the same direction as the concentration with respect to phosphoric acid, but no satisfactory correlation has been made between the two sets of determinations. In solutions of more soluble salts in contact with the phosphates, no generalization whatever seems justified. Potassium chloride, potassium sulphate and sodium nitrate all increase the acidity of solutions in contact with iron phosphate, while potassium chloride and sodium nitrate decrease the amount of the phosphoric acid in the solution. No correlation of the acidity with the amounts of iron in the solution seems possible, although, as is shown by the solutions of potassium chloride, the base in solution is increased.

In contact with calcium phosphate, potassium chloride and sodium nitrate decreased the acidity of the solution instead of increasing it, as in the case of iron phosphate. In both cases, however, the amounts of calcium in the solutions decidedly increased, and in the case of sodium nitrate the phosphoric acid also.

In so far as observations were made, an increase of temperature increased the decomposition of the solid phosphates in either water or salt solutions.

Owing to the complexity of the reactions involved between the hydrolyzed products and the other solutes, and perhaps also to the fact that definite equilibrium conditions were not under observation, attempts to apply the mass law to the results have not been satisfactory. The hypothesis of electrolytic dissociation has, in many of the cases observed, failed to give a satisfactory explanation.

The importance of the phenomena here described for agricultural and mineralogical studies is obvious. Its discussion will, however, be given at a later stage of the study.

BUREAU OF SOILS,
U. S. DEPARTMENT OF AGRICULTURE,
WASHINGTON, D. C.

A MODIFICATION OF THE FREEZING-POINT METHOD.

S. W. YOUNG AND W. H. SLOAN.

Received May 25, 1904.

THE usual method of determining molecular weights by measuring the lowering of the freezing-point depends upon slightly supercooling the solution and then allowing ice to form. This is accompanied by a rise in temperature, and the highest reading which the thermometer shows is taken as the melting-point of the solution. Thus equilibrium between ice and solution is always reached with ascending temperature and by separation of ice.

It is theoretically possible to obtain the same temperature reading, however, in an entirely different way. If a solution be thoroughly stirred in contact with ice the ice will continue to melt and cool the solution even after the solution has reached the melting-point of the pure solvent, and the lowest temperature attainable by stirring a solution with ice will be the melting-point of the solution. The equilibrium will be the same whether it is reached with melting ice or with freezing ice.

Some time after we had begun the investigation of which this paper is a preliminary report,[1] there appeared a description of a very simple method for molecular weight determination, based upon this principle,[2] and which can be readily applied in all cases where the strength of the solution is readily obtainable by direct analysis. The method upon which we have been working, while based upon the same general principle, is, nevertheless, carried out by very different mechanical methods, and avoids the necessity for an analysis of the solution in all cases. In fact, the method is almost the exact counterpart of the Landsberger method as applied to boiling-point determination. In the Landsberger method vapor is passed into the solution until the maximum temperature is reached, and the composition of the solution is determined by weighing both the dissolved substance and the total solution.

DESCRIPTION OF THE METHOD.

Briefly described, our method consists in the preparation of a stirrer of ice, by means of which first the pure solvent is thoroughly agitated and the thermometer reading taken in order to know the melting-point of the pure solvent. Next a quantity of the substance whose molecular weight is to be determined is added and brought into solution by shaking. The solution thus obtained is then thoroughly stirred with the ice-stirrer and the melting-point of the solution is found.

In order to obtain the concentration of the solution the tube in which the determinations were made was first weighed empty,

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[1] The publication is made on account of the departure of Mr. Sloan from this laboratory.

[2] Richards: *Ztschr. phys. Chem.*, 44, 563; This Journal, 25, 291.

then, after a determination had been made, the total weight was again determined. Subtracting from the total weight the weight of the tube and of the dissolved substance the weight of the solvent is obtained, and thus all the data necessary for the computation of the molecular weight.

THE APPARATUS.

(1) *The Tube.*—The first determinations were carried out in the ordinary Beckmann apparatus, but as the results obtained

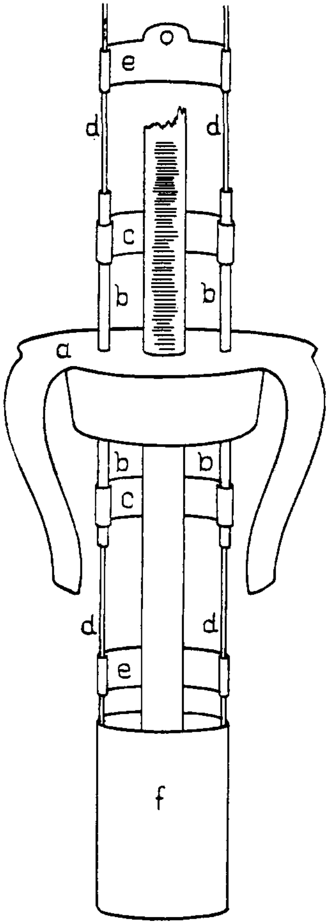

Fig. 1.

showed very considerable fluctuations, recourse was finally had to a vacuum jacket whereby the rate of radiation was very materially reduced. The tube which we used was 260 mm. long and 45 mm. inner diameter.

(2) *The Ice-stirrer.*—The device for using the ice-stirrer is shown in Fig. 1. First there was a carrier for the stirrer frame. This carrier consisted of a brass plate, *a,* with three prongs, which were bent down so as to grip the vacuum tube firmly. Upon the under side of this plate was cemented a cork stopper which fitted the mouth of the vacuum tube nicely. Both the brass plate and the stopper were perforated at the center so as to carry the Beckmann thermometer. At either side of the perforations for the thermometer was placed a smaller perforation, and through each of these perforations was passed a ⅛ inch brass tube, *b b,* which was soldered firmly into the brass plate. In addition to this these two tubes were braced so as to remain in a position parallel to one another, by means of the strips of brass, *c c.* These tubes served as guides for the rods of the stirrer frame proper. The stirrer frame consists of the two upright rods, *d d,* held parallel to one another and in position to follow smoothly through the guides by means of the brass braces, *e e.* At the upper brace, connection is made with a rod which runs to the wheel which moves the stirrer. At the lower end of the rods is soldered the cylindrical roll of silver foil on which the ice is to be frozen, *f.* The stirrer is run very easily by means of a small motor.

(3) *The Freezing of the Stirrer.*—In freezing the ice on to the stirrer frame the following device was made use of (Fig. 2): A piece of glass tube, *a,* slightly smaller than the inner dimensions of the vacuum jacket to be used, was fitted with a rubber stopper carrying another piece of glass tubing, *b,* somewhat larger than the diameter of the thermometer. The stirrer frame of silver foil, *c,* was then placed in the tube, cooled boiled water poured in to the upper level of the frame and the whole apparatus then placed in a freezing-mixture and the water allowed to freeze on the stirrer frame. The stirrer was then easily removed by slightly warming the outer and inner tubes. After removal it was placed in a vacuum jacket for some time before being used in order to avoid having it at a temperature below zero when starting in on

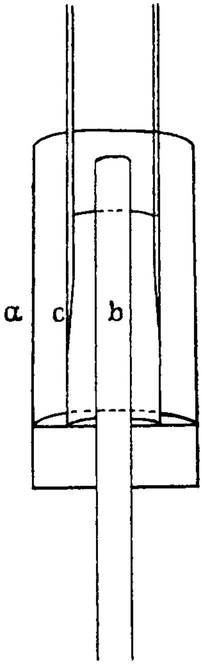

Fig. 2.

the determinations. In this way there was obtained a stirrer of ice that, with reasonable precautions, could be depended on for from six to eight, or even more, determinations without cracking off or becoming too far reduced in size.

(4) In order that the temperature outside the vacuum tube should be held reasonably near to that in the inside of the tube the whole apparatus was packed in a large can of shaved ice.

THE DETERMINATION.

To make a series of determinations the procedure was as follows: About 125 cc. of water, cooled to nearly 0°, was placed in the vacuum jacket and the ice-stirrer placed in position in the tube. After properly adjusting the thermometer, the jacket was placed in the ice-pack and covered over with shaved ice. The water was then briskly agitated with the stirrer, by mechanical means, until the constant reading of the thermometer showed that equilibrium had been obtained. The stirrer and thermometer were then removed to another vacuum jacket, and a weighed amount of the substance to be used was added. The ice-stirrer and the thermometer were then replaced in position, the jacket was put into the ice-pack and again thoroughly covered with the shaved ice. The solution was now again briskly agitated by means of the ice-stirrer until equilibrium was attained. Then the apparatus was taken out of the ice-pack, the thermometer and ice-stirrer removed, after allowing them to drip a moment, to the other vacuum tube, and the vacuum tube with water and solute weighed.

By subtracting the weight of the solute and the weight of the vacuum tube the weight of the solvent was determined. Another weight of solute was now added, the stirrer placed in position and the apparatus returned to the ice-pack. The solution was again agitated until equilibrium was attained, the weight of the solvent again determined as before, another portion of solute added and the whole process repeated. This was continued until six different readings were obtained, representing as many different concentrations. The rate of stirring was about 300 per minute, preliminary experiments having shown that this rate gave a reading of the thermometer which did not change when the rate was increased. If the solutions used are not too concentrated, eight determinations could easily be made with one stirrer. No difficulty was experienced in the ice not sticking to the stirrer frame. Boiled water is essential to making a good stirrer, because the presence of air spaces in the ice tends to loosen the ice around the frame, which may cause trouble.

THE RESULTS.

In the gradual development of the apparatus into its present form there were obtained a very large number of results which need not be given here, as they serve merely to illustrate the increasing effectiveness of the apparatus. The results which are given in the following tables are those last obtained when the apparatus was in its most nearly perfect form. That there are still a number of sources of error which we have not as yet eliminated will be shown later. Determinations were made with cane-sugar and with sodium and potassium chlorides.

For cane-sugar we give here but two series of determinations (Table I), bar-sugar being used in all determinations.

TABLE I.

$C_{12}H_{22}O_{11}$. Series I. Mol. wt. = 342.2.

H_2O. Grams.	Sugar. Grams.	Per liter. Grams.	Normal.	Lowering.	Molecular lowering.
128.60	3.00	23.328	0.068	0.126°	1.848
137.10	10.00	72.939	0.213	0.395	1.853
142.20	20.00	140.647	0.411	0.771	1.875
147.15	30.00	203.873	0.595	1.132	1.900
153.40	40.00	260.756	0.762	1.469	1.928
159.80	50.00	312.891	0.914	1.780	1.947
		Series II.			
131.65	3.00	22.787	0.067	0.122	1.845
137.25	10.00	72.932	0.213	0.395	1.853
142.80	20.00	140.055	0.409	0.766	1.871
148.00	30.00	202.702	0.592	1.124	1.897
154.20	40.00	259.403	0.758	1.463	1.930
160.70	50.00	311.138	0.909	1.775	1.952

The two series here given are the last two performed, and were made under as nearly like conditions as possible. It will be noticed that while all the results are lower than those of Loomis,[1] Raoult,[2] Jones,[3] and Nernst and Abegg,[4] those of the smallest concentration vary the least, the difference being greater as the concentration increases. This is probably on account of the increasing percentage of error due to radiation of heat as the lowering increases.

However, while the results obtained by this method are likely to be low, from the fact that the rapid radiation of heat probably prevents one from obtaining a sufficiently low reading of the thermometer, the tendency in the other method is to obtain too low a reading, because the temperature surrounding the tube is lower than that of the solution used. Again, the freezing out of part of the solvent lessens the volume of the solution, tending to high results.

Corrections are, of course, made for these errors, but these corrections are necessarily more or less arbitrary. Probably the correct lowerings would lie somewhere between those of Raoult and ours, and nearer to Raoult's, because of certain errors still not avoided by our apparatus.

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[1] *Ber. d. chem. Ges.*, **26**, 797 (1893) ; also *Ztschr. phys. Chem.*, **32**, 578 (1900).

[2] *Ztschr. phys. Chem.*, **27**, 617 (1898).

[3] *Ibid.*, **12**, 642 (1893).

[4] *Ibid.*, **15**, (1894).

In passing, attention may be called to the general variations in the results of different investigators, especially those of Jones, where, in some cases, he approximates 25 per cent. higher than any other investigator.

Two series of results using potassium chloride as solute are given in Table II.

TABLE II.

KCl. Series I. Mol. wt. = 74.6.

H_2O. Grams.	KCl. Grams.	Grams per liter.	Normal.	Lowering.	Mol. lowering.
130.52	0.20	1.532	0.020	0.073°	3.554
135.31	0.60	4.434	0.059	0.204	3.432
138.40	1.20	8.656	0.116	0.395	3.404
141.80	2.40	16.925	0.227	0.753	3.323
148.18	4.80	32.393	0.435	1.425	3.282
151.87	7.80	51.359	0.689	2.235	3.245

Series II.

H_2O. Grams.	KCl. Grams.	Grams per liter.	Normal.	Lowering.	Mol. lowering.
129.50	0.20	1.544	0.021	0.072°	3.478
132.90	0.60	4.514	0.061	0.207	3.420
135.45	1.20	8.859	0.120	0.401	3.377
138.39	2.40	17.342	0.232	0.774	3.329
141.80	4.80	33.855	0.454	1.491	3.285
145.45	7.80	53.626	0.719	2.331	3.244

In Table III are given two series of results with sodium chloride as solute.

TABLE III.

NaCl. Series I. Mol. wt. = 58.5.

H_2O. Grams.	NaCl. Grams.	Per liter. Grams.	Normal.	Lowering.	Molecular lowering.
130.70	0.20	1.530	0.026	0.090°	3.441
134.10	0.60	4.474	0.076	0.260	3.399
137.30	1.20	8.741	0.149	0.503	3.366
141.30	2.40	16.985	0.290	0.971	3.344
146.20	4.80	32.831	0.561	1.873	3.334
152.50	8.80	57.704	0.986	3.293	3.334

Series II.

H_2O. Grams.	NaCl. Grams.	Per liter. Grams.	Normal.	Lowering.	Molecular lowering.
131.27	0.20	1.528	0.026	0.090°	3.445
138.75	0.60	4.324	0.074	0.252	3.410
143.45	1.20	8.365	0.143	0.478	3.342
148.25	2.40	16.188	0.276	0.923	3.334
154.90	4.80	30.987	0.530	1.759	3.321
161.90	8.80	54.354	0.929	3.096	3.322

If one takes the trouble to compare our results, as given in the three tables above, with those of Jones,[1] Abegg,[2] Richards,[3] and Raoult,[4] which may best be done by plotting the variation of the molecular lowering with the variation in the concentration, it will be found that they are systematically lower than the others, but, at the same time, are more uniform than any of the others except Raoult's, and in some portions of the curve, also those of Richards. These facts allow us to hope that, when all of the sources of error are eliminated or provided for in some way, our method may give results of the greatest accuracy, and it is our present purpose that the work shall be carried on at an early date.

THE SOURCES OF ERROR.

The chief sources of error which have affected the results above are given here. It may seem strange to those who are familiar with this sort of work that some of these errors were not avoided from the start. The reason is that we have put in all of our time up to the present in perfecting the mechanical part of the method, which at first gave very erratic results. While carrying on this part of the work it seemed wholly unnecessary to work with a too great refinement of method in other respects. Greater or less errors are then due to

(1) The fact that the thermometer used was not calibrated.

(2) The thermometer was not kept continually in ice water when not in use. This should be done, as, when a thermometer has stood at room temperature for some time and is then brought to zero, it takes some hours before the final zero reading is obtained.[5] This is due to the slow contraction of the glass.

(3) The still uncertain effect of variations of the barometer on the readings of a Beckmann thermometer. This is probably a factor that must be separately worked out for each thermometer.

(4) Probably a very considerable source of error arose from the fact that no attempt was made to follow the temperature of the solution at all closely with the temperature of the pack outside. We have reason to believe that there was considerable radiation even across the walls of the vacuum tube.

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[1] *Ztschr. phys. Chem.*, **11**, (1893).

[2] *Ibid.*, **20**, 207 (1896).

[3] *Ibid.*, **44**, (1903).

[4] *Ibid.*, **27**, 617 (1898).

[5] Compare Richards: *Loc. cit.*

We propose in the near future to see that a thorough test of the apparatus is made, taking account of all known sources of error, and we have reason to hope that the results so obtained will compare with the best of the older investigators.

STANFORD UNIVERSITY,
May 17, 1904.

THORIUM; CAROLINIUM, BERZELIUM.[1]

BY CHARLES BASKERVILLE.

Received June 24, 1904.

SYNOPSIS.

THIS paper presents a brief historical account of the discovery of thorium and the questions raised as to its elementary character.

The published evidence is considered in conjunction with experimental data obtained and the conclusions arrived at that thorium is not a primary radioactive body.

The complex nature of thorium is proved by the conduct of salts with certain organic bases, as phenyl hydrazine, for example. Fractions were had, giving atomic weights from 212 to 252, the original being 232.5.

Pure thorium oxide from several sources was converted into the chloride by heating it, mixed with pure sugar carbon, within quartz tubes during the passage of dry chlorine. A volatile chloride, "weisser dampff" of Berzelius, was obtained decreasing in amount according to the duration and temperature of the reaction. The purified, delicately green oxide obtained from this gave a specific gravity of 8.47 and the element, berzelium, an atomic weight of 212 (tetrad).

The temperature of the porcelain tube was raised and thorium tetrachloride distilled away. The residue in the carbon boat on purification gave a grayish pink oxide with a specific gravity of 11.26 and an atomic weight of (tetrad) 255.6 (carolinium). The new thorium, or that in a large measure freed from the berzelium and carolinium, gave an atomic weight of 220.6 and a white oxide with a specific gravity of 9.2. The original thorium gave atomic weights 232.5 to 232.6 and its oxide had a specific gravity of 10.5.

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[1] Presented before the New York Section of the American Chemical Society, April 8, 1904.