1	1.0203	.784	.686	.098	.354	.157	.203	− .046
.2	1.0435	.795	.713	.082	.309	.137	.156	− .019
.3	1.0663	.828	.762	.066	.295	.131	.140	− .009
.4	1.0888	.866	.819	.047	.294	.130	.134	− .004
.5	1.1105	.909	.879	.030	(.299)	.133	.134	− .001
.6	1.1327	.954	.940	.014	.309	.137	.138	− .001
.7	1.1545	1.003	1.002	.001	.323	.143	.143	.000
.8	1.1762	1.053	1.064	− .011	.341	.151	.151	.000
.9	1.1978	1.105	1.126	− .021	.362	.161	.163	− .002
1.0	1.2190	1.159	1.188	− .029	(.388)	.172	.172	.000
1.1	1.2402	1.216	1.250	− .034	.418	.186	.187	− .001
1.2	1.2608	1.275	1.313	− .038	.453	.201	.201	.000
1.3	1.2813	1.335	1.375	− .040	.494	.219	.219	.000
1.4	1.3015	1.399	1.438	− .038	.539	.239	.238	.001
1.5	1.3214	1.464	1.500	− .036	(.592)	.263	.260	.003
1.6	1.3410	1.529	1.562	− .033	.653	.290	.285	.005
1.8	1.3798	1.662	1.686	− .024	.800	.355	.343	.012
2.0	1.4176	(1.809)	1.809	.000	1.0017	.445	.414	.031
2.2	1.4553	1.940	1.932	.008				

( ) show reference points used in theoretical calculations.

plotted against the square root of the ionic strength in Fig. 5. This plot in Fig. 5 is characteristic of all seven salts.
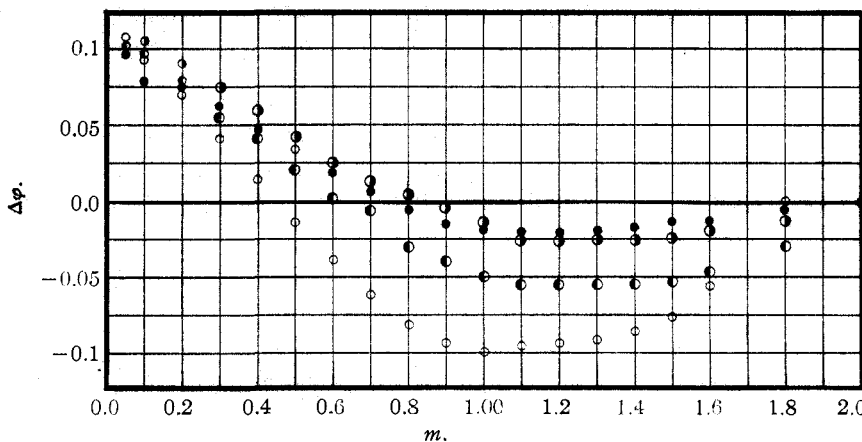

Fig. 6.—Deviations of osmotic coefficients: O. AlCl₃; ●. ScCl₃; ◐. YCl₃; ◑. LaCl₃.

Examination of the values for $\Delta\gamma$ shows wide divergence in the dilute solutions. This is to be expected and the values for $\gamma_{corr.}$ are probably too low in this region, because of the increased error in the isotonic measurements at lower concentrations. The values of γ_D fall off above an ionic strength of ten but this is quite readily understood because the linear term in Hückel's equation may not be enough to correct for the variation of the dielectric constant in such concentrated solutions.

The smoothed osmotic coefficients given in Table II have been used to test the equation of Scatchard[13] for osmotic coefficients of salts in concentrated solutions. This equation was used in the form

$$\varphi_D = 1 + \frac{A z_1 z_2}{\mu}\left[1 + \sqrt{\mu} - \frac{1}{1 + \sqrt{\mu}} - 2\ln(1 + \sqrt{\mu})\right] + b\mu \quad (8)$$

where μ is the ionic strength and b is the linear constant. The value −1.165 was used for A. b was calculated by fixing $\varphi_D = \varphi_{exptl.}$ at 2.0 molal and the values so obtained have been included in Table III. The values of φ_D were computed by

(13) Scatchard, Chem. Rev., 19, 309 (1936).

means of equation (8) and are given in Table IV. The corresponding values of $\Delta\varphi(\varphi_{\text{exptl.}} - \varphi_{\text{D}})$ have also been calculated and are included in the same table (III). For some of the salts $\Delta\varphi$ has been plotted against m in Fig. 6. Cerium, praseodymium and neodymium chlorides were omitted from the plot because the values of $\Delta\varphi$ for these salts were so close to lanthanum chloride which has been included.

The values of $\Delta\varphi$ representing the deviation from Scatchard's equation are not proportionately large when compared to those given by him for the higher valence sulfates measured by Robinson and Jones.[14] In fact, the actual values of $\Delta\varphi$ found in this investigation are less than those for the sulfates.

(14) Robinson and Jones. THIS JOURNAL. **58**. 959 (1936).

I am indebted to Professor Scatchard and Dr. Wood for the use of their data for the osmotic coefficients of potassium and sodium chlorides prior to publication and for several suggestions regarding the use of equation (8). For these courtesies I wish to express thanks.

Summary

1. The osmotic coefficients of aluminum, scandium, yttrium, lanthanum, cerium, praseodymium and neodymium chlorides have been determined in aqueous solution at 25° by the isotonic method of Robinson and Sinclair.[2]

2. The activity coefficients of these salts have been computed from the osmotic coefficients.

3. The data obtained in both 1 and 2 have been compared with theory.

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Ternary Systems. XXIV. Calcium Sulfate, Sodium Sulfate and Water

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Early study of this system by Fritsche[2] disclosed the existence of two double salts, glauberite ($CaSO_4 \cdot Na_2SO_4$) and a salt of the composition $CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O$, which has been variously known as syngenite, from a mistaken reading of its composition, and as the labile double salt, from its metastable relationship to other double salts. Isotherms of the system have been studied at 22° by Cameron and Seidell,[3] and at 25° by Cameron and Breazeale,[4] in both cases without inclusion of double salts. Barre[5] compiled the concentrations of isothermally invariant solutions saturated with two salts, glauberite and each of the components of the system and the labile salt with each of the components, giving an outlined polytherm of the system from room temperature to 100°. D'Ans and Schreiner[6] discussed the two double salts and added a point of saturation by glauberite and gypsum at 60°. Van't Hoff[7] determined the invariant points of saturation by each of these

double salts with gypsum and mirabilite (Glauber's salt) as 30.2° for the transition involving the labile double salt and 29° for that involving glauberite. The present research contains a repetition of the 25° isotherm and additional isotherms at 35, 50 and 75°, including in addition to the previously known double salts, anhydrite at the higher temperatures and a new double salt, sodium pentacalcium sulfate; these data permit the construction of a fuller polytherm than was previously possible.

In carrying out work in this system in which there occur so many degrees of metastability at any given temperature, much use has been made of van't Hoff's[8] generalization that the retardation of salts in coming to equilibrium with their solutions is related to the mean valence, calculated by dividing the total valence representing all the ions in the formula by the total number of such ions, giving each water molecule in a hydrate an arbitrary mean valence of $4/3$; this rule guided us in this research, as in other related researches,[9] in deciding upon appropriate time of contact for

(1) This paper is an abridgment of the thesis presented by Mr. Wills in partial fulfilment of the requirements for the degree of Ph.D. at New York University. June. 1935.

(2) Fritsche. *J. prakt. Chem.*. **72**, 291 (1857). Glauberite had been prepared previously only in the dry way.

(3) Cameron and Seidell. *J. Phys. Chem.*. **5**, 643 (1901).

(4) Cameron and Breazeale. *ibid.*. **8**, 335 (1904).

(5) Barre. *Ann. chim. phys.*. [8] **24**, 145 (1911).

(6) D'Ans and Schreiner. *Z. anorg. Chem.*. **62**, 129 (1909).

(7) Van't Hoff. *Z. physik. Chem.*. **45**, 257 (1903).

(8) Van't Hoff. "Zur Bildung der ozeanischen Salzablagerungen." F. Vieweg und Sohn. Braunschweig. 1905; Vol. I. p. **32**; Vol. II. p. 17.

(9) Hill. THIS JOURNAL. **56**. 1071 (1934); Hill and Yanick. *ibid.*. **57**, 645 (1935).