water which was irreversible in the calorimetric process; *i.e.*, evolved water condensed as liquid in the capsule during cooling and did not recombine with alumina. For these reasons the data of Table III may be uncertain by as much as a few per cent. They are adequate, however, for ordinary heat-balance calculations.

Heat-content values read from smooth curves at 25°-intervals and the corresponding graphically computed entropy increments are given in Table IV.

TABLE IV

MOLAL HEAT CONTENTS AND ENTROPIES ABOVE 298 16°K.

	$Al_2O_3 \cdot 3H_2O$		$Al_2O_3 \cdot H_2O$	
	$H_T - H_{298.16}$, cal.	$S_T - S_{298.16}$, E. U.	$H_T - H_{298.16}$, cal.	$S_T - S_{298.16}$, E. U.
325	1180	3.79	770	2.47
350	2390	7.37	1515	4.68
375	3680	10. 3	2295	6.83
400	5010	14. 6	3115	8.95
425	6390	17.41	3970	11.02
450			4860	13.05
475			5810	15.11
500			6850	17.24

Summary

The heat capacities of $Al_2O_3 \cdot 3H_2O$ and $Al_2O_3 \cdot H_2O$ were measured in the temperature range 52 to 298°K.

The following molal entropies at 298.16°K. were computed: $Al_2O_3 \cdot 3H_2O$, 33.51 ± 0.1; and $Al_2O_3 \cdot H_2O$, 23.15 ± 0.1 E.U.

High-temperature heat contentsa bove 298.16°K. were measured for the two hydrates. These data have been summarized by a table of heat contents and entropies above 298.16°K. at 25° intervals.

BERKELEY, CALIF. RECEIVED JUNE 12, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY]

A New Type of Precision Capillarimeter

BY JOSEPH J. JASPER AND KERMIT D. HERRINGTON

During the investigation of the molar surface energies and the related properties of a series of addition compounds in this Laboratory, it became evident that truly comparable values could be obtained only from high precision surface tension measurements of pure compounds. To obtain data restricted to these requirements plans were made to prepare the compounds in a high vacuum system and to subsequently transfer them to a capillarimeter sealed into the line. The capillarimeter was then to be sealed off from the line and the surface tension measurements carried out under orthobaric conditions. In this way the effects due to moisture and other impurities are eliminated.

This method, however, is by its nature restricted to relatively small quantities of liquids. The primary problem, therefore, was to design and construct a capillarimeter embodying all known features which contribute to the precision of the measurements, and which required a small volume of liquid.

Although the capillary rise method is generally recognized as the ultimate standard for the determination of surface tension, high precision is obtained only by conforming rigorously to certain structural and dimensional specifications in designing the capillarimeter. These specifications arise from the necessity of eliminating, or reducing to negligible proportions, uncertainties introduced by (a) the mathematical theory in the treatment of curved liquid surfaces, and (b) the difficulties attending the measurement of radii of curvature. The uncertainties, however, are reflected in the capillary constant, *rh*, and equations for its calculation have been derived by Rayleigh,[1] Verschaffelt,[2] and other earlier workers, giving approximations within the range of their applicability.

Results from the exact experiments of Richards and Carver[3] show that the major error in the capillary constant can be reduced to a minimum if (a) the radius of the capillary is constant and of such value that the curvature of the liquid meniscus approaches closely that of a hemisphere for liquids which wet the tube, and (b) if the reference surface varies but slightly from that of a geometric plane. It is evident, therefore, that the structural and dimensional specifications of a precision capillarimeter are largely determined by these fundamental requisites.

A capillarimeter, conforming to the precision and volume requirements outlined above, was designed by one of us. It was later constructed and tested with compounds of known purity and surface tensions under orthobaric conditions. In the design additional features were added which eliminate, or minimize, several possible sources of error. Since the experimental details of the capillary rise method have been worked out by Richards and his co-workers,[3,4,5] and by Harkins and Brown,[6] it seemed expedient to follow their

---

[1] Lord Rayleigh, *Proc. Roy. Soc.* (London), **A92**, 184 (1915).

[2] J. E. Verschaffelt, *Proc. Koninkl. Akad. Wetenschappen Amsterdam.*, **21**, 357, 836 (1919).

[3] T. W. Richards and E. K. Carver, THIS JOURNAL, **43**, 827 (1921).

[4] T. W. Richards and J. W. Shipley, *ibid.*, **36**, 1828 (1914).

[5] T. W. Richards and L. B. Coombs, *ibid.*, **37**, 1656 (1915).

[6] W. D. Harkins and F. E. Brown, *ibid.*, **41**, 499 (1919).

procedures as closely as possible and to compare the results with the best accepted orthobaric values in the literature. The purpose of this paper, therefore, is to describe the capillarimeter and to present the results of the measurements carried out over an appreciable temperature range.

The Capillarimeter

Since one of the chief requisites of a capillarimeter is a capillary tube of small but constant bore, considerable time and effort were devoted to its selection. Equal care was taken in selecting the larger tubing from which the liquid reservoir was constructed since it is imperative that the inner and outer walls be cylindrical and parallel. The procedure employed in the preliminary treatment of the capillary, and the determination of the radius and constancy of bore, was similar to that of Harkins and Brown.[6]

The diagram of the instrument is shown in Fig. 1. The essential features consist of a horizontal arm a, which carries the liquid receiver c, the capillary chamber d, and the capillary tube f. The instrument is connected to the vacuum system through tube b while tube a is either sealed closed or provided with a break tip. In operation the liquid is transferred from the vacuum system to c by immersing the latter in a freezing-bath. The capillarimeter is removed by sealing off arm b, and the liquid is transferred to d by tipping the instrument. The capillary tube extends into housing g to prevent the liquid from flowing into it from above. The diameter of the capillary chamber d is 50 mm., and this provides a reference surface much greater than the minimum required to produce a flat surface, according to Richards and Carver.[3] The reëntrant bottom e of the capillary chamber offers two advantages. First, the quantity of liquid needed to produce the flat reference surface is small when compared with the usual quantities required, 10 ml. being sufficient. Second, the additional surface area provides better contact with the liquid medium of the bath and, therefore, hastens thermal equilibrium. Furthermore, the axis of the capillary f coincides with that of chamber d, thus making it possible to measure the capillary rise without revolving the cathetometer telescope. Since no portion of the capillary tube is horizontal, the vertical motion of the liquid within the capillary tube is unrestricted. The housing g, into which the capillary tube extends, can be opened readily for direct cleaning of the capillary if the need arises. Tests for possible distortion were made through both walls of the capillary chamber above the reëntrant surface by focussing the cathetometer telescope on a scale and viewing it along the diameter of the tube.

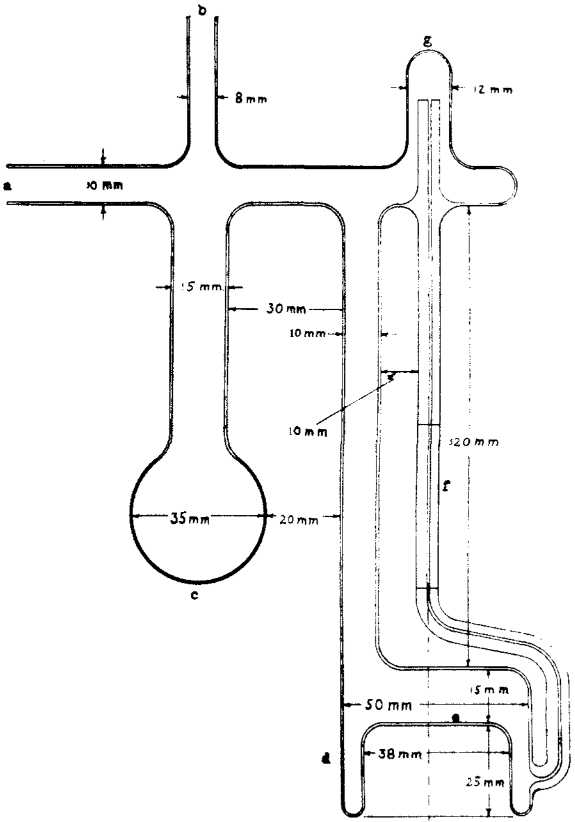

Fig. 1.—Capillarimeter.

To test the capillarimeter the surface tension measurements of several carefully purified liquids were made at 20, 40 and 60°. The results are compared with values found in the "International Critical Tables" and are shown in Table I.

TABLE I

SURFACE TENSION–TEMPERATURE DATA FOR VARIOUS LIQUID COMPOUNDS

Compound	t, °C.	Surface tension J. and H.	 I. C. T.
Benzene	20	28.92	28.93[a]
	40	26.27	
	60	23.62	
Toluene	20	28.51	28.50
	40	26.22	26.20
	60	23.88	23.80
p-Xylene	20	28.36	28.37
	40	26.20	
	60	24.04	24.20

[a] T. W. Richards and E. K. Carver (ref. 5).

Summary

1. A brief review of the fundamental errors inherent in the capillary rise method was given, together with the necessary measures to be taken in eliminating or minimizing them.

2. A capillarimeter was described which conformed to the structural and dimensional specifications of a precision instrument, offering the advantage of small volume requirement and convenience of manipulation. Additional features were added which serve to reduce other possible errors. A diagram of the instrument was presented.

3. To test the capillarimeter, liquids of known

purity and surface tension were measured over a temperature range and the results compared with those given in the "International Critical Tables." A table is given in which the results for the temperatures 20, 40 and 60° are tabulated.

DETROIT, MICH. RECEIVED MAY 11, 1946

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, AND FROM THE RICHARDSON MEMORIAL LABORATORY, THE TULANE UNIVERSITY OF LOUISIANA]

Ozonolysis of Pyridine Homologs, a Method of Structural Elucidation[1]

BY WILLIAM SHIVE,[2] EDWARD G. BALLWEBER[3] AND W. WILBUR ACKERMANN[2]

Utilization of ozonolysis in the degradation of certain derivatives of pyridine[4,5] and quinoline[6] has indicated that this reaction may be generally useful in the proof of structure of bases of these types. In the present work, a study of the ozonolysis products of pyridine, 2-, 3- and 4-picoline, 2,6-lutidine, 2,4,6-collidine, and 2-*s*-butyl-4,5-dimethylpyridine was made in order to determine the value of ozonolysis in structural elucidation of pyridine homologs.

Experimental

Source of Pyridine Homologs.—Commercial grades of anhydrous pyridine and 2-picoline obtained from Pittsburgh Coke and Chemical Co. were purified by redistillation through a six-foot Stedman-packed column. 3-Picoline, Eastman Kodak Co. "practical" grade, 90–95% purity, was purified by the method of Lidstone.[7] 4-Picoline and 2,6-lutidine, Eastman Kodak Co. "Eastman" grade, were also purified by the same process. 2,4,6-Collidine, Eastman Kodak Co. "Eastman" grade, was redistilled. A sample of 2-*s*-butyl-4,5-dimethylpyridine which was isolated from petroleum[5] was kindly supplied by Dr. H. L. Lochte and Dr. W. W. Crouch.

Ozonization.—The ozone used in these experiments was generated by passing dry oxygen through a silent electric discharge in a set of six Berthollet tubes connected in series by mercury-filled joints. Unless otherwise indicated, all solutions were ozonized for ten hours by passing, at a rate of 2 liters per hour, a stream of ozonized oxygen containing 5% ozone through a solution of 5 g. of the anhydrous pyridine homolog in 30 cc. of dry solvent. Ozonides as such were not detected, and these solutions of ozonized pyridine homologs consisted of relatively complex mixtures from which derivatives were isolated or in which materials were identified by specific tests. The tendency of unreacted pyridine homologs to destroy some of the more reactive compounds made the isolation of derivatives of these compounds difficult. The following experimental work is arranged according to the products of ozonolysis in order to interrelate these products and the structures of the pyridine homologs.

Formic and Acetic Acid.—An ozonized solution of each pyridine homolog was extracted with 15 cc. of water, and the aqueous layer was acidified with dilute sulfuric acid and mildly heated with 1 g. of 2,4-dinitrophenylhydrazine to convert pyruvic acid to the phenylhydrazone; otherwise, the pyruvic acid interfered with the acetate test. The mixture was cooled, filtered and distilled until 8 cc. of distillate was collected. One 3-cc. portion of the distillate was treated with magnesium, sulfuric acid and chromotropic acid as described by Eegriwe.[8] The appearance of a violet coloration indicates the presence of formic acid.

Another 3-cc. portion was treated with 2% iodine, 5% lanthanum nitrate, and ammonium hydroxide as described by Kruger and Tschirch.[9] A blue precipitate is obtained with acetic acid but not with formic acid. Other aliphatic acids also give this test.

Application of these testing procedures to ozonized solutions of pyridine, 2-, 3- and 4-picoline, and 2,6-lutidine in cyclohexane[10] and to 2,4,6-collidine in chloroform gave the results listed in Table I for formic and acetic acid.

The insoluble layer and the cyclohexane layer of an ozonized cyclohexane solution of 3-picoline were separated and tested for formic and acetic acid. A deep violet coloration was obtained only with the insoluble layer in testing for formic acid whereas neither layer gave the characteristic blue coloration in the acetate test.

Pyruvic Acid: Isolation of Derivatives.—An ozonized solution of 2,4,6-collidine in chloroform was treated with 20 cc. of 50% acetic acid containing 4 g. of phenylhydrazine. After standing for several minutes, the mixture was diluted with water and heated to remove the chloroform. The viscous, orange liquid which separated was extracted with ether, and the portion insoluble in ether or dilute acetic acid was removed by filtration. The ether solution was evaporated to dryness, and the residue was recrystallized from benzene to obtain 0.52 g. of yellow-brown, needle crystals, m. p. 171–172° with gas evolution. This product is evidently identical with the pyruvic acid phenylhydrazone obtained by Fischer and Jourdan,[11] but not with the isomeric form, m. p. 192°, which is usually obtained.

Anal. Calcd. for $C_9H_{10}O_2N_2$: C, 60.66; H, 5.66; N, 15.72. Found: C, 60.91; H, 5.93; N, 15.74.

With this indication of the presence of pyruvic acid in the ozonolysis products of methyl substituted pyridine homologs, the following procedure was used for the isolation of the 2,4-dinitrophenylhydrazone For example, an ozonized solution of 2,4,6-collidine in chloroform was extracted with 15 cc. of water, and the aqueous layer was treated with 1 g. of 2,4-dinitrophenylhydrazine, 10 cc. of ethanol and 10 cc. of dilute hydrochloric acid. The mixture was heated, cooled and filtered. The insoluble material was washed with hot dilute hydrochloric acid and digested with 5% sodium bicarbonate. The filtrate from the digestion was cooled and acidified with hydrochloric acid to obtain a

---

[1] From theses submitted by Edward G. Ballweber to the University of Illinois in partial fulfillment of the requirements for the degree of Bachelor of Science and by W. Wilbur Ackermann to The Tulane University of Louisiana for the degree of Bachelor of Science and Master of Science.

[2] Present address: Department of Chemistry, University of Texas, Austin, Texas.

[3] Present address: Department of Chemistry, University of Chicago, Chicago, Illinois.

[4] Shive, Roberts, Mahan and Bailey, THIS JOURNAL, **64**, 909 (1942).

[5] Lochte, Crouch and Thomas, *ibid.*, **64**, 2753 (1942).

[6] Schenck and Bailey, *ibid.*, **62**, 1967 (1940).

[7] Lidstone, *J. Chem. Soc.*, 241 (1940).

[8] Eegriwe, *Z. anal. Chem.*, **110**, 22 (1937).

[9] Kruger and Tschirch, *Ber.*, **63**, 826 (1930).

[10] Durland and Adkins, THIS JOURNAL, **61**, 429 (1939), reported the formation of cyclohexanone, formic acid and adipic acid on ozonization of cyclohexane. We have been unable to identify formic acid among the ozonolysis products of cyclohexane, and the other two products did not seriously interfere with our experiments.

[11] Fischer and Jourdan, *Ber.*, **16**, 2241 (1883).