

No simple relationship was found to exist between the increased rate of inversion in the presence of these salts and the activity coefficients of the hydrogen ion in solutions of the same acid and salt concentrations containing no sucrose, but the rough parallelism observed indicates that the activity of the hydrogen ion is probably the most important factor in determining the rate of inversion.

For concentrations of salt above 0.500  $M$  an equation proposed by Schmid and Olsen as describing the neutral salt action,  $K = K_0 \times 10^{rC}$ , has been found to apply fairly well.

The equation of Schmid and Olsen is derived from the Hückel expression for the activity coefficient of an ion in concentrated solutions, with certain assumptions. This also indicates the importance of the activity of the hydrogen ion in determining the rate of inversion.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MCGILL UNIVERSITY]

## A MICRO CALORIMETER

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In this paper is described a small calorimeter with which heats of solution may be determined using only 4 cc. of solvent and corresponding amounts of solute. The heat capacity of the calorimeter itself is approximately 1 calorie. The calorimeter in all its essential details resembles very closely a larger calorimeter which was developed in this Laboratory in connection with work on the surface energy of solid sodium chloride.<sup>1</sup>

For a complete description of the construction and manipulation of this type of calorimeter, the reader is referred to these two papers. The following brief description may, however, be given here. The calorimeter, which is cylindrical in shape and closed at both ends, is placed with its axis horizontal and is able to revolve on an axle at each end. A separate vessel inside the calorimeter contains the solute, this vessel being surrounded by the solvent. On rotation, the solute and solvent mix. The adiabatic method of calorimetry is used. The calorimeter is enclosed in a copper jacket and the whole submerged in a bath of water (about 14 liters). By means of a radiation thermel placed in the air space between the calorimeter and the copper jacket, the temperature of the bath of water is kept always at the same temperature as the calorimeter. The actual temperature of the calorimeter is then determined by means of a platinum resistance thermometer placed in the bath of water.

<sup>1</sup> (a) Lipsett, Johnson and Maass, *THIS JOURNAL*, **49**, 925 (1927); (b) Lipsett, Johnson and Maass, *ibid.*, **49**, 1940 (1927).

**Description of Calorimeter.**—The body of the calorimeter (A, Fig. 1) was made from a platinum crucible which was spun into the required shape. The lid of the crucible was flattened to form the removable end of the calorimeter. This body was cylindrical in shape, 2.2 cm. long and 2.5 cm. in diameter. It was flanged at one end, B. The end, C, which was removable, consisted of a flat disk of platinum carrying an axle in the center. This disk was fastened to the flange, B (which was first coated with a thin film of vaseline), by means of 15 small steel screws (Waltham "Plate Screws" No. 131, size 18). The glass axles on which the calorimeter was supported were 1 mm. in diameter. A piece of brass, D, was cemented to one axle and into this could be screwed a long steel axle, by means of which the calorimeter was rotated.

The solute was placed in a small platinum box, E, which was also cylindrical in shape, 1.7 cm. long and 1.5 cm. in diameter, having a capacity of 2.7 cc. This box was made to slip into the calorimeter, where it was held in position by thin platinum supports projecting from the sides and bottom of the box. The bottom support, F, was forked and fitted over a small platinum projection, G, in the body of the calorimeter. In the top of the box was an opening  $6 \times 9$  mm. The opening was flanged and on the flange the lid of the box rested. The lid was a small piece of platinum  $12 \times 9 \times 1.3$  mm., ground plane on one side, weighing 4 g. When the flange of the box was moistened with glycoline and the lid placed on, the solute inside the box was protected from any possible action of solvent vapor. The solvent was introduced into the calorimeter through the opening, H, which was closed by a tapering platinum plug.

On rotation of the calorimeter, the lid of the inner box fell off and solution of the solute took place.

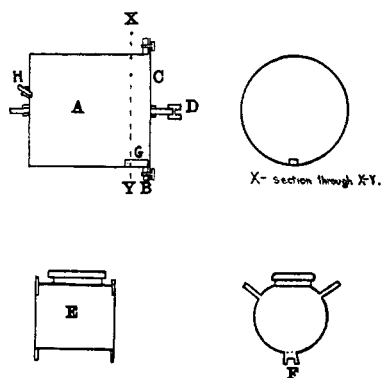


Fig. 1.

TABLE I  
THE HEAT CAPACITY OF THE CALORIMETER AT 25°

Material	Quantity	Spec. heat, cal.	Heat capacity, cal.
Platinum	32.56 g.	0.0314 <sup>a</sup>	1.0224
Glass <sup>b</sup>	0.014 g.	.18	0.0025
Steel screws	.429 g.	.107	.0459
Air inside calorimeter	4.5 cc.	....	.0010
Air in gap <sup>c</sup>	16 cc.	....	.0040
Glycoline, vaseline	0.014 g.	.45	.0061
Gold <sup>d</sup>	.245 g.	.0316	.0077
Total heat capacity			1.090

<sup>a</sup> White, *Phys. Rev.*, **12**, 436 (1918); Gaede, *Physik. Z.*, **4**, 105 (1902); Schlett, *Ann. phys.*, [4] **26**, 201 (1908). This value may be high, as Schlett has shown that hammering decreases the specific heat of platinum.

<sup>b</sup> Half the weight of the glass axles is taken.

<sup>c</sup> The volume considered is that portion estimated to be effective in heating the calorimeter.

<sup>d</sup> Used as solder.

The calorimeter was enclosed in a copper jacket in exactly the same manner as the previously used calorimeter<sup>1</sup> except that the air gap in the present case was only 6 mm. in width. The inside of the copper jacket was gold plated to reduce radiation of heat. The radiation thermel was similar to the one used previously.<sup>2</sup>

The accessory apparatus, namely, outer bath, resistance thermometer, bridge, galvanometer, etc., was the same as had been used before.

**Heat Capacity of the Calorimeter.**—The heat capacity of the calorimeter was calculated as shown in Table I.

### Experimental Part

The large surface of the calorimeter compared to its heat capacity offered opportunity for large errors if the adiabatic control was not accurately maintained. It was found that when the environment was kept 1° hotter than the calorimeter, the temperature of the latter rose at the rate of 0.04° per minute when the calorimeter contained 4 cc. of water. Except for one minute, however, when the solute and solvent were first mixed, the temperature difference between the calorimeter and surrounding jacket was usually so small that, except during this minute, errors due to loss or gain of heat from the environment were negligible. During the greater part of an experiment this temperature difference was less than 0.0002°.

During the solution of the solute, the calorimeter was rotated for ten minutes at the rate of 10 r.p.m. It was found that the heat generated by friction during rotation was sufficient to cause a rise in temperature of the calorimeter and contents (which had a total heat capacity of approximately 5 cal.) of about 0.00015° per minute.

The calorimeter was tested by making several determinations of the heat of solution of sodium chloride at 25°, obtaining in each case a 9.114% solution. For this purpose approximately 0.4 g. of salt was used and dissolved in 4 cc. of water. The change in temperature which was measured was approximately 1°.

TABLE II  
HEAT OF SOLUTION OF SODIUM CHLORIDE AT 25°

Expt.	Heat of solution, cal. per mole (9.114% soln.)	Deviation from mean, %
1	790.1	0.06
2	788.4	.15
3	788.1	.19
4	791.6	.25
5	787.8	.23
6	791.7	.26
	Mean	789.6

<sup>2</sup> It was erroneously stated (ref. 1 a, p. 929) that the thermel was made from wires 0.02 mm. in diameter, rolled flat till about 0.8 mm. wide and 0.03 mm. thick. The original diameter should have read 0.02 cm. instead of 0.02 mm.

The results appear in Table II. The corrections used in making the calculations have been described in the previous papers.

It will be seen that the maximum deviation from the mean value is 0.26%.

The heat of solution of sodium chloride under the same conditions, as determined with the former calorimeter,<sup>1b</sup> was 787.5 cal. per mole. The difference between this and the above results may easily be accounted for by the uncertainty in the values used for the specific heats of the sterling silver and the platinum from which the calorimeters were constructed.

The results obtained show that a fair degree of accuracy may be attained with a calorimeter of this type while requiring the use of only small quantities of material.

Grateful acknowledgment is made to the National Research Council of Canada for a grant to aid in this research and also for a Studentship held by one of us, during the tenure of which the work was carried out.

### Summary

A small calorimeter is described with which heats of solution may be determined using 4 cc. of solvent and corresponding amounts of solute. The heat capacity of the calorimeter is approximately 1 cal.

Several determinations of the heat of solution of sodium chloride at the same concentration gave results which never differed from a mean value by more than 0.26%.

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[CONTRIBUTION FROM THE PHYSICAL LABORATORY OF BRYN MAWR COLLEGE AND THE CHEMICAL LABORATORY OF THE U. G. I. CONTRACTING COMPANY]

## THE NEAR INFRA-RED ABSORPTION BANDS OF SOME HYDROCARBONS

BY JAMES BARNES AND W. H. FULWEILER

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This report, which is a continuation of earlier papers,<sup>1</sup> is on the measurements of the wave lengths of the near infra-red absorption bands of liquid pentane, decane and tetradecane. It also contains some observations on the structure of the 8744 Å. band of benzene and the 8767 Å. band of toluene.

The apparatus used, namely, source of continuous radiation, cells, gratings and densitometer, as well as the methods of photography and of measurement of wave lengths, were the same as those described in the papers referred to above. In addition, a Hilger prism spectrometer of

<sup>1</sup> Barnes and Fulweiler, THIS JOURNAL, 49, 2034 (1927); *J. Opt. Soc. Am.*, 15, 331 (1927).