The 2,3-Epoxypentenes from the 2-Pentene Bromohydrins.—The procedure is similar to that described for preparing the epoxide from the chlorohydrin. When 33.4 g. (0.2 mole) of *erythro*-2-pentene bromohydrin was added slowly with agitation to a solution of 56 g. (1 mole) of potassium hydroxide pellets in 25 ml. of water at 100–110° in a 100-ml. 3-necked flask equipped with mercury sealed stirrer, thermometer, dropping funnel and condenser arranged for distillation, wet epoxypentane distilled over. This was dried with magnesium sulfate and distilled through a 30 cm. Vigreux column with finger condenser at a reflux ratio of ten, yielding 12 g. (70% yield) of *trans*-2,3-epoxypentane, 80% of which distilled between 80.0 and 80.2° at 746 mm. Nothing came over above 80.2°. The refractive index of the last 2 ml. of distillate was n^{25}D 1.3840, identical with the value for pure *trans*-2,3-epoxypentane (Table II). Thus the reaction product was pure *trans*-2,3-epoxypentane, for any *cis* isomer, had it been present, would have become concentrated in the last 2 ml. of distillate.

Similarly 18 g. (0.108 mole) of *threo*-2-pentene bromohydrin with 35 g. (0.6 mole) of potassium hydroxide in 20 ml. of water gave 7 g. (0.08 mole) of *cis*-2,3-epoxypentane, distilling 85.2–85.4° at 750 mm. As soon as the water was removed, the rest of the distillate (90% of the total) was collected in two approximately equal fractions. The refractive index of these two was n^{25}D 1.3915, identical with the value for pure *cis*-2,3-epoxypentane.

Summary

The oxide of 2-pentene has been separated into the *cis* and *trans*-2,3-epoxypentanes by fractional distillation.

cis-2-Pentene and *trans*-2-pentene have been synthesized from the isomeric 2,3-epoxypentanes.

With hydrobromic acid, *trans*-2,3-epoxypentane is converted into 100% pure *erythro*-2,3-dibromopentane and *cis*-2,3-epoxypentane into *threo*-2,3-dibromopentane.

Through the steps, 2,3-pentanediol, 2,3-diacetoxypentane and 2,3-dibromopentane the *cis* oxide yields the *dl-erythro* dibromide, and the *trans* oxide the *dl-threo* dibromide mainly. The formation of the other isomer takes place to the extent of about 7%.

When a pure *dl*-2,3-dibromopentane is converted into the corresponding 2-pentene, and this is allowed to react with bromine, the resulting dibromide contains 2 or 3% of the other isomer.

When a pure *cis* or *trans*-2,3-epoxypentane is converted into the bromohydrin and the oxide regenerated from this, the resulting oxide is pure.

Measurement of the dielectric constant is an accurate method of analysis of mixtures of the diastereomeric *dl*-2,3-dibromopentanes.

PASADENA, CALIFORNIA RECEIVED JUNE 5, 1940

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WASHINGTON]

A Thermodynamic Study of the System Zinc Sulfate–Sulfuric Acid–Water at 25°

BY H. V. TARTAR, W. W. NEWSCHWANDER AND A. T. NESS

During recent years considerable work has been done on the thermodynamics of aqueous solutions containing two electrolytes. In nearly all of these investigations the activity of only one of the three components has been determined and the solutions have been dilute.

In only one case have the thermodynamic properties of all three components been studied. This was done by MacDougall and Blumer[1] in the investigation of the three component system of sulfuric acid, acetic acid and water, a solution containing a strong and a weak electrolyte. This system may be also classified as one composed of one non-volatile and two volatile components.

Since very little work has been accomplished on systems of three components in the more concentrated solutions, it was deemed a worthy task to make a study of some of the thermodynamic properties of each of the components in the system: sulfuric acid–zinc sulfate–water at 25°. These two strong electrolytes are both non-volatile, have a common ion, and are of different valence types.

The data are also of practical interest, particularly here in the Northwest, because the solutions used in industry for the electro-winning of zinc[2] lie within the concentration range used. By means of the free energies which have been calculated it is possible for the first time to determine the electrolysis energy efficiencies of the electrolytic zinc plants throughout the world.

Discussion of Method

The thermodynamic activities of the water, the zinc sulfate, and the sulfuric acid in solutions of varying molalities were determined independently at 25°.

The vapor pressure of the water was determined

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(1) MacDougall and Blumer, THIS JOURNAL, **55**, 2236 (1933).

(2) Mantell, "Industrial Electrochemistry," McGraw-Hill Book Co., New York, N. Y., 1931.

by means of a modification of the method of Washburn and Heuse.[3] The activity was calculated by means of the equation $a = p/p_0$, where p is the measured vapor pressure of the solution and p_0 the vapor pressure of pure water at 25°.

The activity of the sulfuric acid was obtained from the measurement of the e. m. f. of cells of the type

$$H_2/H_2SO_4(m_1),\ ZnSO_4(m_2)/Hg_2SO_4/Hg \qquad A$$

and using the equation

$$\log a_{\pm} = \frac{E^0 - E}{(2.3026)\ \frac{3RT}{2F}} \qquad (1)$$

The e. m. f. of the cells of the type

$$Zn\text{-}Hg(1\ \text{phase})/H_2SO_4(m_1)ZnSO_4(m_2)/Hg_2SO_4/Hg \qquad B$$

was measured and from these values were calculated the e. m. f.'s of the corresponding cells

$$Zn/H_2SO_4(m_1),\ ZnSO_4(m_2)/Hg_2SO_4/Hg \qquad C$$

This calculated e. m. f., E, was that used to determine the activity of the zinc sulfate by use of the equation

$$\log a_{\pm} = \frac{E^0 - E}{(2.3026)\ \frac{RT}{F}} \qquad (2)$$

The concentrations of sulfuric acid and zinc sulfate in the solutions studied were varied within the ranges 0.1 to 4.0 M, and 0.5 to 2.0 M, respectively.

Materials

Zinc Sulfate.—The zinc sulfate, "analyzed reagent" quality, was recrystallized three times. The stock solution of zinc sulfate was analyzed by the pyrophosphate method as described by Hillebrand and Lundell.[4] This was checked by weighing the anhydrous zinc sulfate obtained by evaporation of three samples of the stock solution and then heating in a muffle furnace at 300°. The results by the two methods agreed within 1 part in 2300.

Sulfuric Acid.—The sulfuric acid, "analyzed" reagent, was diluted to 85% with conductivity water and then cooled with cracked ice. The large crystals of hydrogen sulfate monohydrate obtained were filtered in a Buchner funnel without filter paper and then allowed to melt and run into a Pyrex bottle containing conductivity water. The density of this stock solution was then determined; from this datum the concentration was estimated, using the values given in the "International Critical Tables."[5] As a check, a volumetric method was also used in which the sulfuric acid was titrated into hot sodium carbonate solution, using phenol red as an indicator, as suggested by Kolthoff and Menzel.[6] These methods gave results agreeing within 1 part in 1000.

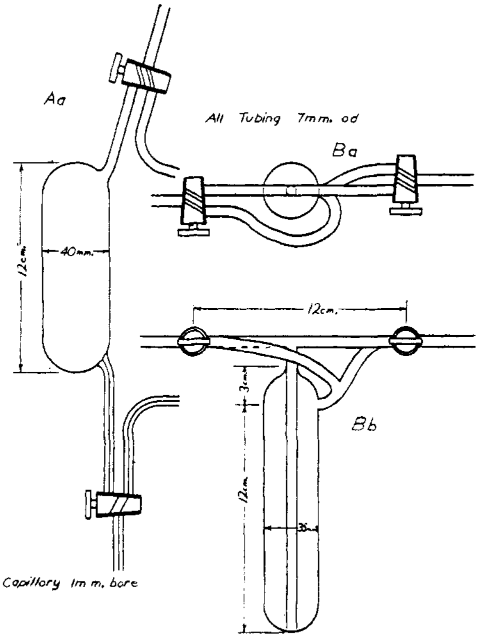

Fig. 1.—Amalgam holder, A, and flask, B.

Water.—Ordinary distilled water was redistilled in an all-glass still after adding some phosphorus pentoxide.

Mercury.—The mercury was subjected to air bubbling for a day, then washed with dilute nitric acid, dried and twice distilled *in vacuo* in a glass still.

Zinc.—The "electrolytic" zinc, 99.99% pure, was obtained through the courtesy of the Anaconda Copper Mining Company of Great Falls, Montana, to whom the authors desire to express their gratitude.

Zinc Amalgam.—Zinc was added to mercury under a concentrated zinc sulfate solution slightly acidified with sulfuric acid and heated in a bath of boiling water for several hours until the amalgam consisted of a single phase. On cooling, the material solidified as a two-phase amalgam.

A single-phase amalgam was prepared and kept under hydrogen by diluting the two-phase amalgam with mercury in a flask and then transferring through an 8-mm. glass tube filled with filter paper and finally through a 1-mm. capillary tube to an amalgam holder devised for the purpose, Fig. 2. The function of these tubes was to remove any zinc oxide; the amalgam had a bright, oxide-free surface.

Two more amalgams were made by diluting portions of the single-phase amalgam previously prepared. Amalgam holders having the mercury for dilution in them were repeatedly filled with hydrogen and then a portion of amalgam from the first container was added. By means of the three-way stopcocks the tubes joining the two amalgam holders were flushed out with hydrogen before any amalgam was run out of the first flask into the mercury of the second.

Mercurous Sulfate.—The mercurous sulfate was prepared by the method of Hulett.[7] It was aged in a brown,

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[3] Washburn and Heuse, THIS JOURNAL, **37**, 309 (1915).

[4] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, New York, N. Y., 1929.

[5] "International Critical Tables," Vol. III, McGraw-Hill Book Co., New York, 1933, p. 56.

[6] Kolthoff and Menzel, "Volumetric Analysis," Vol. II, John Wiley and Sons, New York, N. Y., 1929, p. 87.

[7] Hulett, *Phys. Rev.*, **32**, 257 (1911).

glass-stoppered bottle under 2 *M* sulfuric acid for two years. The mercury–mercurous sulfate electrodes used were very reliable in constancy of e. m. f.

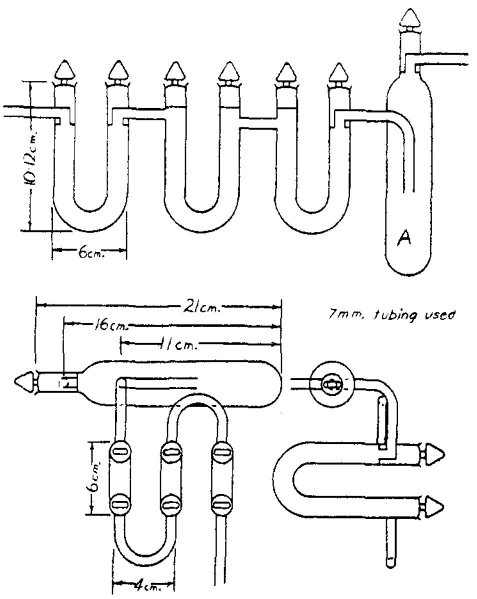

Fig. 2.—Moisture absorber.

Rubber Tubing.—The thick-walled rubber tubing was impregnated with molten paraffin as recommended by Pregl.[8] Except for sleeves used in joining tubes together, rubber was avoided.

Hydrogen.—Tank hydrogen was purified by the method of MacInnes and Cowperthwaite[9] using reduced copper catalyst in a quartz tube maintained near 690°.

Apparatus

Potentiometric Set-up.—A Leeds and Northrup type K potentiometer and galvanometer of 1800 megohms sensitivity were used. The cell was checked against a cell recently standardized by the United States Bureau of Standards. This potentiometric set-up permitted the measurement of the e.m.f.'s of the cells to 0.01 millivolt.

Temperature Control.—A water-bath maintained at 25 ± 0.02° was used for the vapor pressure determinations.

For the e. m. f. measurements, an air-bath was employed with air-stirring and thermostatic control to limit temperature variations to ±0.01°.

Experimental

Vapor Pressure Apparatus.—In principle, the vapor pressure apparatus was the same as that described by Washburn and Heuse.[3] Ideally, if a given volume of dry air passes over water, a certain weight of water is absorbed. If the same volume of dry air passes over a solution, a different weight of water is absorbed. The vapor pressures of the water and of the solution are directly proportional to these weights.

Several modifications were made in the apparatus used by Washburn and Heuse to obtain more rapid and efficient operation.[10] Four saturators were used instead of three, with solutions in saturators 2 and 3 and water in 1 and 4 thus permitting two solutions to be run simultaneously with a considerable saving of time and labor. An all-glass flow meter of the orifice type with taps connected to an oil manometer proved satisfactory for determining the velocity of the air. A simple pressure regulating device with a variable hydrostatic head connected after the flowmeter operated very efficiently with an aspirator in maintaining a quite constant flow of air through the apparatus.

The saturators were of the same design as those used by Washburn and Heuse.[3] The openings for filling the saturators were filled with 00 rubber stoppers, covered with rubber caps, and sealed with paraffin. Two sets of saturators, S_2 and S_3, were fitted with interchangeable ground glass joints. Thus S_2 and S_3 could be removed from the apparatus for cleaning, drying in an oven at 110° and refilling. While one set was in use, the next set was being prepared, and no lost time resulted.

Changes in volume in the air within the saturators due to the pressure drop in the apparatus were not measured; instead, the changes in pressure were correlated with the changes in weight. Small differential manometers containing kerosene of density 0.89 and colored with a red dye, palatine black, were used to measure these changes in pressure.

The greatest modification of the apparatus was in the type of absorbers used, see Fig. 2. They were exceedingly efficient and could be used for a long time without refilling. The vertical bulb A dipped into a Dewar flask containing dry-ice and acetone. The moisture in the air froze on the walls of the bulb and the dry air passed up through the central tube. The bulb was found to remove 99.9% of the moisture from the air. The remaining few milligrams of water were removed by passing over phosphorus pentoxide in three U-tubes, E, which were arranged at right angle to A as shown in C. The water was removed from the bulbs every 3 runs.

After about 30 runs had been made, the first portion of the first U-tube became somewhat messy and the phosphorus pentoxide in the absorbers was changed. This was probably unnecessary because the desiccant in the remaining U-tubes appeared unchanged.

The glass set-up was mounted on an oak frame 17″ × 17″ × 30″. The apparatus was rocked six times a minute during a run.

Vapor Pressure Measurement Technique.—With the solutions in their proper saturators, and with rubber tubing to carry the air stream across the places where the absorbers were to be, the apparatus was lifted into its place in the thermostat by means of a small block and tackle suspended from the end of a swinging arm. The apparatus was started rocking, the switch to the heating coils closed, and finally the aspirator was turned on. After two or three hours to approach steady conditions, the weighed absorbers along with the safety tubes were quickly fitted into place. The absorbers were joined to the apparatus and to the safety tubes by means of tight-fitting sleeves of rubber tubing. The safety tubes served

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(8) Pregl, "Quantitative Organic Microanalysis," 3d ed., P. Blakiston's Son and Co., Philadelphia, Pa., 1937.

(9) MacInnes and Cowperthwaite, This Journal, **53**, 555 (1931).

(10) *Cf.* Newschwander, Doctorate Thesis, University of Washington, 1939; complete details are given concerning the apparatus and its operation.

to protect the dry side of the absorbers against moisture diffusing backward against the stream of air. These tubes were filled with phosphorus pentoxide and fitted to the apparatus by means of ground glass joints. During a run, barometer readings corrected to 0° and manometer readings were taken every two hours. No changes were observed in the manometer readings except toward the end of the run when ice began to clog the absorber bulbs.

Approximately 2 g. of water was collected in a run lasting eight hours.

A special procedure was followed in weighing the absorbers. A_1 was weighed against a tare; A_1 was weighed against A_2; A_1 against A_3; and A_3 against A_4. The weighing against the tare gave the amount of water collected by A_1 to an accuracy of 1 mg. Since there is a ratio of weights in the formula used for calculating vapor pressures, the precision of the method, as far as weighing is concerned, does not depend on how accurately the water absorbed by A_1 is determined, but rather on how accurately are determined the differences in the weight of water absorbed by A_1 and the weights of water absorbed by the other absorbers. By this method of weighing the absorbers against one another, the differences in the weights of moisture collected by the absorbers are accurate to near ±0.1 mg.

Two runs of eight hours duration checked each other with an error in vapor pressure no greater than ±0.004 mm. mercury.

More accurate results were obtained by making a "double run" before weighing the absorbers. Two sets of absorbers were weighed. One set was run until ice began to close the bulb. The other set of absorbers was then put into the apparatus. Meanwhile the first set was allowed to thaw, but was not weighed. When the second set began to clog, the first set was put back on the apparatus while the ice melted in the second set. Two or even three samples of water may be collected by the absorbers before weighing. This method gave results that frequently checked to less than ±0.0005 mm. mercury. With care, this method should assure results to an accuracy of ±0.002 mm. mercury.

Electromotive Force Measurements.—The hydrogen electrodes were of the form recommended by Clark.[11] They were platinized by electrolysis of a 3% solution of chloroplatinic acid containing a trace of lead acetate as recommended by Britton,[12] just enough platinum black being deposited to remove the metallic sheen. Before each run the electrodes were replatinized.

The glass apparatus used in determining the e. m. f.'s of the cells, Fig. 3, was designed for simplicity of operation, despite its complex appearance. With this apparatus the e. m. f.'s of two types of cells, giving activities of both sulfuric acid and zinc sulfate, could be determined simultaneously. Flask B, Fig. 1, was very useful in effecting the introduction of (a) the amalgam under an atmosphere of hydrogen, and (b) the solution.

The mercurous sulfate half-cells, 5, were half-filled with mercury and then covered with a paste of mercurous sulfate which had been washed on a Buchner funnel with distilled water and a portion of the solution. The solution was introduced into flask B and the apparatus assembled as shown in Fig. 3. Flask B was fitted to the cell by means of the sleeve 16. After placing the assembled apparatus into the air-bath, hydrogen, partially saturated by passing over water, was bubbled for a few minutes through B to remove most of the oxygen above the solution. Then the hydrogen was passed down through the tubes 13 of the amalgam holders into the cell. The cell was flushed out by this method for a period of at least two hours, in some cases overnight. During this time A was closed with a rubber stopper; the hydrogen escaped through 12 and a rubber tube to the outside of the air-bath.

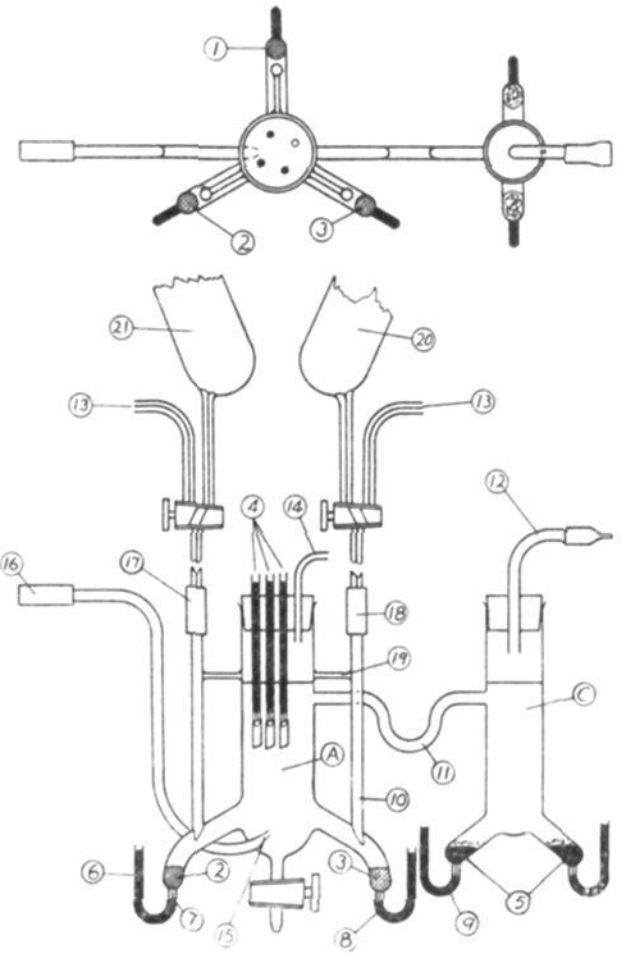

Fig. 3.—Apparatus for electromotive force measurements.

When the apparatus was considered free of oxygen, the amalgams were run into the 3 half-cells, 1, 2 and 3. The stopcocks on flask B were turned to force the solution into the cell. Some liquid was left in the flask to presaturate the hydrogen used for the hydrogen electrodes. When the cell had been successfully filled, the stopcocks on B were turned so that hydrogen bubbled through this flask and into the cell. Then the hydrogen electrodes 4 were fitted into place, tube 12 closed with a rubber policeman, and the hydrogen allowed to escape through the tube 14.

The bend in tube 11 helped to keep mercurous sulfate out of compartment A. The rod 19 was used to strengthen tube 10. The seals 7 were tungsten with the exposed portions platinum. The amalgam holders were joined to the cell by heavy rubber sleeves 17 and 18. The electrical contacts were made in mercury as is indicated by 4, 6, 8, and 9.

Since a voltaic cell of type B has a negative temperature coefficient, the room temperature was kept somewhat higher than that of the cell. After the thermostat was

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[11] Clark, "Determination of Hydrogen Ions," 3d ed., Williams and Wilkins Co., Baltimore, Md., 1928.

[12] Britton, *J. Chem. Soc.*, **127**, 2111 (1925).

closed the values of the e. m. f., E, increased as the cell cooled. Since some time after equilibrium had been reached the value of E began to drop, due to action of the sulfuric acid on the zinc amalgams, this effect was readily discerned and not confused with the change in E toward equilibrium.

The amalgams gave constant readings in less than an hour, and held for one to four hours. These e. m. f.'s were reproducible to ±0.05 mv. The experimental values with the 3 amalgam electrodes on a single run agreed among themselves to ±0.01 mv. Care was taken that solution did not become entrapped between the amalgam and the glass as this was found to cause erratic results. Small bubbles often appeared, after several hours, between the amalgam and the glass. On a single run the hydrogen electrodes checked each other to ±0.01 mv. and on separate runs to ±0.05 mv.

Very seldom was there any measurable difference between the mercurous sulfate electrodes; any differences were of the order of 0.02 mv.

Standardization of Zinc Amalgam Electrodes.—To standardize the zinc amalgams, a procedure quite similar to an ordinary run was used. Flask B contained the zinc sulfate solution. Metallic zinc was not used as the standard electrode owing to possible structural variations in different samples. According to Clayton and Vosburgh,[13] the two-phase amalgam gives the same value for E^0 as does crystalline metallic zinc. Therefore, this type of amalgam was chosen as the reference electrode.

After the cell had been flushed out with hydrogen, melted two-phase amalgam was sucked up into a heated, hydrogen-filled pipet, and quickly introduced into what was normally the mercurous sulfate half-cell. The dilute amalgams and solution were run into the cell as previously described. Greater precautions were taken to remove any oxygen and during a run hydrogen was bubbled through the solution used. The value of E for each electrode checked to ±0.01 mv. The e. m. f. of this type of cell is independent of the concentration of zinc sulfate.

This standardization of the dilute amalgams was done at both 25 and 35°.

The results gave directly the corrections to be added to E for the cell B to give E for the cell C, for which E^0 is known to be 1.3765_5 from the work of Harned and Hamer[14] and of Clayton and Vosburgh.[13]

Calculations

Vapor Pressures.—At a given temperature the mass of water picked up by a moving stream of air will vary directly with the volume of the air V and the vapor pressure P of the liquid solution.

$$m = KV_p \tag{3}$$

If, for example, there is water in saturator S_1 and solution in S_2, the volumes V_1 and V_2 will vary inversely with the partial pressures of the air. These partial pressures are the barometric pressure B diminished by both the vapor pressure p and the sum of the manometer readings P which show the difference between the atmospheric pressure and the pressure in the apparatus before entering an absorber. Then

$$\frac{V_1}{V_2} = \frac{B - P_2 - \Delta P_2}{B - P_1 - \Delta P_1} \tag{4}$$

Using equation 3 we find that

$$\frac{V_1}{V_2} = \frac{m_1 p_2}{m_2 p_1} \tag{5}$$

Equating the right-hand portions of equations 4 and 5 and rearranging

$$p_2 = \frac{B - \Delta P_2}{\dfrac{m_1(B - p_1 - \Delta P_1)}{m_2 p_1} + 1}$$

Using the value 23.75 mm. as the vapor pressure of water at 25° and substituting for p_1 a more general formula

$$p_s = \frac{B - \Delta P_s}{\dfrac{m_w(B - 23.75 - P_w)}{m_s 23.75} + 1}$$

where s refers to solutions (subscript 2 or 3) and w to water (subscript 1 or 4).

Activities of Water.—The activities of water were determined by the ratio

$$a_w = p_s/p_w$$

Even if the value of p_w, 23.75, were changed by ±0.01 mm., which is the variation to be found in the literature, the ratio which gives us the activities is unchanged. For any completed run, m_1, m_2, V_1 and V_2 are fixed quantities. Therefore p_2 (equation 5) varies directly with any value assigned to p_1 and the ratio of the two numbers remains the same.

Mean Activities and Activity Coefficients of Zinc Sulfate.—The mean activities were calculated by using the equation 2 where E is the e. m. f. of cell C. Activity coefficients γ were calculated from the relation

$$\gamma = \frac{a^{\pm}}{m^{\pm}} = \frac{a^{\pm}}{(m_{\mathrm{Zn}^{++}} m_{\mathrm{SO}_4^{--}})^{1/2}} = \frac{a^{\pm}}{[(m_2)(m_1 + m_2)]^{1/2}}$$

Mean Activities and Activity Coefficients of Sulfuric Acid.—The mean activities of sulfuric acid were calculated by equation 1 where E is the e. m. f. of the cell A; E^0 of this cell is 0.61515 volts.[4] The activity coefficients were calculated from

$$\gamma = \frac{a^{\pm}}{m^{\pm}} = \frac{a^{\pm}}{[(2m_1)^2(m_1 + m_2)]^{1/3}}$$

Calculation of Free Energies.—During the electrolysis of zinc sulfate to form zinc the reaction is

$$\mathrm{ZnSO_4} + \mathrm{H_2O} \longrightarrow \mathrm{H_2SO_4} + \mathrm{Zn} + {}^1/_2\mathrm{O_2}$$

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[13] Clayton and Vosburgh, This Journal, **58**, 2093 (1936).

[14] Harned and Hamer, *ibid.*, **57**, 27 (1935).

This reaction and its change in free energy ΔF_8 is equal to the sum of two equations and their free energies

$$ZnSO_4 + H_2 \longrightarrow H_2SO_4 + Zn;\ \Delta F_6 \quad (6)$$
$$H_2O \longrightarrow H_2 + {}^1/_2O_2;\ \Delta F_7 \quad (7)$$
$$\overline{ZnSO_4 + H_2O \longrightarrow H_2SO_4 + Zn + {}^1/_2O_2;\ \Delta F_8} \quad (8)$$

Equation 6 in turn is the sum of the reactions studied in this paper.

$$ZnSO_4 + 2Hg \longrightarrow Zn + Hg_2SO_4;\ \Delta F_9 \quad (9)$$
$$H_2 + Hg_2SO_4 \longrightarrow 2Hg + H_2SO_4;\ \Delta F_{10} \quad (10)$$
$$\overline{ZnSO_4 + H_2 \longrightarrow H_2SO_4 + Zn;\ \Delta F_6 = \Delta F_{10} - \Delta F_9}$$

Since

$$\Delta F = -nFE$$

the free energy for equation 6 is

$$\Delta F_6 = nF(E_9 - E_{10}) \quad (11)$$

where E_9 and E_{10} are the e. m. f.'s corresponding to equations 9 and 10, respectively.

For equation 7

$$\Delta F_7 = \Delta F^0 + RT \ln \frac{1}{a_{H_2O}} \quad (12)$$

where ΔF^0 at 25° is 56,560 calories and at 35° is 56,180 calories.[15]

The final equation for the change in free energy at 25° for equation 8 is obtained by adding 11 and 12

$$\Delta F_8 = nF(E_9 - E_{10}) + 56{,}560 + RT \ln \frac{1}{a_{H_2O}} \quad (13)$$

At 35° 56,560 calories is replaced by 56,180 calories in 13.

Results and Discussion

Eleven sets of solutions were used, seven in which the concentration of the sulfuric acid was constant and the zinc sulfate concentration varied, and four with a fixed concentration of the zinc sulfate and variable concentrations of the sulfuric acid. The activities of the water, the mean activities and activity coefficients of sulfuric acid and of the zinc sulfate, and the free energies for the electrodeposition of a gram mole of zinc have been determined for each set of solutions. The data are given in Table I which also includes appropriate data obtained by Harned and Hamer[14] and by Robinson and Jones.[16] By means of the graphs presented, it is possible to estimate any of these thermodynamic quantities for any solution containing zinc sulfate and sulfuric acid through the range of concentration studied.

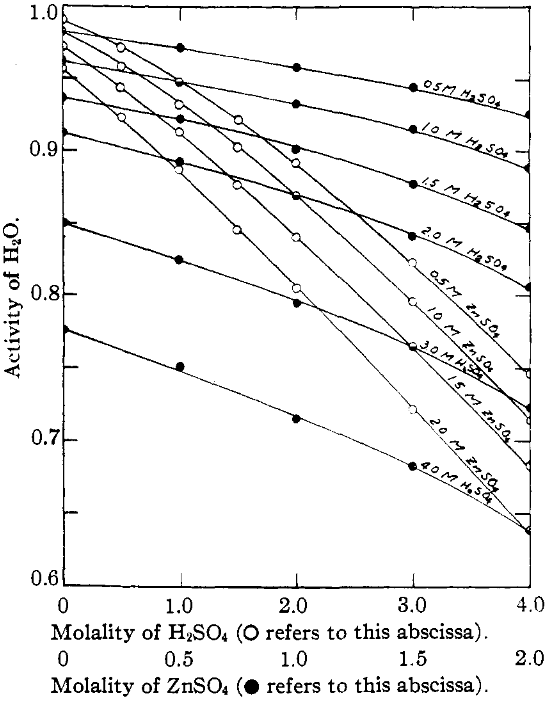

Fig. 4.—Activity of water in aqueous solutions containing both zinc sulfate and sulfuric acid.

The data have been found to have good consistency when checked by the application of the familiar thermodynamic equation

$$55.51 \text{ d} \ln a_0 + m_1 \text{ d} \ln a_1 + m_2 \text{ d} \ln a_2 = 0$$

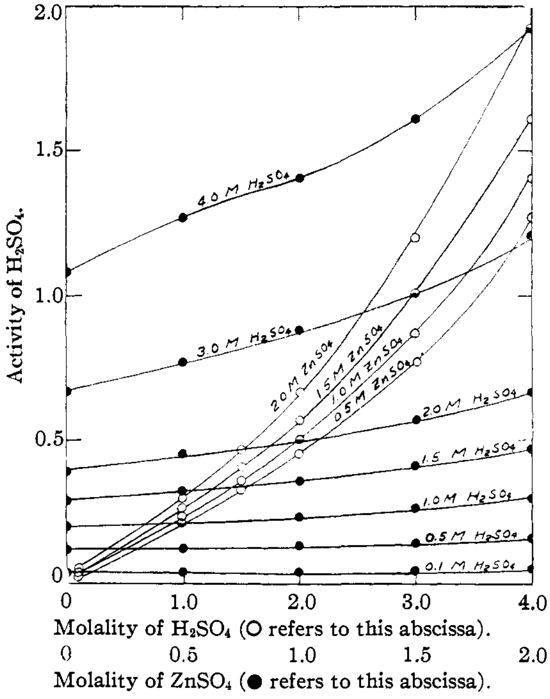

Fig. 5.—Activity of sulfuric acid in aqueous solutions of zinc sulfate.

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(15) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, N. Y., 1923, p. 485.

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

TABLE I

RESULTS OF VAPOR PRESSURE AND ELECTROMOTIVE FORCE MEASUREMENTS USING SOLUTIONS OF SULFURIC ACID AND ZINC SULFATE

		Water		Sulfuric acid				Zinc sulfate		
H_2SO_4, m_1	$ZnSO_4$, m_2	Vapor pressure, mm.	Activity, a_1	E. m. f., E_5	Activity, $a^{\pm}$	Activity coeff., γ	E. m. f., $a^{\pm}$	Activity, $a^{\pm}$	Activity coefficient, γ	Free energy change, ΔF cal.
		25°								
0.1	0			0.73714	0.0421	0.265				
0.5	0		0.9821	.69609	.122	.154				
1	0		.9620	.67600	.206	.130				
1.5	0		.9385	.66213	.295	.124				
2	0		.9136	.65088	.396	.125				
3	0		.8506	.63041	.673	.141				
4	0		.7774	.61201	1.085	.171				
0	0.5	23.544	.9913							
0.1	.5			.74070	0.0384	.133	1.46504	0.0319	0.0582	89,990
0.5	.5	23.107	.9729	.69600	.123	.123	1.46470	.0323	.0457	92,050
1	.5	22.512	.9479	.67281	.224	.123	1.46218	.0356	.0412	93,020
1.5	.5	21.914	.9227	.65848	.325	.124	1.45920	.0400	.0400	93,540
2	.5	21.186	.8921	.64600	.449	.131	1.45480	.0475	.0425	93,950
3	.5	19.583	.8246	.62499	.775	.155	1.44532	.0687	.0520	94,530
4	.5	17.735	.7467	.60589	1.272	.193	1.43423	.1058	.0706	94,960
0	1	23.324	.9829							
0.1	1			.73909	0.0401	.114	1.45572	.0458	.0437	89,640
0.5	1	22.787	.9594	.69408	.129	.113	1.45374	.0495	.0404	91,640
1	1	22.180	.9339	.67068	.237	.118	1.45075	.0556	.0393	92,600
1.5	1	21.428	.9022	.65436	.361	.128	1.44636	.0660	.0417	93,170
2	1	20.709	.8720	.64157	.504	.139	1.44161	.0794	.0458	93,560
3	1	18.895	.7956	.62029	.875	.167	1.43081	.1209	.0605	94.090
4	1	16.986	.7152	.60197	1.407	.206	1.41977	.186	.0831	94,490
0	1.5	23.092	.9723							
0.1	1.5			.73637	0.0430	.108	1.44906	.0594	.0384	89.470
0.5	1.5	22.454	.9454	.69021	.143	.113	1.44561	.0673	.0389	91,450
1	1.5	21.713	.9142	.66649	.264	.122	1.44180	.0788	.0407	92,390
1.5	1.5	20.842	.8776	.64943	.411	.137	1.43675	.0960	.0453	92,970
2	1.5	19.965	.8406	.63635	.577	.151	1.43116	.1193	.0521	93,340
3	1.5	18.152	.7643	.61474	1.011	.185	1.42000	.184	.0709	93,890
4	1.5	16.209	.6825	.59671	1.614	.229	1.40915	.281	.0978	94,310
0	2	22.741	.9575							
0.1	2			.73329	0.0466	.106	1.44271	.0761	.0371	89,330
0.5	2	21.958	.9245	.68565	.160	.118	1.43824	.0905	.0405	91.340
1	2	21.094	.8882	.66115	.303	.132	1.43301	.111	.0453	92,250
1.5	2	20.116	.8470	.64416	.471	.149	1.42741	.138	.0522	92,800
2	2	19.148	.8062	.63039	.673	.168	1.42140	.174	.0617	93.190
3	2	17.16	.7225	.60803	1.203	.213	1.41027	.269	.0851	93,773
4	2	15.13	.6371	.59003	1.920	.264	1.39892	.419	.1208	94.160
		35°								
1	0.5			.67086			1.45807			92.540

in which a_0 is the activity of water and m_1, a_1 and m_2, a_2 represent the molalities and activities of the acid and the salt, respectively. The curves also appear to pass quite easily through the points of Harned and Hamer[14] for pure sulfuric acid, and the points of Robinson and Jones[16] for pure zinc sulfate.

Of interest are the minima that occur (Figs. 6 and 8) in the activity coefficients of sulfuric acid and zinc sulfate when the concentration of sulfuric acid remains constant and the zinc sulfate concentration varies.

Minima are also to be noted (Fig. 8) in the activity coefficients of zinc sulfate when the concentration of zinc sulfate is held constant and the concentration of sulfuric acid is allowed to vary.

As might be expected (Fig. 9) the free energy decreases with decreasing sulfuric acid concentration and with increasing zinc sulfate concentration. The free energy decreases quite rapidly as the concentration of the acid approaches zero.

It has been found that single-phase zinc amalgams will give reproducible results in four molal

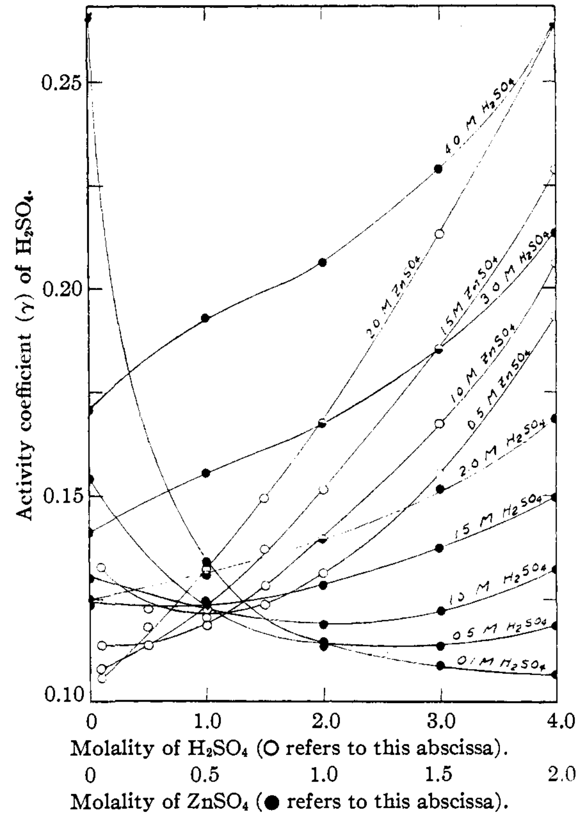

Fig. 6.—Activity coefficient of sulfuric acid in aqueous solutions of zinc sulfate and sulfuric acid.

sulfuric acid. Richards and Dunham[17] found that the zinc amalgam electrode gave steady values in 2 molal sulfuric acid.

From the data on the solution of zinc sulfate 0.5 *M* and sulfuric acid 1.0 *M* at 25° and 35° and using the Gibbs–Helmholtz equation the average value for the change in heat content Δ*H* for this temperature range was computed for the reaction given in equation 8 and found to be 78,236 cal. per gram mole of zinc.

At the present time no worker has developed a satisfactory theory for explaining the changes in the thermodynamic properties of strong electrolytes in the more concentrated solutions. When such a theory is developed, it is hoped that the data presented herein will be useful toward further consideration of this three component system, composed of water and two strong electrolytes of different valence types.

The Thermodynamic Energy Efficiency of the Electrolytic Zinc Process.—In the commercial "low acid" process the production of 1 pound of zinc from a bath which is approximately 0.5

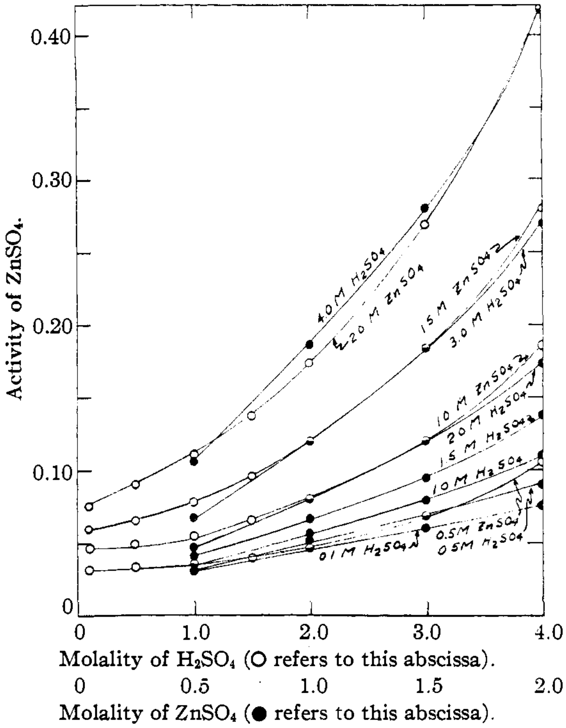

Fig. 7.—Activity of zinc sulfate in aqueous solutions of sulfuric acid and zinc sulfate.

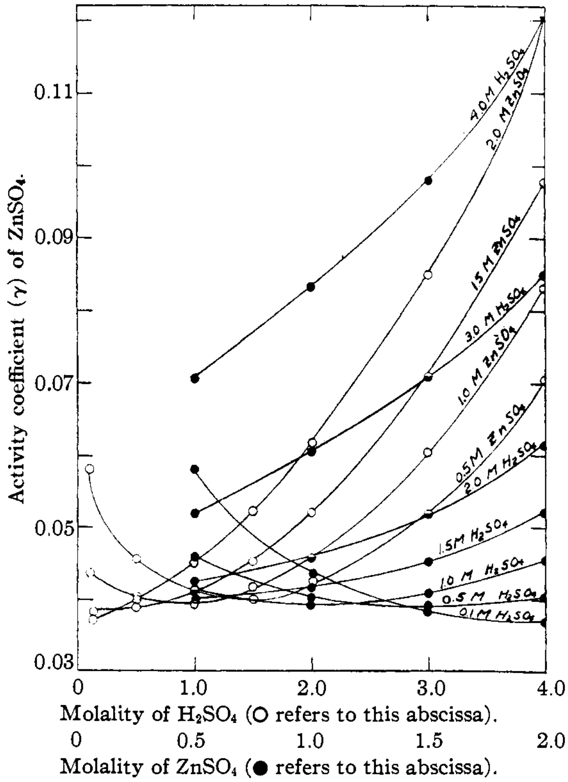

Fig. 8.—Activity coefficient of zinc sulfate in aqueous solutions of sulfuric acid and zinc sulfate.

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[17] Richards and Dunham, This Journal, **44**, 678 (1922).

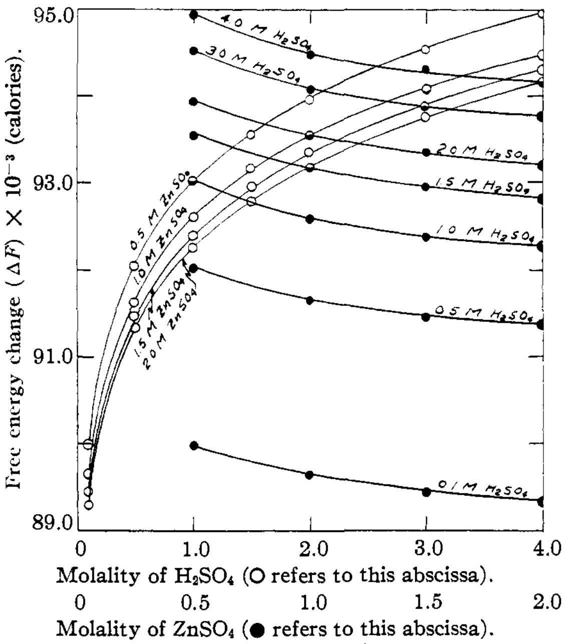

Fig. 9.—Free energy change for the reaction $ZnSO_4 + H_2O \rightarrow H_2SO_4 + {}^1/_2O_2 + Zn$.

molal zinc sulfate and 1.0 molal sulfuric acid requires approximately 1.46 kilowatt hours of electrical energy; 181,000 calories per gram atomic weight of zinc. The electrolysis is carried out commercially at about 35°. We have found that at 35° under reversible conditions 92,540 calories are required. Then the energy efficiency of the commercial electrolysis compared the reversible process

$$\frac{92{,}540(100)}{181{,}000} = 51.1\%$$

The excess energy, 48.9 per cent., is used in *IR* drop through the solution, maintaining the requisite overvoltage, etc., and is dissipated in the form of heat.

In the "high acid" process the concentration of the electrolyte does not remain the same, but changes gradually. At the beginning of the run the solution is sulfuric acid 2.4 *M* and zinc sulfate 1.6 *M*. During the run the zinc sulfate diminishes to 0.8 *M* while the acid increases to 3.2 *M*. The points in Fig. 10 were obtained by interpolation; using these and by graphical integration it was found that at 25° it would be necessary to use 93,900 calories under reversible conditions to obtain a gram mole of zinc by means of the "high acid" process. At 35° due to the temperature coefficients for equations 11 and 12 it is necessary to subtract 550 calories. This gives a final value of 93,450 calories at 35°.

In the commercial "high acid" process 1.53 kilowatt hours are required to produce 1 pound of zinc. From this we find that it takes 189,000 calories to get one mole of zinc. Then the energy efficiency of this process as compared with one operating under reversible conditions is

$$\frac{93{,}450(100)}{189.000} = 49.4\%$$

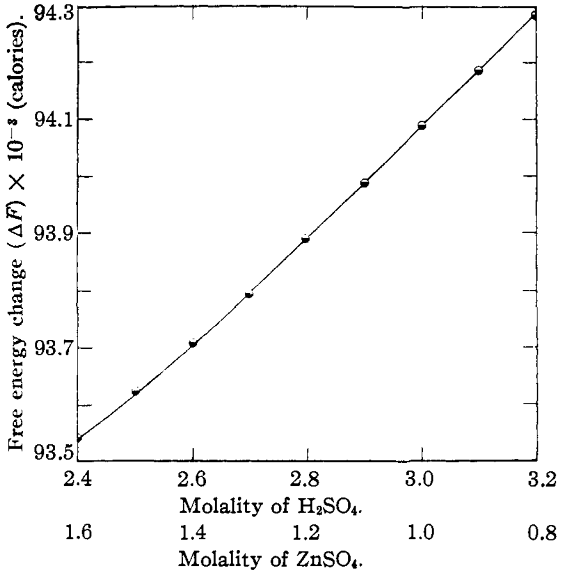

Fig. 10.—Free energy change at particular concentrations of sulfuric acid and zinc sulfate in solution.

Summary

1. The activities of each component of the system zinc sulfate–sulfuric acid–water (concentrations, zinc sulfate 0.5 to 2.0 *M*, sulfuric acid 0.1 to 4 *M*) were determined experimentally by measurement of the vapor pressures of the solutions, and by measurement of the e. m. f.'s of the cells

$$H_2/H_2SO_4(m_1),\ ZnSO_4(m_2)/Hg_2SO_4/Hg$$
$$Zn/H_2SO_4(m_1),\ ZnSO_4(m_2)/Hg_2SO_4/Hg$$

2. A dynamic vapor pressure apparatus of improved design has been built and used.
3. Zinc amalgam electrodes were used successfully in relatively concentrated acid solution.
4. The changes in free energy for the reaction

$$ZnSO_4 + H_2O \longrightarrow Zn + H_2SO_4 + {}^1/_2O_2$$

in this series of solutions has been computed.

5. The change in heat content has been computed for the above reaction within the temperature range 25° to 35° using solutions of sulfuric acid 1 *M* and zinc sulfate 0.5 *M*.
6. For the first time, the free energy has been determined for the reaction occurring in the electrolytic zinc processes.

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