Peroxide in the dioxane was determined by titrating the iodine liberated from sodium iodide in glacial acetic acid, using 0.0811 *N* sodium thiosulfate solution. (A blank correction was made, using 10 ml. of water instead of 10 ml. of dioxane, with the same period of heating, to allow for air oxidation of iodide.) An old sample of dioxane showed about one milliequivalent of peroxide per liter. Air was bubbled through a sample of treated dioxane, using a fine frit to ensure small bubbles. After 30 min., the dioxane contained 0.81 meq./l. peroxide, and after 1 hr., 1.10 meq./l. Apparently an equilibrium between formation and decomposition of peroxide was then reached, because the titer remained unchanged after bubbling air through the dioxane for an additional 30 min.

In another experiment, 1.18 g. of polyvinylpyridine was dissolved in 10 ml. of methanol, and precipitated with untreated dioxane. The precipitate was allowed to stand in contact with the dioxane for a week. The volume of the precipitate was 3.0 ml. The dioxane was decanted carefully and 55 ml. of methanol was added; the precipitate expanded in 2 days to 6.0 ml. This methanol (plus extracted dioxane) was decanted and 50 ml. of fresh methanol was added. After 5 days, the volume of precipitate had expanded to 8 ml. The methanol was decanted and combined with the first portion; evaporation under vacuum gave a residue of 0.724 g. for the soluble polymer. The gel portion was also dried under vacuum; it weighed 0.457 g., so approximately 40% of the polymer had been insolubilized. The specific volumes of the gel were 6.5, 13 and 18 cc./g. as first precipitated, and after the first and second soakings in methanol, respectively. As the precipitating liquid was extracted with methanol, the gel naturally expanded while it imbibed good solvent.

It is therefore clear that dioxane which is to be used in polymer work should be carefully freed from oxygen and peroxides, and further that polymers should not be allowed to stand in contact with dioxane and air.

STERLING CHEMISTRY LABORATORY
YALE UNIVERSITY
NEW HAVEN, CONNECTICUT

Activity Coefficient of Gallium Perchlorate in Water at 25°[1]

BY C. STUART PATTERSON, S. YOUNG TYREE, JR., AND KERRO KNOX

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Extensive compilations of activity coefficients by Stokes and Robinson[2,3] indicate that for a strongly hydrated cation the salts exhibiting the highest activity coefficients are usually those of large anions. The iodide and perchlorate of lithium, for example, reach the greatest value. With potassium, on the other hand, which is not so highly hydrated, the perchlorate and nitrate have low values. Where there is evidence of a chemical nature for complex halide formation, as with zinc, the polyatomic anions of strong acids, especially the perchlorate, give the largest activity coefficient. This behavior is presumably due to the fact that there is the least possible amount of complex or ion-pair formation between perchlorate ion and cations. Thus, perchlorates are widely used to study the chemistry of cations.

We have measured the osmotic coefficients of aqueous solutions of pure gallium perchlorate by the isotonic method of Sinclair and Robinson[4,5] as part of a study of the hydrolysis–polymerization of gallium ion produced by added base. The activity coefficients have been calculated over the concentration rate, 0.05 to 2.0 molal gallium perchlorate.

Experimental

Materials.—Gallium perchlorate was prepared by the method of Foster[6] from gallium metal. One sample of gallium was obtained from the Aluminum Company of America; another was donated by the Eagle-Picher Company. The most satisfactory method found for drying the salt was to place it in a glass tube, the closed end of which fitted into the drying chamber of an Abderhalden drying pistol. The tube was made long enough for perchloric acid to condense between the sample and a sodium hydroxide trap. The tube was evacuated through this trap by a vacuum pump. A solvent with a b.p. of 125° was used, and the sample was heated under vacuum overnight. Dry air was then admitted and the tube sealed between the condensed acid and the sample. The tube was opened in a dry-box and the sample stored in a weighing bottle until used. All weighings were done in the dry-box. The material was analyzed for perchlorate by precipitation with tetraphenylarsonium chloride solution saturated with tetraphenylarsonium perchlorate after solution in water saturated with tetraphenylarsonium perchlorate. Following digestion on a hot plate, the solution was brought back to its volume after precipitation by the addition of distilled water.[7] The precipitate was filtered at room temperature on a sintered glass crucible, washed with water saturated with tetraphenylarsonium perchlorate and then with ice-cold distilled water. It was dried at 110° and weighed as tetraphenylarsonium perchlorate. Triplicate samples run in this manner agreed to within a few tenths of 1%. Analysis for gallium was made both by precipitation as the hydrous oxide and ignition to the oxide, and by direct ignition of the hydrated perchlorate to the oxide. The results of both methods agreed.

Anal. Calcd. for $Ga(ClO_4)_3 \cdot 6H_2O$: Ga, 14.64; ClO_4, 62.66. Found: Ga, 14.96; ClO_4, 63.78; ratio, ClO_4/Ga, 2.989; formula, $Ga(ClO_4)_3 \cdot 5.5H_2O$.

The sample prepared in this manner is thus somewhat less hydrated than the stoichiometric 6-hydrate.

Potassium chloride of reagent grade was recrystallized repeatedly from water and dried at 120°. This material was found to give the same results as that taken directly from the bottle without further purification.

Calcium chloride 2-hydrate of reagent grade was analyzed for chloride by precipitation with silver nitrate. The calcium chloride content was found to be 75.62%, the remainder being water. The stoichiometric 2-hydrate is 75.49% $CaCl_2$.

Apparatus and Procedure.—The apparatus was similar to that described by Mason.[8] The cups of 25-ml. capacity were machined out of silver rod. A nickel collar was soldered around the outside top of each cup, fitting a tapered stainless steel lid. The cups were made to fit tightly into six holes in a copper block 7.5 in. in diameter by 2.5 in. thick. Slight depressions around the edge of the block fitted the lids, so that they could be quickly placed on the proper cup upon opening the unit. Platinum gauze strips stood up in the cups to give increased surface area. A magnetically driven fan with two 3 × 5 cm. flat blades was fastened vertically in the center of the block and ran at about 60 r.p.m. The fan hastened equilibrium, especially in the more dilute solutions where the time required without it became excessive. The container was a 250-mm. glass vacuum desiccator. The whole assembly was clamped on a flat brass rack which rocked back and forth at seven round trips per min. in a 45-gal. thermostat. Temperature was controlled at 25 ± 0.005°. The fluctuations in the region of the samples was doubtless much less than this limit.

At the beginning of a series of runs, samples of gallium perchlorate were weighed directly into the cups. For the more concentrated solutions, the calcium chloride was also

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[1] From the doctoral research of C. S. Patterson.

[2] R. H. Stokes, *Trans. Faraday Soc.*, **44**, 295 (1948).

[3] R. A. Robinson and R. H. Stokes, *ibid.*, **45**, 612 (1949).

[4] D. A. Sinclair, *J. Phys. Chem.*, **37**, 495 (1933).

[5] R. A. Robinson and D. A. Sinclair, THIS JOURNAL, **56**, 1830 (1934).

[6] L. S. Foster, *Inorg. Syntheses*, **2**, 26 (1946).

[7] The authors are grateful to Professor W. T. Smith, Jr., for informing them of this way of increasing the accuracy of the procedure described by H. H. Willard and G. M. Smith, *Ind. Eng. Chem., Anal. Ed.*, **11**, 305 (1939), for perrhenate.

[8] C. M. Mason, THIS JOURNAL, **60**, 1638 (1938).

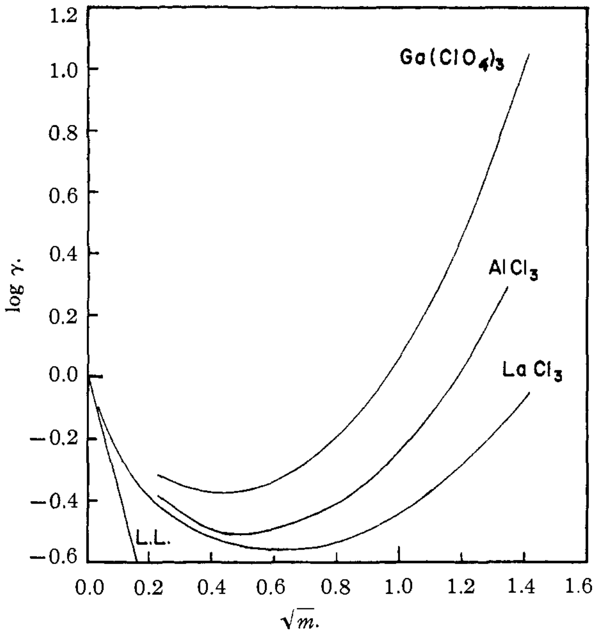

Fig. 1.—Activity coefficients of $Ga(ClO_4)_3$ (this research) and $LaCl_3$ and $AlCl_3$ (12) at 25°. L. L. designates the Debye–Hückel limiting law.

weighed in the dry-box, but the potassium chloride could be weighed in the laboratory. As nearly the equilibrium amount of water as possible was placed in each cup by a pipet. The system was evacuated carefully, to prevent spattering, by opening a two-liter bottle alternately to a water aspirator and then the system. After this was done several times the system was opened directly to the aspirator and pumped with the fan running until several drops of water, placed in the bottom of the desiccator to sweep out the air, had evaporated completely. The system rocked in the bath for a period of from 24 hr. for the most concentrated solutions to one week for a few of the most dilute. Dried air was admitted to the desiccator before opening. After weighing, the procedure was repeated occasionally to make sure equilibrium had been reached, but the agreement of duplicates was usually taken as indicative of equilibrium. To begin another run, water was added to each cup, carefully adjusting the concentration in each cup in order to hasten equilibrium. It was found desirable to keep the total volume of solution below 3 ml. When this volume was reached, a smaller sample was weighed out and the process continued.

In a few of the first runs, three samples of reference salt opposed three of gallium perchlorate, but in the majority of cases, duplicate samples were run, the third pair having added base. The results of these hydrolysis experiments will be reported later. Agreement in the more concentrated solutions was generally 0.1% or better, but, as reported by Mason,[8] the error below 0.25 *m* was considerably larger. Although analysis of the gallium perchlorate showed the water content to be slightly low, the vapor pressure data were reproducible for the products of two different preparations carried out under the conditions given above.

Results and Discussion

From the experimental results given in Table I the osmotic and activity coefficients of gallium perchlorate given in Table II were calculated using the method that Mason[9] developed for trivalent chlorides. Recent values of the osmotic coefficients of the reference salts[10] and of the fundamental physical constants[11] were used. The values of a' and B chosen were 3.05 and 1.0660, the former corresponding to an $\mathring{a}$ of 9.28.

TABLE I

ISOTONIC SOLUTIONS OF GALLIUM PERCHLORATE AND POTASSIUM CHLORIDE OR CALCIUM CHLORIDE AT 25°

$m_{Ga(ClO_4)_3}$	m_{KCl}	$m_{Ga(ClO_4)_3}$	m_{KCl}	$m_{Ga(ClO_4)_3}$	m_{KCl}
0.0549	0.1020	0.3557	0.8063	0.9408	3.179
.0818	.1542	.4181	.9940	1.065	3.862
.1038	.1969	.4733	1.173	1.168	4.460
.1539	.2982	.5009	1.269	1.184	4.562
.1955	.3886	.6264	1.742	1.219	4.770
.2341	.4744	.6514	1.843		m_{CaCl_2}
.2559	.5361	.6562	1.860	1.511	2.790
.2930	.6355	.7248	2.147	1.825	3.472
.3172	.6971	.7649	2.328	2.002	3.857
.3319	.7384	.9248	3.100		

TABLE II

OSMOTIC AND ACTIVITY COEFFICIENTS OF GALLIUM PERCHLORATE AT 25°

m	φ	γ	m	φ	γ
0.05	0.861	0.484	1.1	1.784	1.392
.1	.867	.443	1.2	1.912	1.704
.2	.903	.422	1.3	2.045	2.105
.3	.971	.439	1.4	2.185	2.629
.4	1.051	.477	1.5	2.330	3.314
.5	1.139	.532	1.6	2.479	4.211
.6	1.233	.604	1.7	2.627	5.365
.7	1.332	.697	1.8	2.774	6.846
.8	1.436	.814	1.9	2.920	8.746
.9	1.545	.961	2.0	3.068	11.203
1.0	1.661	1.150			

The activity coefficients given in Table II are plotted in Fig. 1, along with the recalculated values for $LaCl_3$ and $AlCl_3$.[12] It is seen that gallium perchlorate deviates even more widely from the Debye–Hückel limiting law (designated L.L. in Fig. 1) than these other two 3–1 electrolytes. The activity coefficient rises sharply in concentrated solution, in fact, more rapidly than any other previously studied electrolyte. Calculations of $\Delta\varphi$ showed that the extended Debye–Hückel equation using the $\mathring{A}$ parameter or the further extended expression with the $2Bm$ term were unsatisfactory for fitting the data to a semiempirical equation. The only expression found that would give a reasonable fit at low concentrations was the two-parameter equation of Stokes and Robinson.[13] Using a modified least-squares method, the best fit in the range 0.05–0.5 *m* was obtained with $\mathring{a} = 7.93$ and $n = 24.5$. The maximum deviation in this range is 0.013 and the average deviation 0.007 in log γ. In terms of the size of the *n* term, this is essentially the same range covered by Stokes and Robinson for 1–1 and 2–1 electrolytes. The $\mathring{a}$ value of 7.93 used here is somewhat lower than the 9.28 used in Mason's equation for the calculation of φ_D. The former value has perhaps more physical significance since the equation in which it is used fits the data over a concen-

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(9) C. M. Mason, THIS JOURNAL, **63**, 220 (1941).

(10) KCl: R. A. Robinson, *Trans. Roy. Soc., New Zealand*, **75**, [II] 203 (1945); reprinted by R. H. Stokes and B. J. Levien, THIS JOURNAL, **68**, 333 (1946). $CaCl_2$: ref. 2.

(11) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 586.

(12) Ref. 11, pp. 428, 573.

(13) R. H. Stokes and R. A. Robinson, THIS JOURNAL, **70**, 1870 (1948).

tration range while the larger figure comes from an extended Debye–Hückel equation which fits at only one point, 0.05 *m*, and deviates widely at all other concentrations. The value of 7.93 is somewhat larger than the numbers derived for rare earth perchlorates by Spedding and Jaffe,[14] but the difference is probably not significant since different methods of calculation for different concentration ranges were used in the two cases. In any case, the $\mathring{a}$ is large and approaches the size of Bjerrum's *q*, which has a value of 10.5 Å. for 3-1 electrolytes.[15] Comparing the relative sizes of $\mathring{a}$ and *q* for gallium perchlorate with those of 2-1 electrolytes,[16] it is seen that ion-pair formation is negligible for this salt. Gallium perchlorate is, thus, a very strong, highly hydrated electrolyte.

[14] F. H. Spedding and S. Jaffe, This Journal, **76**, 884 (1954).

[15] Ref. 11, pp. 42–45.

[16] Ref. 11, pp. 422–423.

Department of Chemistry
University of North Carolina
Chapel Hill, N. C.

The Preparation of Dicalcium Phosphate Dihydrate and Calcium Pyrophosphate

By P. D. S. St. Pierre

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In a high temperature phase equilibrium investigation of the system $Ca_3(PO_4)_2$–Al_2O_3–SiO_2,[1] a source of phosphorus pentoxide was required whose composition and purity was clearly established. It was found that commercial C.P. tricalcium phosphate was normally hydroxyapatite. Further to this the salts tested contained notable quantities of sodium and iron. The combination of non-stoichiometric composition and the presence of impurities had a notable effect on certain properties. For instance the melting point was depressed by approximately 330°, from 1730 to 1400°.

Barrett and McCaughey[2] met with the same difficulty in their investigation of the system CaO–P_2O_5–SiO_2, but found that calcium pyrophosphate obtained by calcining dicalcium phosphate ($CaHPO_4 \cdot 2H_2O$) was a good source of phosphorus pentoxide for their mixtures. Contrary to Barrett and McCaughey's experience, tests made during the present investigation showed that the C.P. dicalcium phosphate obtained commercially was just as liable to compositional variation and alkali contamination as the tricalcium salt. The powerful fluxing action of alkalies renders salts containing them useless for phase studies.

Attempts to synthesize tricalcium phosphate by MacIntyre's method[3] met with no success. In this method $Ca_3(PO_4)_2 \cdot nH_2O$ is precipitated from chilled calcium sucrate solution by the addition of concentrated phosphoric acid in very slight excess. Although instructions were carefully followed, a gelatinous precipitate was obtained each time. Melting point and refractive index determinations indicated that the material produced was a hydroxyapatite.

It was noted that if MacIntyre's procedure was reversed, and chilled calcium sucrate added to dilute phosphoric acid, neutralization proceeded only to the displacement of the second hydrogen atom from the acid molecule. Further investigation indicated that this was an ideal method for the preparation of pure dicalcium phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$) of stoichiometric composition. This salt is easily converted into calcium pyrophosphate ($Ca_2P_2O_7$) by ignition at 900° and if combined with the stoichiometric proportions of pure calcium carbonate may be converted to tricalcium phosphate on high temperature ignition. Tricalcium phosphate in the low temperature form (β) is obtained from such mixtures by prolonged heating (12 hours) at approximately 1000°. If the mixture is heated at 1500° or above, the reaction is rapid and the high temperature form (α) obtained.

The preparation of these two compounds ($CaHPO_4 \cdot 2H_2O$ and $Ca_2P_2O_7$) was carefully studied and the optimum conditions for their formation determined.

Experimental

All the preliminary experiments indicated that provided the calcium sucrate was added to chilled dilute phosphoric acid, neutralization always stopped at the second stage of hydrogen replacement even when a large excess of calcium sucrate was present. Thus, provided the additions were made correctly, and the solutions kept chilled (10°) a good product was obtained without any special attention being paid to the quantities mixed. However, it is recommended that the quantity of reactants be carefully measured and only a slight excess of calcium sucrate used.

The stock of dicalcium phosphate was prepared as follows: 322.5 g. of C.P. calcium carbonate was calcined at 1000° for one hour and the lime so obtained dissolved in 5 liters of 22.5% CO_2-free aqueous sugar solution. Freshly ignited lime dissolved easily and completely in the sugar solution. The sucrate solution was chilled to 10° and added to 190 cc. of concentrated phosphoric acid (1.05 g. P_2O_5 per cc.) diluted to 3 liters with water. The phosphoric acid had previously been assayed by titration with standard sodium hydroxide solution, using phenolphthalein as indicator and a little sodium chloride to sharpen the end-point.

The phosphoric acid was contained in a large stoneware vessel maintained at 10° by an ice-bath. The acid was vigorously stirred and the sucrate added slowly, in eleven stages. Samples for *p*H determinations were taken two minutes after each sucrate addition. Figure 1 shows how the *p*H changes as the acid is gradually neutralized. After stirring for one hour following neutralization the *p*H dropped to 8.2.

It will be noted that there is a slight inflexion in the neutralization curve at 2.5 liters calcium sucrate, the point of formation of monocalcium phosphate. The completion of the reaction, however, is clearly shown by the rapid rise in *p*H once the second hydrogen atom has been displaced from the phosphoric acid.

The dicalcium phosphate prepared by this method settles readily and may be filtered very easily. After filtration the precipitate was washed with 10 liters of cool distilled water. The excess calcium sucrate was washed out easily since it is a very soluble compound. The precipitate was dried at 50° for several days and stored ready for conversion to calcium pyrophosphate.

Since the ultimate aim was to produce tricalcium phosphate in mixtures used in the phase study, it was found convenient to calcine the dicalcium salt at 900° to obtain calcium pyrophosphate. Thus when tricalcium phosphate was required, calcium pyrophosphate and calcium carbonate were mixed in the proportions shown by the equation

$$Ca_2P_2O_7 + CaCO_3 \longrightarrow Ca_3(PO_4)_2 + CO_2$$

and the required tricalcium salt formed *in situ* when the mixture was heated to 1600–1700°.

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[1] P. D. S. St. Pierre, *J. Am. Ceram. Soc.*, **37** [6] 243 (1954).

[2] R. L. Barrett and W. J. McCaughey, *Am. Mineralogist*, **27**, 680 (1942).

[3] W. H. MacIntyre, G. Palmer and H. L. Marshall, *Ind. Eng. Chem.*, **37**, 164 (1945).