above the un-ionized curve at a value of 1.000 for log $1/N_1$, thus even on this latter assumption the maximum deviation of the solution from Raoult's law is only 200 calories or about 5%.

Similar results were found for solutions of lead bromide in silver bromide[3] where agreement of the observed free energy of dilution of silver bromide by lead bromide with that calculated on the assumption that Raoult's law is obeyed and that both salts were un-ionized was very good, while assumption of complete ionization of both salts yielded a higher curve which agreed less well with the observed values. The molal volumes of these two solutions were also found to be in essential agreement with those predicted on the assumption of additivity. Moreover, the agreements of the free energies of dilution of silver bromide by lead bromide and of silver chloride by lead chloride with those predicted by Raoult's law were found to be equally as good at the higher temperatures as at lower temperatures. These solutions thus show the partial molal free energies, partial molal entropies and molal volumes of ideal solutions. The slightly poorer agreement of both series of solutions with Raoult's law curves based upon complete ionization is, the author believes, hardly sufficient to be particularly significant.

Summary

E. m. f. measurements of the cells, Ag(s), AgCl in $PbCl_2$(liq.), Cl_2(g), have been measured at mole fractions of silver chloride varying between 1.00 and 0.10 at temperatures from 460 to 620°.

Density measurements have been made upon a fifty mole per cent. solution of silver chloride and lead chloride which may be expressed by the equation $d^t = 5.547 = 0.00128t$ between the temperatures of 428 and 576°.

Calculations of the activity, activity coefficient, free energy of formation, and partial molal free energy of silver chloride have been made at the temperatures 500 and 600°.

The activity of the solvent, a_1, agrees very well with that predicted by Raoult's law throughout the entire range of temperature studied.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Cadmium Sulfate as a Basis for Acidimetry

BY SAMUEL E. Q. ASHLEY AND GEORGE A. HULETT

Upon crystallization from aqueous solution, cadmium sulfate forms large, hydrated crystals ($CdSO_4 \cdot 8/3\ H_2O$) of two sorts—some cloudy from inclusions of mother liquor and others of water clearness. These last possess uniformity of composition rare in salt hydrates and have been used in the determination of the atomic weight of cadmium.[1] In the present paper the authors describe a method of preparing standard sulfuric acid from these clear crystals by weighing them, dissolving in water and then depositing the cadmium in a mercury cathode—thus leaving a precisely known amount of sulfuric acid which may be diluted to a known volume or used to standardize an alkali solution.

Preparation of Material

Our method of preparing clear crystals has been to start with a concentrated filtered solution of chemically pure salt and allow it to evaporate spontaneously in 30-cm. crystallizing dishes closely covered with large pieces of filter paper. The solution is usually added to a depth of somewhat more than a centimeter. After about two weeks, crystals appear on the bottom of the dish; and, after they have reached a convenient size, the clear ones are removed with tweezers and the cloudy ones are redissolved for further crystallization. Although it not infrequently happens that a crop of crystals contains no clear crystals, the average yield of clear crystals is 7–10% by weight. A marked variation in the yields of these crystals made it seem possible that we might discover the conditions which favored their formation. An extensive investigation of the crystallization of the salt has not revealed any means of improving the yield of clear crystals, so we have been forced to rely upon the small yield normally obtained. This is quite sufficient for practical purposes if a large quantity of cadmium sulfate is crystallized.

Purity of Hydrated Cadmium Sulfate

The purity of cadmium sulfate has been disputed chiefly on the basis that the hydrate contains considerable amounts of "dissolved" or "included" water.[2] According to Baxter and Wilson, this water may be present in

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(1) Perdue and Hulett, *J. Phys. Chem.*, **15**, 155 (1911); Baxter and Wilson, THIS JOURNAL, **43**, 1230 (1921).

(2) T. W. Richards, *ibid.*, **33**, 888 (1911).

amounts as high as 0.2%.[3] Our analyses of crystals selected at random from material prepared over a considerable period of time have failed to show any such variation in composition, and it does not seem to have been conclusively shown that the variation in the analyses of Baxter and Wilson has come from the presence of water in the cadmium sulfate crystals beyond the suspicion which invariably attaches itself to hydrated materials. Assuming the accepted value for the atomic weight of cadmium, it is possible from the determination of the sulfate carried out in this paper to calculate the percentage composition of water in each sample of cadmium sulfate analyzed. The mean value for this determination is 18.725% while the theoretical value calculated from the accepted atomic weights is 18.728%. No determination varies from the mean value by more than 0.07%, and the precision of the experimental method was such that it would be unreasonable to assume that such a variation could be due only to the variation in the proportion of water in the crystal. We have grown cadmium sulfate crystals in solutions containing the dyes methylene blue and picric acid, and have failed to detect any material included in the clear crystals although dye was found deposited in the cracks of the cloudy crystals. Previous workers have been unable to detect any inclusions in the clear crystals by examining them with a microscope. Although the crushed crystals have an aqueous tension of 17.8 mm.[4] at 25°, the individual clear crystals if unmarred by scratches, fractures, etc., may be maintained indefinitely in a low humidity without showing any tendency to lose water of crystallization, and hence are very well suited for quantitative work. However, it is difficult to handle the crystals, remove them from the dishes in which they are grown, wipe them free of mother liquor with filter paper and store them, without inflicting some small damage which ultimately leads to efflorescence of the crystal. To prevent this, we have stored our cadmium sulfate in a desiccator over a paste of sodium chloride and water whose aqueous tension is less than half a millimeter higher than the dissociation pressure of the salt hydrate. Crystals have been preserved in this Laboratory for over a year in this manner with complete satisfaction.

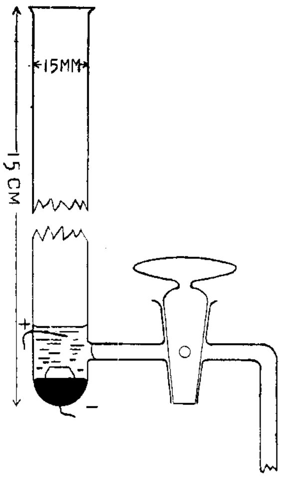

Fig. 1.—Diagram of electrolytic cell showing crystal of cadmium sulfate on mercury.

Analytical Method

Ten determinations of the concentration of a solution of approximately tenth normal sodium hydroxide were carried out in the following manner.

An electrolytic cell of the form depicted in Fig. 1 was made by sealing a stopcock to a test-tube (15 cm. × 15 mm.) about 15 mm. from the test-tube bottom. The external diameter of the side tube used was 6 mm. The anode is a short piece of platinum wire sealed through the side of the test-tube about 25 mm. from the bottom, and the cathode contact is made by sealing a short bit of platinum wire through the bottom. The weighed crystal (or crystals) is placed on top of a layer of mercury 6–7 mm. deep in the bottom of the tube, and then distilled water is carefully added by means of a pipet until the anode has just been covered. Cadmium sulfate though very soluble has a slow rate of solution so that this may be done without getting an appreciable amount of cadmium sulfate in the upper portion of the electrolyte. Air trapped in the side tube prevents the entrance of the liquid, and hence no liquid is separated from the main portion into the "dead space" of the apparatus. A resistance of 100 ohms was connected in series with the cell and a milliammeter and twelve volts potential applied to the circuit.

The cadmium sulfate dissolves, forming a layer of concentrated solution on the surface of the mercury. If the cell has been carefully assembled, the cadmium is deposited in the mercury without ever getting into the upper portion of the solution to any large extent. The conductivity of the solution is at first quite low, but as sulfuric acid is formed and the distribution of the sulfate ions becomes more general throughout the solution, the conductance increases and reaches a maximum value. A voltage lower than twelve volts may be used without the hundred ohm resistance, but the migration of ions proceeds more slowly, the current is lower and the whole process takes considerably longer. The total number of coulombs passed in each experiment was obtained by plotting the current against the time and integrating graphically by counting the squares under the curve. A typical curve of this sort is reproduced in Fig. 2. It will be noticed that at one point on the curve there is a definite break. This point marks the time at which hydrogen begins to be evolved. The falling off in the current presages the appearance of the hydrogen on the bright mercury surface by fully sixty seconds. Despite the fact that the deposition potential for cadmium is higher than that of hydrogen,

Fig. 2.—Typical curve showing course of electrolysis of cadmium sulfate (obtained with sample No. 5) "H_2 evolved" when 85.2% of cadmium is removed.

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[3] Baxter and Wilson, THIS JOURNAL, 43, 1237 (1921).

[4] Carpenter and Jette, *ibid.*, 45, 578 (1923).

because of the high over-voltage of hydrogen on mercury and the high concentration of cadmium ions at the mercury surface, no hydrogen has been evolved up to this point and hence the current efficiency for the decomposition of cadmium sulfate has been 100%. We are able to get 85% of the cadmium out of the solution in this way. It is an easy matter to calculate the amount of the crystal decomposed from the current that has passed, and, since we know the weight of the original material, we can calculate the percentage decomposed. From the data obtained in the electrolyses of the ten samples, it was found that the appearance of the hydrogen regularly occurs very close to the same place in each electrolysis. At this point the spray which has collected on the walls of the tube is washed down with a few cc. of water from a pipet. The electrolysis is continued until current approximately 33% in excess of the amount necessary to decompose the cadmium sulfate has passed and then the electrolysis may be assumed to be complete. Empirical determinations have shown no cadmium in the solution when tested with hydrogen sulfide after 25% excess current has passed—but, as this seems to be close to the liminal value, a larger amount of current is best employed for safety's sake. During the latter part of the electrolysis the solution is vigorously stirred by the evolution of hydrogen and oxygen. If the vessel has been carefully cleaned, no droplets of spray adhere to the walls, but a film of solution covers the glass as high as the spray is carried (about 50 mm. above the surface). As the droplets of spray strike the walls of the tube they run back into the electrolyte and thus a continuous efficient washing is obtained. When the electrolysis has reached completion, the electrolyte is run into a flask for titration. The current is left on and the cell is washed with a stream of carbon dioxide-free water until the milliammeter reads zero. The mercury should be shaken gently to release any acid trapped between it and the glass.

The acid was then titrated with carbonate-free alkali prepared by treating the alkali with calcium hydroxide after the method of Kolthoff.[5] The indicator used was brom thymol blue. The flask was swept free of carbon dioxide by carbon dioxide-free air, then stoppered with a rubber stopper fitted with a soda lime tube, weighed and the alkali added rapidly until the end-point was reached. The flask was again weighed to determine the amount of alkali added. The amount of excess alkali if any was now determined by a back titration with hundredth normal sulfuric acid from a micro-buret. Each solution was then made acid with a drop of concentrated hydrochloric acid and saturated with hydrogen sulfide to determine whether any cadmium or mercury were present in the sample. The volume of the solution was not greater than 100 cc. No heavy metal was detected by this means in any sample. The results of the ten determinations of the strength of the alkali made in this fashion are shown in Table I.

TABLE I

$CdSO_4 \cdot 8/3H_2O$, g.	NaOH soln., g.	Normality	H_2SO_4, %
0.46425	32.383	0.11178	38.252
.46379	32.319	.11189	38.214
.44638	31.134	.11179	38.249
.48942	34.155	.11173	38.270
.49533	34.512	.11191	38.209
.43558	30.378	.11180	38.246
.43395	30.251	.11185	38.229
.42124	29.379	.11180	38.249
.46626	32.499	.11187	38.224
.43528	30.352	.11182	38.239
	Average	.11182	38.238

Mean deviation—3.5 parts per 10,000

Probable error of the arithmetical mean, ±0.000016

The weights of material given in the above table are corrected for weight in vacuum. The weight of sodium hydroxide has also been corrected for the weight of material in excess of the end-point, found by back titration.

The "per cent. of sulfuric acid" given in the last column is calculated by dividing the weight of the sulfuric acid obtained from the electrolysis by the weight of the sample of cadmium sulfate. The weight of sulfuric acid was calculated by taking the normality of the sodium hydroxide to be that obtained by the three other methods used, *i. e.*, 0.11183 *N*.

The normality of the sodium hydroxide was now determined by the three most generally used methods, *i. e.*, by constant boiling hydrochloric acid, acid potassium phthalate and benzoic acid. The hydrochloric acid was prepared by Dr. N. H. Furman and its composition of 20.240% was checked by him by a silver chloride gravimetric analysis. The acid potassium phthalate and benzoic acid were obtained from the Bureau of Standards and possessed a purity of 99.97 and 99.98%, respectively. The acid potassium phthalate was dried at 120° according to the Bureau's instructions. The benzoic acid was spread on a watch glass in a desiccator over calcium chloride for several months. It seemed undesirable to fuse the acid to drive out the possible water because of the danger of forming the resinous polymer, a reaction which takes place even below the melting point.[6] Since the results agree well with the other methods, it may be assumed that no serious amount of moisture was retained by the material. Table II shows the results obtained.

The normality of the alkali as determined by the cadmium sulfate shows an agreement with the mean value of the other methods to within 1 part in 10,000. The result of each method agrees within the experimental error with the value obtained by means of cadmium sulfate, and hence establishes it as a method at least comparable with the others in the degree of precision obtainable. Since both of the organic acids must be calibrated in terms of constant boiling hydro-

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(5) I. M. Kolthoff, *Z. anal. Chem.*, **61**, 48 (1922).

(6) Weaver, THIS JOURNAL, **35**, 1309 (1913).

TABLE II

Vacuum weight of material, g.	Corrected weight of NaOH, g.	Normality	
HCl 20.240% Mol. wt. 36.468			
0.9125_7	45.296	0.11181	
$.8997_2$	44.679	.11176	Average 0.11179
$.9018_6$	44.780	.11178	Av. dev. 2.2 parts per
$.9332_1$	46.320	.11182	10,000
Acid potassium phthalate 99.97% Mol. wt. 204.180			
1.3388_4	58.563	0.11193	
1.1865_2	51.978	.11177	Average 0.11186
1.4629_5	64.024	.11188	Av. dev. 4.2 parts per
1.4835_2	64.928	.11187	10,000
Benzoic acid 99.98% Mol. wt. 122.083			
0.4460_1	32.642	0.11190	
$.8561_0$	62.717	.11179	Average 0.11183
$.4924_2$	36.081	.11177	Av. dev. 4.2 parts per
$.7644_5$	55.973	.11185	10,000

Mean value for twelve titrations 0.11183

chloric acid, which in turn is dependent on the gravimetric analysis by silver chloride, the use of cadmium sulfate provides an independent standard of acidimetry comparable with the hydrochloric acid.

We have carried out some preliminary experiments to determine the suitability of the pentahydrate of copper sulfate for determinations of the kind just described. Although the efficiency with which copper can be removed from the electrolyte is greater than in the case of cadmium, the color of the crystals makes the selection of the flawless ones difficult, and the low solubility of copper in mercury is a distinct disadvantage over the cadmium.

Hart and Croasdale[7] have removed the copper from dilute copper sulfate solutions by electrolysis and then determined the amount of acid produced, by weighing the copper; but the work has not been done with a degree of precision that would enable one to draw any conclusions regarding the possible usefulness of this method.

Summary

A new and independent method for preparing standard solutions of sulfuric acid by the electrolysis of cadmium sulfate in aqueous solution has been described.

The method has been compared with three established standards in acidimetry and shown to yield quite as precise results.

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(7) Hart and Croasdale, *J. Anal. Appl. Chem.*, **4**, 424 (1890).

PRINCETON, NEW JERSEY RECEIVED FEBRUARY 20, 1934

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Para-normal-butylphenylarsonic Acid as a Reagent for the Determination of Iron

BY K. A. CRAIG AND G. C. CHANDLEE

In a recent investigation of phenylarsonic acid as a reagent for the determination of tin,[1] it was observed that iron showed some tendency to precipitate. A large number of substituted phenylarsonic acids were investigated but *p-n*-butylphenylarsonic[2] was the only one found that would precipitate iron quantitatively in the presence of mineral acids.

Procedure.—The unknown sample containing not over 70 mg. of iron is dissolved in nitric acid or aqua regia, if necessary, the solution diluted to 200 cc. and carefully neutralized with ammonium hydroxide until a barely permanent precipitate is formed. Hydrochloric, nitric or sulfuric acid is then added in sufficient quantity so that the solution after addition of the reagent is approximately but not over 0.4 *N*. The solution is then heated nearly to boiling and 0.75 g. of reagent dissolved in 100 cc. of water at 80–90°,[3] is added slowly with stirring, whereupon a white flocculent precipitate is obtained. The mixture is then digested for twenty to thirty minutes, allowed to stand until completely cold, usually overnight, and the precipitate washed first by decantation and then on the filter paper with warm 0.02 *N* hydrochloric acid and finally with warm water until free from chloride.

The precipitate is ignited in a porcelain crucible over a low flame until the filter paper has been burned off. It is then heated for half-hour intervals over a strong Bunsen flame to constant weight. Usually one heating suffices. It is not possible to expel all the arsenic by heating in an open crucible, but by employing a propped lid this can be accomplished. The residues, tested by the Gutzeit method, never show more than 0.05 mg. and in many cases are entirely free of arsenic.

Thirteen determinations of pure solutions of iron salts whose iron content had been established by well-known methods, using samples containing approximately 0.05

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[1] Knapper, Craig and Chandlee, THIS JOURNAL, **55**, 3945 (1933).

[2] The *p-n*-butylphenylarsonic acid used in this work was prepared by Mr. D. M. Jones of this Laboratory according to a method developed by Dr. W. L. Evers (M.S. Thesis, Northwestern University) and as yet unpublished.

[3] This compound is only slightly soluble in cold water and in all determinations the excess reagent was recovered by evaporating the filtrate.