Λ/Λ_∞. If the values corrected for viscosity were used, the results for potassium chloride would be little changed, but no approach to a constant could be obtained in the case of sodium chloride. This work with constant silver concentration was interrupted when barely begun, but it promises to be of much interest, as also determinations in which chloride concentration is kept constant, but total silver is varied, which would help greatly in the interpretation. No conclusion can at present be drawn as to the significance of the difference in shape, slope, or position of the two curves given.

Summary.

The activity of chloride ion in concentrated solutions of sodium and of potassium chloride saturated with silver chloride is calculated from potential measurements, using silver electrodes, and a junction of concentrated potassium nitrate, to eliminate diffusion potentials. The solubility product, for want of a better hypothesis, is assumed constant, and evidence is offered to show that its variations do not greatly affect the conclusions.

The values obtained by this method are always smaller than those calculated from conductivities except in the most concentrated solutions of sodium chloride. The dissociation calculated from them reaches a minimum at 1.7 *N*.

Solutions variable in alkali chloride, but constant in silver chloride, afford results supporting the hypothesis that the complex K_3AgCl_4 exists in concentrations above 1.7 *N*.

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EQUILIBRIUM IN THE SYSTEM DISODIUM HYDROGEN ARSENATE, LEAD NITRATE, AND WATER AT 25° C.

BY B. E. CURRY AND T. O. SMITH.

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In the course of an investigation of commercial lead arsenates the writers experienced the need of more definite information than the literature affords concerning the theoretical compounds of lead and arsenic acid. The compounds reported by previous workers have evidently been formed under ordinary synthetic rather than equilibrium conditions. The methods of preparation in most cases have apparently been selected with the view of duplicating those used by the manufacturer.

The most important source of arsenic used in the preparation of commercial lead arsenate is disodium hydrogen arsenate. This is the cheapest source of arsenic in suitable form. The lead salts used are the nitrate and the acetate. The nitrate is given the preference because it is the cheaper salt on the basis of lead content; also, because the product formed from the nitrate under manufacturing conditions possesses more desirable physical properties and has a higher arsenic content. For practical purposes the data secured from an equilibrium study would be most valuable if these salts were taken.

The composition of most brands of commercial lead arsenate is very near that of lead hydrogen arsenate. They contain, in general, more lead and less arsenic than the theoretical salt and are said to be mixed with the triplumbic arsenate in varying amounts, depending upon the method and conditions of manufacture.

Lead hydrogen arsenate, $PbHAsO_4$, contains theoretically 64.28% PbO; 33.13% As_2O_5 and 2.59% H_2O. Triplumbic arsenate, $Pb_3(AsO_4)_2$, contains theoretically 74.42% PbO and 25.58% As_2O_5.

The thermostat used in this work was maintained at 25° ± 0.2°. The rotating shaft was equipped to carry the bottles with their length in the plane of rotation, so that the contents of the bottle by breaking on its ends were thoroughly shaken. The salts were pure disodium hydrogen arsenate, $Na_2HAsO_4.7H_2O$ and pure lead nitrate, $Pb(NO_3)_2$. For convenience in making up the bottles, standard solutions were prepared and the required amount of each measured from a buret. The percentages were computed so that their combined weight was 2 g. in each bottle. The bottles, 500 cc. in volume, were weighed and, after the standard solutions had been measured into them, water was added to make the total contents 450 g., as shown in the following table:

TABLE I.

Bottle.	% As_2O_5.	G. As_2O_5.	% PbO.	G. PbO.	Total g. salts.	Total g. contents.
1	5	0.10	95	1.90	2.00	450
2	10	0.20	90	1.80	2.00	450
3	20	0.40	80	1.60	2.00	450
4	25	0.50	75	1.50	2.00	450
5	26	0.52	74	1.48	2.00	450
6	27	0.54	73	1.46	2.00	450
7	28	0.56	72	1.44	2.00	450
8	29	0.58	71	1.42	2.00	450
9	30	0.60	70	1.40	2.00	450
10	31	0.62	69	1.38	2.00	450
11	32	0.64	68	1.37	2.00	450
12	33	0.66	67	1.34	2.00	450
13	34	0.68	66	1.32	2.00	450
14	35	0.70	65	1.30	2.00	450
15	37	0.74	63	1.26	2.00	450
16	40	0.80	60	1.20	2.00	450

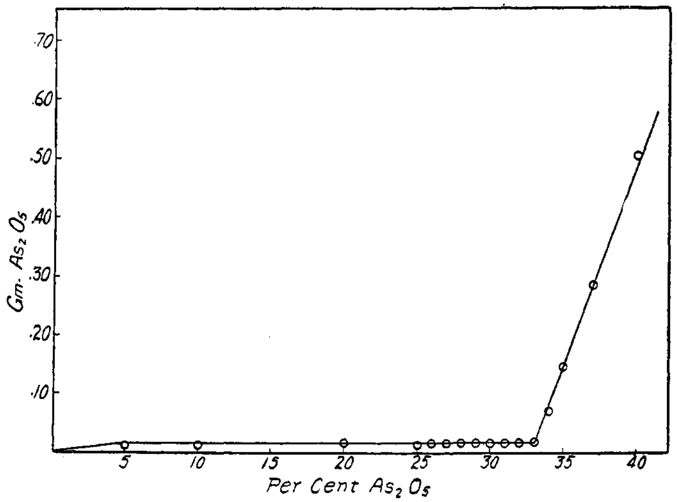
The bottles were allowed to remain in the thermostat three months. Doubtless equilibrium was reached in a much shorter time. They were then taken from the rotating shaft and allowed to stand in the thermostat until the solid phase had separated out. The supernatant liquid was then filtered off, the solid phase being left in the bottles. The arsenic oxide was determined in 100 cc. portions of the filtrates by the usual iodine method. The data are given in Table II.

TABLE II.

Bottle.	% As_2O_5.	G. As_2O_5 in 100 cc. filtrate.	Bottle.	% As_2O_5.	G. As_2O_5 in 100 cc. filtrate.
1	5	0.0086	9	30	0.0144
2	10	0.0115	10	31	0.0144
3	20	0.0153	11	32	0.0144
4	25	0.0115	12	33	0.0173
5	26	0.0144	13	34	0.0690
6	27	0.0144	14	35	0.1495
7	28	0.0144	15	37	0.2875
8	29	0.0144	16	40	0.5060

The above data are plotted in Fig. 1, using as ordinates the weight in grams of As_2O_5 in 100 cc. of the filtrate as abscissae the percentage of As_2O_5 in the combined weight of the reacting compounds.

FIG. 1



The above data show that a compound is formed at about 33%, which is the As_2O_5 content of lead hydrogen arsenate. They also show that only one compound is formed, unless the solubilities are so nearly equal as not to be detected by a change in the curve. In order to show that other compounds do not exist in an equilibrium of these salts at the given temperature, an analysis was made of the solid phase in several of the bottles. To procure the sample for analysis the bottle was taken from the thermostat and the solid phase was poured upon a suction filter by aid of the mother liquor remaining with it. The mother liquor was removed as completely as possible by strong suction. The solid was dried and the lead determined by the usual method of weighing the sulfate. Table III gives the results.

TABLE III.

Bottle.	% PbO found.	Variation from theoretical PbO content of lead hydrogen arsenate.
3	65.49	+1.21%
5	64.45	+0.17%
8	64.66	+0.38%
12	64.44	+0.16%

Conclusion.—In the system disodium hydrogen arsenate, lead nitrate and water there exists at 25° only one compound, lead hydrogen arsenate.

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THE SOLUBILITY CURVES OF SALT HYDRATES: CALCIUM NITRATE.

BY HUGH STOTT TAYLOR AND WILLIAM NOLAND HENDERSON.

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Systems formed of two components have attracted considerable attention from phase rule investigators. The phase relationships of systems composed of mixtures of salts and water have been the chief object of experimental study. They may broadly be classified according as the components separate from solution in the pure state or as combination occurs between them with the formation of definite compounds. To the latter class belong the salt hydrates. They form a class of extreme importance, owing to their frequent occurrence in the field of inorganic chemistry. Study of such systems leads to a subdivision of hydrates into two classes, those possessing a definite melting point forming a liquid phase of the same composition as the solid hydrate and those which do not so behave.

Of the latter class of crystalline hydrates, which show no true melting point, but on the other hand a transition point, the classical example is sodium sulfate decahydrate, $Na_2SO_4.10H_2O$. Below 32.4° the saturated solution exists in stable equilibrium with the salt hydrate. Above that temperature, solutions are in stable equilibrium with the anhydrous salt and the solubility curve shows a sharp break at the transition temperature. At this temperature partial fusion occurs, during which the temperature remains constant. This is no true melting point, however, for the composition of the liquid phase is not the same as that of the original solid. The system also shows unstable solubility curves. For example, the curves of the decahydrate and the anhydrous salt may be continued some distance into the unstable region. That of the anhydrous salt, if sufficiently prolonged, meets the solubility curve of the unstable heptahydrate, which exists in equilibrium with solutions of higher concentrations than