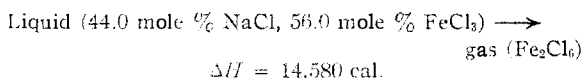
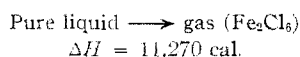
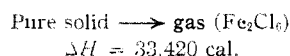


ride and chlorine becomes appreciable above 300°. It is evident, therefore, that ferric chloride cannot be volatilized from a mixture containing excess sodium chloride.

The following heat quantities have been calculated from the vapor pressure data



Thus, the heat of solution of solid ferric chloride in a solution having a concentration just below that of the eutectic is 18,840 cal. per gram formula weight of Fe₂Cl₆.

Other Properties.—The molten eutectic mixture conducts electricity readily with the evolution of chlorine at the anode, and reduction to ferrous chloride at the cathode. Corrosion tests were made with various metals in the mixture both exposed to air and in a nitrogen atmosphere. Copper and copper alloys are attacked rapidly. Steel is slightly corroded in moist air. Chromium

alloys and stainless steel are quite resistant to the molten salt.

Summary

1. The phase diagram of the system ferric chloride-sodium chloride was determined. A eutectic, having the composition of 46 mole per cent. sodium chloride, 56 mole per cent. ferric chloride, fuses at 158°.

2. The vapor pressures of pure ferric chloride and of three mixtures with sodium chloride were measured. The observed vapor pressures of solutions saturated with ferric chloride agree with the values reported by Stirnemann for the pure substance.

3. No evidence was found for the existence of a compound between the two chlorides. The extremely low vapor pressure of ferric chloride in the presence of sodium chloride at temperatures above the boiling point of the pure compound is due to the normal effect of the solute in lowering the vapor pressure. This prevents the possibility of volatilizing ferric chloride during chlorination of ores in the presence of excess sodium chloride.

URBANA, ILLINOIS

RECEIVED AUGUST 4, 1941

[CONTRIBUTION No. 186 FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

Activity Coefficients of Strontium Chloride by an Isopiestic Method¹

BY BENJAMIN A. PHILLIPS AND GEORGE M. WATSON WITH W. A. FELSING

Introduction

The purpose of this investigation was the determination of the activity coefficients of strontium chloride in aqueous solution by the isopiestic method first proposed and used by Bousfield and Bousefield² and subsequently improved and made practical by numerous investigators.³ It was decided to develop this method still further, contemplating certain changes in the ap-

paratus which would increase the accuracy of the determinations.

The reference electrolyte chosen for use in this study was barium chloride, the activity coefficients of which have been determined with highly satisfactory agreement by the different methods of Tippetts and Newton,⁴ by Newton and Tippetts,⁵ and by Robinson.⁶ Harned and Åkerlöf⁷ have recalculated the data of Lucasse,⁸ and Pearce and Gelbach⁹ have presented a limited number of values.

Experimental determinations of the activity coefficients of strontium chloride are not numerous. Lucasse,⁸ Hepburn¹⁰ and Harned and

(1) Constructed from a portion of a thesis presented to the Graduate Faculty of the University of Texas by Benjamin A. Phillips in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1939. Original manuscript received October 7, 1940.

(2) Bousfield and Bousefield, *Proc. Roy. Soc. (London)*, **A103**, 429 (1923).

(3) (a) Sinclair, *J. Phys. Chem.*, **37**, 495 (1933); (b) Robinson, *THIS JOURNAL*, **56**, 1830 (1934); (c) Robinson, *ibid.*, **57**, 1161, 1165 (1935); (d) Robinson and Jones, *ibid.*, **58**, 938 (1936); (e) Robinson, *ibid.*, **59**, 84 (1937); (f) Robinson, *Trans. Faraday Soc.*, **34**, 1142 (1938); (g) Owen and Cook, *THIS JOURNAL*, **59**, 2273 (1937); (h) Mason and Ernst, *ibid.*, **58**, 2032 (1936); and (i) Mason, *ibid.*, **60**, 1638 (1938).

(4) Tippetts and Newton, *ibid.*, **56**, 1675 (1934).

(5) Newton and Tippetts, *ibid.*, **58**, 280 (1936).

(6) Robinson, *ibid.*, **59**, 84 (1937).

(7) Harned and Åkerlöf, *Physik. Z.*, **27**, 424 (1936).

(8) Lucasse, *THIS JOURNAL*, **47**, 732 (1925).

(9) Pearce and Gelbach, *J. Phys. Chem.*, **29**, 1023 (1935).

(10) Hepburn, *J. Chem. Soc.*, 1204 (1932).

Åkerlöf⁷ have presented data; the agreement, however, is not very satisfactory.

Experimental

In order that the isopiestic method may yield precise results, it is necessary that true equilibrium in every sense be attained and that the concentrations of the solutions at equilibrium be known with certainty. If true equilibrium is established by providing proper conditions, the accuracy of the method will depend upon the determinations of the concentrations of solutions having identical vapor pressures at the same temperature.

Only changes in technique and in apparatus developed during this investigation will be described.

Thermal Contact Procedure.—To improve thermal contact between solutions, this investigation used liquid mercury between and around nickel¹¹ cups placed upon a heavy steel plate.

The Solution Cups.—The round, flat-bottomed nickel cups for the solutions were 1.6 cm. deep and 3.8 cm. in diameter and were drawn from a sheet of 22 gage stock. They were polished to a mirror finish before gold-plating; great pains were taken to secure a non-porous gold-plate thereby eliminating corrosion and contamination. Concentrated solutions of chlorides will cause corrosion of the nickel, if a pinhole in the gold-plating exists. The inside walls, but not the bottoms, of each cup were then given a thin coating of an acid-, alkali-, and water-proof baked resin varnish to prevent amalgamation of the exposed gold-plate with the mercury vapor. Even though the vapor pressure of mercury at 25° is only 0.00184 mm.,¹² in a partially evacuated system this pressure is sufficient over a period of thirty-six to seventy-two hours to bring about amalgamation of an exposed gold surface. The cups were fitted, as shown in Fig. 1, with flat covers overlapping the edges and ground to a loose fit; a short fin extending

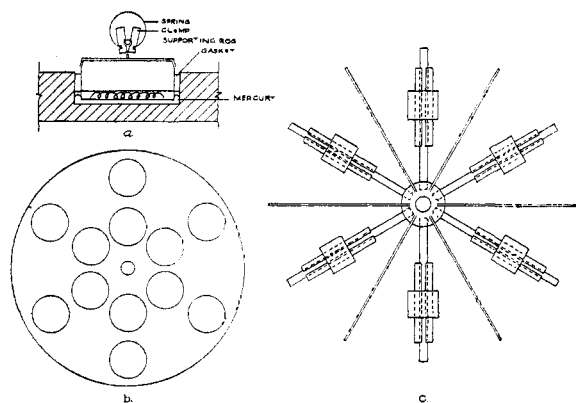


Fig. 1.

(11) Experiments were also conducted with platinum cups. After allowing these cups to remain in contact with mercury for several days, the cups were put into actual service. Wiped with a clean towel and dried at room temperature, the cups were used as if they had been nickel cups. The data obtained with these platinum cups were about as accurate as those obtained with nickel cups, especially if the cups were weighed before and after a run (drying the cups in air at room temperature). At first, the cups gained from one to three milligrams during a run, but this gain became less with use. The average weight of the solution was about three grams.

(12) "International Critical Tables," Vol. III, p. 206.

upward served as a handle for these covers. With one type of rocking device, short platinum wire helices were placed directly into the solutions in the cups to aid in stirring and to provide better heat transfer from the liquid surfaces to the bottoms.

The Steel Desiccator.—The desiccator, shown in Fig. 2, was 25.4 cm. in diameter and 15.2 cm. high. A standard tubulated glass cover was ground to fit the flanged rim; vacuum stopcock lubricant¹³ was used. No difficulty whatsoever was encountered in removing mercury globules from the bottom and sides of the cups because of lubricant vaporization. A 17.8 cm. diameter aluminum plate, suspended above the cups, prevented accidental entry of dust particles into the solutions.

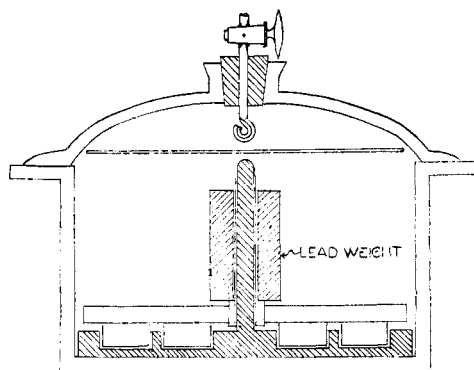


Fig. 2.—Steel desiccator.

The Heat Transfer Plate.—The steel plate used to promote thermal equilibrium between cups was 1.9 cm. thick and 25.4 cm. in diameter. Twelve flat-bottomed holes, 1.27 cm. deep, were drilled into the plate spaced as shown in Fig. 1(b). A triangle of heavy steel spring wire was set into the bottom of each hole to ensure a continuous layer of mercury between the cup and the plate. A steel post, 12.7 cm. long and screwed into the center of the plate, served both as a handle and as a support for the mechanisms necessary in the removal and replacement of covers.

The Cover-Removal Mechanism.—A steel tube, 10.2 cm. long, fitted around the center post; at its lower end was located a "hub" from which extended 6 flat blades and 6 rods. The rods were part of the clip mechanism used to catch and hold the cup covers; on raising the whole mechanism the covers were lifted. On rotating through a 30° angle, the blades of the mechanism could be lowered to rest on the top edge of each cup; each cup was thus held down equally on its wire triangle base. A heavy lead weight, resting on the hub, kept the cups securely in their holes in the plate. This whole mechanism could be operated from the outside of the desiccator through the tubulature in the cover.

The Rocking Device.—Two rocking devices were used: one employed a simple to-and-fro rocking motion while the other added a rotating motion. In the *first*, the framework containing the desiccator was pivoted at the bottom and rocked back and forth at any speed or through any angle desired by means of variable speed pulley ratios and crank-arm lengths. In the *second*, a steel rod extending downward from the bottom of the desiccator was set in a

(13) Central Scientific Company, Chicago, Ill., No. 15520 A.

socket bearing at the bottom of the thermostat. The top of the frame above the desiccator was connected by means of a bearing to the end of a crank arm. By rotating this arm in a horizontal plane the desiccator was made to describe a circle and, in so doing, caused the plate and cups to be tilted through all directions. This motion caused the solution to flow in the cups with a circular motion, thus constantly presenting fresh liquid surfaces. The speed and amount of tilting were varied to obtain best results.

With this type of rocking device, which was considered quite superior to the first in regard to the time required for equilibration, the platinum helices were found unnecessary. Smaller amounts of solutions could also be used in the cups with this type of rocking device. The thermostat temperature was held constant at $25 \pm 0.005^\circ$.

Purification of Materials. (a) **The Solvents.**—All water used had a specific conductance of 1.2×10^{-6} reciprocal ohms at 25° . All hydrochloric acid was re-distilled c. p. material.

(b) **The Salts.**—**Barium chloride** of reagent quality was twice recrystallized from an aqueous hydrochloric acid solution. This salt was dried to remove the hydrochloric acid and was again recrystallized twice from conductivity water. After centrifuging, the crystals were dried over "Dehydrite" in a vacuum oven. The salt was placed into a cold oven, the oven exhausted, and the temperature raised slowly to 165° , at which temperature the salt was kept for twenty-four hours. **Strontium chloride** of reagent grade was purified in a similar manner, except that it was recrystallized three times from conductivity water. All salts were stored in a vacuum desiccator over "Dehydrite."

Preparation of Solutions.—Large volumes of solutions were not required; hence stock solutions were prepared directly in weight burets of about 70 ml. capacity. Samples of the anhydrous salts of approximately the weight desired were placed into tared weighing bottles; these were heated in a vacuum oven at 165° for ten hours. The closed bottles were cooled and weighed and the salts transferred into the weight burets; the proper weight of water was then added. The weights of salts used varied from 2 to 6 grams.

Details of Operation.—The solutions were weighed into the tared metal cups directly from the weight burets; at least three samples of each salt solution were used in any one determination. The times required for equilibration, as determined experimentally, varied from twenty-four hours for the concentrated solutions to thirty-six and up to seventy-two hours for the increasingly dilute solutions. At the end of the equilibration period, dry air was admitted to the desiccator (which had been evacuated at the beginning of the period). On removal of the cups, now covered, any small droplets of mercury adhering to the outside of the cups were brushed off with a camel's hair brush and the weighings made quickly.

As a means of testing out the efficiency of the method, the isopiestic ratio, $M_{(KCl)}/M_{(NaCl)}$ was determined as a function of the concentration of the sodium chloride solutions over the range 1.0 to about 3.0 molal. The relation obtained was $M_{(KCl)}/M_{(NaCl)} = 1.0075 + 0.03310 M_{(NaCl)}$. This relation is to be compared with that given by Robinson¹⁴ for the same concentration range

$$M_{(KCl)}/M_{(NaCl)} = 1.0082 + 0.03237 M_{(NaCl)}$$

(14) Robinson, *Trans. Faraday Soc.*, **35**, 1217 (1939).

The agreement is satisfactory for the range of concentrations covered in this investigation.

The Data Obtained

The observed molalities of isopiestic solutions are listed in Table I; each value listed is the mean of the concentrations found in three or four cups present in the desiccator during a given run. The deviations of individual values from the recorded mean was never greater than ± 0.0002 molal. The last two columns give a comparison of the isopiestic ratio, $M_{(BaCl_2)}/M_{(SrCl_2)}$ as found in this investigation and as calculated from isopiestic data of $BaCl_2$ -KCl and $SrCl_2$ -KCl solutions as given by Robinson.¹⁵

TABLE I
WEIGHT MOLALITIES OF ISOPIESTIC SOLUTIONS AT 25°
(MOLES/1000 G. OF WATER)

Barium chloride	Strontium chloride	$R = \left[\frac{M_{(BaCl_2)}}{M_{(SrCl_2)}} \right]_{obs.}$	R (calcd. from Robinson ¹⁵)
1.4079	1.3020	1.0813	1.0673
1.4020	1.2964	1.0814	1.0669
1.0040	0.9440	1.0635	1.0480
0.7868	.7490	1.0504	1.0418
.7831	.7455	1.0504	1.0402
.6929	.6630	1.0450	1.0335
.4550	.4380	1.0388	1.0268
.3997	.3865	1.0341	1.0230
.2374	.2290	1.0366	1.0202
.0410	.0396	1.0353	
.0339	.0328	1.0335	

Treatment of Results

The experimental data were treated according to the methods of Robinson and Sinclair.^{3b} The reference values for the activity coefficients, as selected, were 0.561 for a 0.05 molal barium chloride solution and 0.464 for a 0.2 molal strontium chloride solution. The value for barium chloride is due to Scatchard and Tefft¹⁶ and the value for strontium chloride is the mean of the experimental and calculated values (0.465 and 0.463) of Harned and Åkerlöf.¹⁷ Should these reference values be replaced in the future by more accurate measurements, the activity coefficients of this investigation may readily be adjusted to the more correct value. The activity coefficients and osmotic coefficients at rounded concentrations, as calculated by the usual procedures, are presented in Table II. The activity coefficients are presented graphically in Fig. 3.

These results are believed to have an over-all

(15) Robinson, *ibid.*, **36**, 735 (1940).

(16) Scatchard and Tefft, *This Journal*, **52**, 2272 (1930).

(17) Harned and Åkerlöf, *Phys. Z.*, **27**, 424 (1926).

TABLE II
OSMOTIC AND ACTIVITY COEFFICIENTS FOR BARIUM AND STRONTIUM CHLORIDE SOLUTIONS

Weight molality (moles/1000 g. water)	Barium chloride ϕ (Osmotic coef- ficient)	Barium chloride γ (Activity coef- ficient)	Strontium chloride ϕ (Osmotic coef- ficient)	Strontium chloride γ (Activity coef- ficient)
0.05	0.860	(0.561)	0.892	0.572
.10	.844	.498	.871	.514
.20	.833	.440	.861	(.464)
.30	.834	.412	.865	.441
.40	.843	.396	.877	.430
.50	.857	.389	.894	.426
.60	.873	.386	.914	.427
.70	.888	.385	.936	.432
.80	.903	.385	.959	.438
.90	.919	.387	.983	.448
1.00	.934	.390	1.007	.458
1.10	.950	.394	1.032	.470
1.20	.965	.399	1.056	.484
1.30	.981	.405	1.080	.498
1.40	.997	.411		
1.50	1.013	.417		
1.60	1.030	.422		
1.70	1.048	.429		
1.80	1.067	.436		

accuracy of better than 1 part in 500, provided the reference activity coefficient is assumed correct.

The activity coefficients calculated in this investigation for barium chloride agree well with those of Robinson,⁶ of Tippetts and Newton⁴ and of Harned and Åkerlöf.¹⁷ The data of Scatchard and Tefft¹⁶ are in fair agreement, while the data of Lucasse,⁸ of Jones and Dole¹⁸ and Hepburn¹⁰ deviate more extensively.

The activity coefficients for strontium chloride, as calculated from the experimental data, agree quite well with those calculated by Harned and

(18) Jones and Dole, *THIS JOURNAL*, **51**, 1035, 1073 (1929).

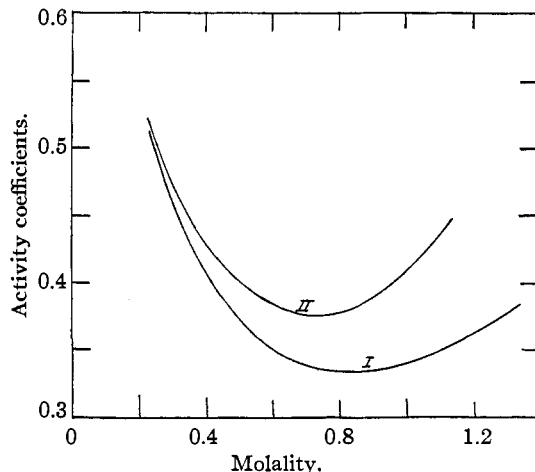


Fig. 3.—Activity coefficients of barium and strontium chlorides: I, BaCl₂; II, SrCl₂.

Åkerlöf,⁷ but they do not agree with those of Lucasse⁸ or of Hepburn.¹⁰

A series of determinations on calcium chloride has been made; however, the investigation is still in progress. The results will be reported at a later date.

Summary

1. Certain improvements in technique and in design of apparatus for the isopiestic method of determining activity coefficients have been described.

2. The activity coefficients have been determined for aqueous solutions of strontium chloride, using barium chloride as the reference standard. The values obtained are believed to have an accuracy better than 1 part in 500.

AUSTIN, TEXAS

RECEIVED NOVEMBER 10, 1941

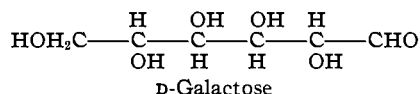
[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

Crystalline Modifications of D-Manno-D-gala-heptose, and the Preparation of Some of Its Derivatives¹

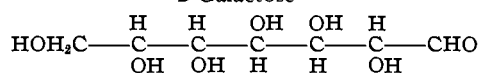
BY EDNA M. MONTGOMERY AND C. S. HUDSON

D-Manno-D-gala-heptose, originally called *d*- α -mannoheptose by Emil Fischer,² who prepared it from D-mannose by the cyanohydrin synthesis, was shown by George Peirce³ to have the configuration of carbon atoms one to five like that of

D-galactose; because this heptose is related thus to D-mannose and to D-galactose, it has been termed D-manno-D-gala-heptose.⁴



D-Galactose



D-Manno-D-gala-heptose

(1) Publication authorized by the Surgeon General, U. S. Public Health Service. A preliminary report on the crystalline modifications of D-manno-D-gala-heptose was presented in part at the meeting of the National Academy of Sciences, Washington, D. C., April, 29, 1930. Not copyrighted.

(2) Fischer and Passmore, *Ber.*, **23**, 2226 (1890).

(3) Peirce, *J. Biol. Chem.*, **23**, 327 (1915).

(4) Hudson, *THIS JOURNAL*, **60**, 1537 (1938).