Structure I appears unlikely because of adjacent positive charges, which cause it to violate the principle of minimum kernel repulsion[8] or the adjacent charge rule.[9] Structures II, III, IV and V do not violate this adjacent charge rule; however, in II, III, and V the sulfur atom has more than an octet, *i. e.*, $3d^2$, $3d^4$ and $3d^2$ electrons, respectively, are assumed. The use of *d*-orbitals makes structures II, III, and V neither more nor less probable. However, the introduction of one double bond increases the calculated value of the parachor from 396.8 to 420.2, which is substantially greater than the observed value. Therefore, structure IV appears most probable.

Summary

The effect of temperature on the molecular surface energy of the readily dissociated addition compound of sulfur dioxide with dimethylaniline, $C_6H_5(CH_3)_2N{\cdot}SO_2$, has been determined. Equations are presented for density and surface tension over the temperature range 0 to 30°.

Values for the parachor seem to indicate a nitrogen to oxygen (N–O) linkage in this compound.

Detroit, Michigan Received October 15, 1941

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[8] Lucas, "Organic Chemistry," American Book Company, New York, N. Y., 1935, p. 19.

[9] Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 184.

[Contribution from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, No. 829]

A Low Temperature Adiabatic Calorimeter. The Calibration of the Platinum Resistance Thermometers

By Don M. Yost, Clifford S. Garner, Darrell W. Osborne, Thor R. Rubin and Horace Russell, Jr.

During the last five years there has been constructed in this Laboratory the calorimetric apparatus necessary for the measurement of heat capacities and heat contents of substances in the temperature range 12 to 300°K. It is the purpose of the present paper to describe briefly the construction and operation of the calorimeters developed, as well as to discuss the calibration of the set of five platinum resistance thermometers that serve for the accurate measurement of the temperatures in the range of interest.

Construction of the Calorimeters.—The advantages in accuracy and convenience of the adiabatic calorimeter as described by Southard and Brickwedde[1] make it undoubtedly most suitable for measurements of heat capacities and heats of transition and fusion in the range 12–300°K. However, for measurements of heats of vaporization and vapor pressures, the constant temperature environment provided by the massive shield of a non-adiabatic Nernst–Giauque[2] type calorimeter is very convenient. Accordingly a calorimeter of each type has been built.

The adiabatic calorimeter is shown to scale in Fig. 1. Details of construction of this type of apparatus have been given by several authors[3] or are indicated in the legend of Fig. 1. The whole assembly is supported in a Pyrex-glass dewar flask 11 cm. i. d. × 85 cm. depth which serves as a liquid air container. The dewar was mounted in a kapok insulated wooden box. Vacuum and filling tubes were constructed of monel metal tubing, this alloy being superior to german silver for the purpose. The platinum-cased thermometer-heater is held in the re-entrant tube with heavy stopcock grease. It was found helpful, but not essential, to provide the 1-mm. filling tube to the calorimeter with a heater of a single layer of no. 30 constantan wire.

The Nernst–Giauque calorimeter, used exclusively for the determination of vapor pressures and heats of vaporization, differs but little from those described by other investigators, and the scale drawing shown in Fig. 2 will suffice for its description. The calorimeter is of gold-plated copper and is provided with three separate heaters: one is contained inside the resistance thermometer, the second of no. 30 manganin is wound on the lower half of the calorimeter, and the third fills about three-fourths of the space above the second heater. A layer of no. 26 bare copper wire is wound over these outer heaters; the junctions of two copper–constantan difference thermocouples are soldered to it at two points, and the other junctions are thermally anchored to the heavy (2 kg.), silver-plated, copper radiation shield. An absolute thermocouple is soldered to the 1-mm. i. d. monel filling tube at the point where it leaves the calorimeter. With this arrangement

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[1] Southard and Brickwedde, This Journal, **55**, 4378 (1933).

[2] Giauque and Egan, *J. Chem. Phys.*, **5**, 45 (1937).

[3] Blue and Hicks, This Journal, **59**, 1962 (1937). References (1) and (2). Since this apparatus was built, an article by Aston and Eidinoff, *ibid.*, **61**, 1533 (1939), has appeared describing a low temperature, adiabatic calorimeter.

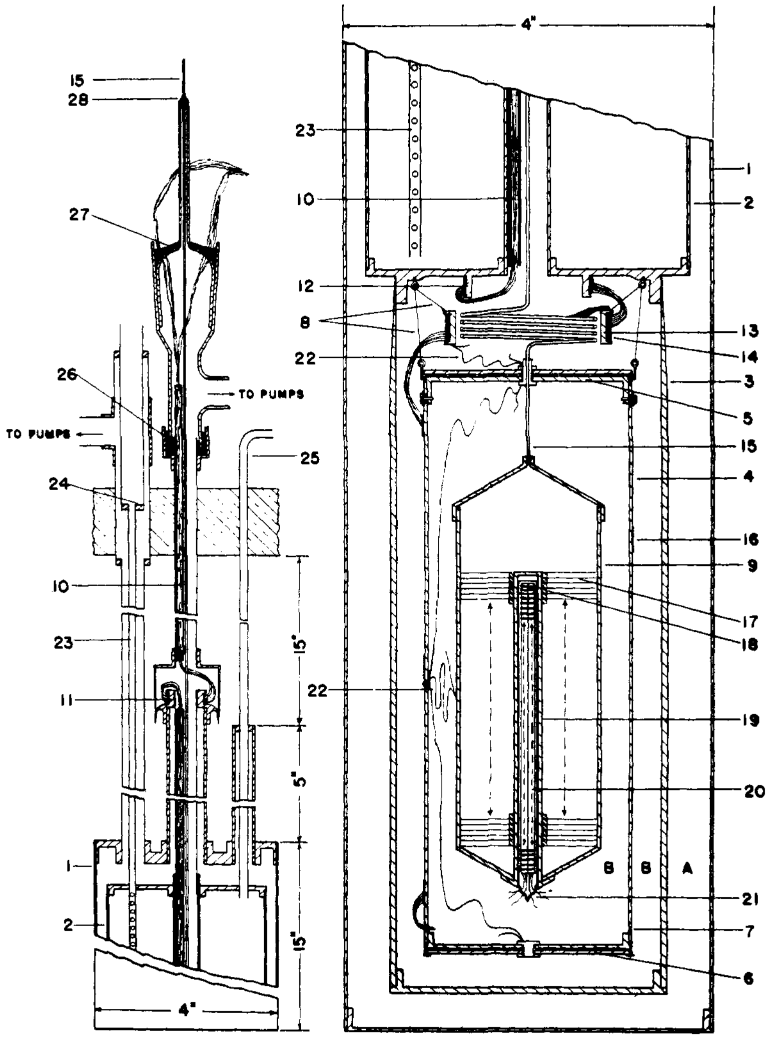

Fig. 1.—Adiabatic calorimeter assembly: 1, outer brass can; 2, 600-cc. brass liquid hydrogen container; 3, outer chromium-plated copper shield, bismuth-soldered (40 Bi, 40 Pb, 20 Sn, m. p. 111°) to hydrogen container; 4, electrically-controlled, chromium-plated, copper inner radiation shield; 5 and 6, top and bottom of inner radiation shield, both individually electrically controlled; 7, vent holes for admission of helium gas and for evacuation; 8, silk fish line supports; 9, gold-plated copper calorimeter I, vol. 126 cc., wall thickness 0.5 mm.; 10, twenty-eight no. 36, double silk covered, copper lead wires; 11, "anchoring" junction maintained at temperature of contents of dewar flask; 12, "anchoring" junction maintained at temperature of contents of hydrogen container; 13, copper "floating" ring; 14, heating coil of no. 30 constantan for regulating temperature of "floating" ring; 15, 1-mm. i. d., 0.1-mm. wall monel metal filling tube; 16, heating coils of no. 30 constantan or manganin for regulating temperature of inner radiation shield (sides, top and bottom); 17, thin, perforated, gold-plated, copper disks for thermal equilibrium; 18, gold-plated copper disk separators; 19, reentrant tube which holds resistance thermometer-heater; 20, thermometer-heater, in platinum case; 21, thermometer and heater leads passing through glass seal; 22, copper–constantan difference thermocouples from calorimeter to side of inner radiation shield, from side to top and bottom of shield, and from top of shield to "floating" ring, all electrically-insulated from each other; 23, 3 mm. o. d. 0.1-mm. wall monel metal filling tube for hydrogen container; 24, shoulder against which rests the end of the dewar filling tube from liquid hydrogen supply flask; 25, 5-mm. o. d. 0.1-mm. wall monel metal exit and evacuation tube for hydrogen container; 26, de Khotinsky or picein joint; 27, perforated glass stopper, sealed with picein cement, through which leads pass; 28, sealing wax joint.

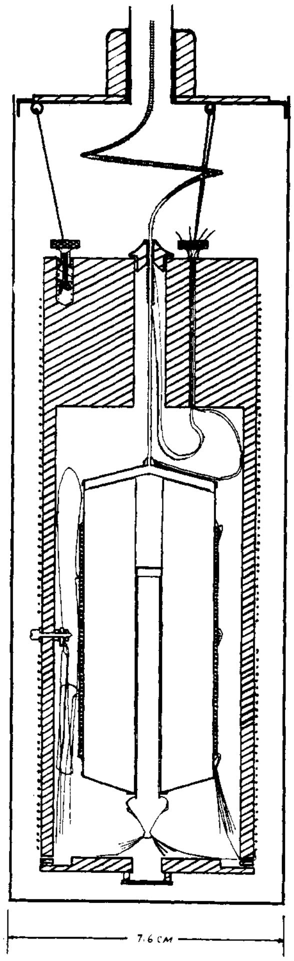

Fig. 2.—Non-adiabatic calorimeter for measuring heats of vaporization and vapor pressures.

of heaters and thermocouples, it is possible to vaporize the liquid in the calorimeter by means of internal or external heating, and at the same time make observations on the temperature gradient along the calorimeter. The absolute thermocouple on the filling tube serves to measure the temperature of the vapor leaving the calorimeter. The free volume of the calorimeter is 80 cc. It is provided with sixteen vertical, gold-plated copper vanes soldered to the re-entrant tube holding the resistance thermometer; the upper ends of the vanes are provided with a conical deflecting cover. The monel filling tube is covered by a layer of no. 30 constantan wire to which are soldered at 25-cm. intervals no. 36 copper wires to serve as heater and thermocouple leads.

Auxiliary Apparatus and Operation.—Energy and temperature measurements are made in all cases with an auto-calibrated White double potentiometer. The standard cell is frequently compared with cells certified by the National Bureau of Standards. The important resistors in the energy circuit are calibrated in place against Leeds and Northrup or Bureau of Standards certified resistors.

Lead storage cells are used as a source of current. Heating periods are usually ten minutes or longer, although the first few at hydrogen temperatures may be as short as five minutes. A correction is made for the heat generated in the two 6-cm., no. 36 copper current leads from the radiation shield to the thermometer-heater, it amounts at most to 0.07%. Both an electric clock and calibrated stop watch are used for time measurements; the over-all accuracy in energy measurements is 0.03–0.05%.

The operation of the adiabatic calorimeter is described by Southard and Brickwedde.[1] The substance to be studied is condensed into the calorimeter, and any residual vapor in the warmer filling tube is swept into the calorimeter with helium. The calorimeter is cooled from liquid air to hydrogen temperatures by first breaking the vacuum in compartment B with 1–2 cm. pressure of helium while maintaining a high vacuum in A and then filling the hydrogen container (2) slowly with liquid hydrogen. About two liters are required to cool the inner compartment and fill the 600-cc. container. The filling tube is then closed, and a high capacity vacuum pump to the hydrogen container is started and allowed to run until all measurements are completed. The temperature of the hydrogen drops in a few minutes to the triple point, and remains constant there for fifteen to thirty minutes until all the hydrogen is frozen. After the calorimeter has cooled to 12°K., compartment B is evacuated. About two and one-half hours are required for these operations. The frozen hydrogen is not completely evaporated until some fifteen to twenty hours later; thus in the temperature range 12 to 90°K., two complete series of heat capacity measurements can be made with a single, two liter filling of liquid hydrogen. Since the temperature of the radiation shield is maintained within ±0.01 to ±0.02° of the calorimeter, no heat interchange corrections are necessary. It is found, experimentally, that the calorimeter can be maintained indefinitely at a given temperature to ±0.001°. The resistance of the thermometer is ordinarily determined at five-minute intervals after energy input until the temperature is constant to 0.001°; about ten minutes are required for the attainment of equilibrium except in regions of thermal transition. The final temperature of one run is usually the initial temperature of the next. The current of about 1 ma. through the platinum resistance thermometer is measured across a 100-ohm standard resistor whose constancy is periodically checked. Temperature intervals are measured to 0.002° except at the lowest temperatures.

Calibration of the Resistance Thermometers.—The five platinum resistance thermometers, H-22, CT-26, CT-2, CT-4, and CT-7, that form an important part of the calorimetric apparatus were constructed according to the designs of Meyers[4] and the specifications of the National Bureau of Standards. The platinum cases are 0.762 cm. in diameter and five to eight centimeters in length. Four of the thermometers, CT-26, CT-2, CT-4 and CT-7, contain two separate coils each, one of C. P. annealed platinum wire (0.0036 inch diameter) and the other of no. 40 bare constantan wire. Two platinum leads are gold soldered to the constantan coil, and where they emerge through the glass head of the thermometer case, each is soft soldered to two copper wires which serve as current and potential leads to the heater. Each end of the platinum thermometer coil is welded to two platinum lead wires, the branch points in this case being inside the thermometer case. The fifth thermometer, H-22, contains a coil of platinum only, and was calibrated later over the range 14°K. to 444.60°C. by the National Bureau of Standards.

Thermometer CT-26 was constructed and calibrated some time before the others. Its resistance was determined at the ice point, the mercury freezing point and the normal oxygen boiling point. At the steam point it was compared with a Leeds and Northrup resistance thermometer certified by the National Bureau of Standards. From these points the constants R_0, α, δ and β in the Callendar–Van Dusen equation

$$= \frac{R - R_0}{\alpha R_0} + \delta\left(\frac{t}{100} - 1\right)\frac{t}{100} + \beta\left(\frac{t}{100 - 1}\right)\left(\frac{t}{100}\right)^3$$

(for $t > 0$°C. the β term is omitted)

were determined. For thermometers CT-2, CT-4 and CT-7, α and δ were obtained from the measured R_0 and by comparison with the certified Leeds and Northrup thermometer in baths of boiling water and boiling *o*-toluidine (200°C.). The β was fixed by comparison with CT-26 at the normal oxygen point. Further checks at the oxygen point were obtained by comparison at or near this temperature with the Leeds and Northrup thermometer. It may be remarked that thermometers of the type described here suffer somewhat when heated repeatedly and over long times at the temperature of boiling sulfur. Accordingly the determination of the Callendar equation constants at 200° and lower is to be recommended for the glass sealed platinum capsule-type thermometer

In order to test whether or not the thermometers would give correct temperatures on the international scale, their resistances at the freezing and melting point of mercury were determined. Thermometers CT-26, CT-2, CT-4 and CT-7, together with H-3, belonging to Professor Hugh M. Huffman of this Institute, were then placed to-

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(4) Meyers, *Bur. Standards J. Research*, **9**, 807 (1932).

TABLE I

RESULTS OF THE CALIBRATION AND COMPARISON OF THE RESISTANCE THERMOMETERS

Thermometer	CT-26	CT-2	CT-7	H-22[a]	CT-4
R_0 (Int. ohms)	26.2820	45.7726	45.1231	22.6393	46.0268
$\alpha \times 10^2$	0.39094	.391757	.391751	.391349	.390622
δ	1.509	1.499	1.494	1.5118	1.551
β	0.1264	.1221	.1233	.12143	.1336
F. p. Hg[b]	−38.87°	−38.871°	−38.872°		−38.888°

Values of $\epsilon_n = t_{\text{CT-26}} - t_{\text{CT-n}}$ in °C.

Temp. °C.	23.8	−117.9	−180.8
ϵ_2	0.002°	0.010	0.001
ϵ_7	.001°	.022	.001
ϵ_4	.000°	.062	.004

[a] The constants of this thermometer were determined by the National Bureau of Standards. [b] The f. p. of Hg is −38.864° on the international scale.[5]

gether in a copper block in the adiabatic calorimeter and compared with each other over the range 90–300°K. The above table presents the constants of the thermometers together with the comparisons for a few significant temperatures.

It is believed that our temperature scale as defined by CT-26, 2, 7 and H-22 does not differ from the international scale by more than 0.02° at the most unfavorable points. It is noteworthy that the value of δ for CT-4 is greater than the allowed maximum of 1.50 and this is reflected in the large deviation from the other thermometers at −117.9°, a point near which the deviations will approach a maximum. Because of this a smoothed table was constructed using the deviation plot resulting from the comparison measurements.

Below 90°K. thermometer CT-26 was calibrated by means of a helium gas thermometer, according to the procedure described by Hoge and Brickwedde.[6] The calorimeter in the adiabatic apparatus served as the gas thermometer bulb in these measurements, a calculation having shown that the error due to stretching of the copper walls (0.5 mm. thick) by varying gas pressures was entirely negligible. The obnoxious volume of the 1-mm. monel metal filling tube was 2.09 cc., and that in the manometer about 0.3 cc. The manometer, which was enclosed in a glass case, had an inside diameter of 18.65 mm., and the mercury levels were read with a Henson cathetometer whose scale had been calibrated against a glass decimeter from the National Bureau of Standards. The helium used was purified by passing it slowly through a carefully prepared charcoal trap cooled with liquid air. Two series of measurements were made over the range 14.5–90°K., and the results were used to construct a smoothed table of R/R_0 against T. The maximum deviation of the experimental values of T from the smoothed values was 0.02°, and the average deviation was less than 0.01°. Accordingly, in the range 14.5–90°K., thermometer CT-26 measures temperatures that probably do not differ by more than 0.02° from the thermodynamic scale.

The thermometers CT-2, CT-4, CT-7 and H-3 were later compared with CT-26 in the low temperature range. Recently Professor Huffman has compared H-3 with a thermometer, H-25,[7] certified by the National Bureau of Standards and has found one deviation to be 0.026° (at 50°K.), the remaining deviations being 0.01° or less, both above and below 50°K. We feel confident, therefore, that the temperature scales of this Laboratory are in satisfactory accord with those provisionally accepted by the Bureau of Standards.

It is evident from the above that our temperature scale consists of two parts, one being the thermodynamic scale (14.5–90°K.) and the other being the international scale (above 90°K.). It is known that the international scale may differ by as much as 0.05° from the thermodynamic scale at some temperatures,[8] but until a reliable method for making the corrections is discovered, all results from this Laboratory will be reported in terms of the international scale in the region above 90°K.

Acknowledgments.—We wish to state here our gratitude for the advice and many helpful sugges-

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(5) Heuse and Otto, *Ann. Physik*, [5] **9**, 486 (1931); Wilhelm, *Bull. Bur. Standards*, **13**, 655 (1918). A correction of −0.009° must be applied to the published result to include effect of the β term which was not originally used.

(6) H. Hoge and F. Brickwedde, *J. Research, Natl. Bur. Standards*, **22**, 351 (1939).

(7) We are indebted to Doctors Brickwedde and Hoge for the calibration of thermometers H-22 and H-25.

(8) Heuse and Otto, *Ann. Physik*, [5] **14**, 181 (1932); Keesom and Dammers, *Physica*, **2**, 1051, 1080 (1935).

tions given to us by Professor Hugh M. Huffman. We also wish to express our thanks to Mr. Meyer Test, an NYA assistant, and to Dr. Robert Ruehrwein for constructing the resistance thermometers. The liquid hydrogen necessary in the measurements was kindly furnished by Professor A. Goetz of the Cryogenic Laboratory at this Institute.

Summary

A precision adiabatic low temperature calorimeter is described which is comparatively simple to construct and operate, and which requires only two liters of liquid hydrogen for a complete series of heat capacity measurements in the range 14–90°K. A calorimeter for vapor pressure and heats of vaporization measurements is also described.

The calibration of a set of four platinum resistance thermometers over the range 14°K. to 200°C. is described.

PASADENA, CALIFORNIA RECEIVED JUNE 23, 1941

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 832]

The Heat Capacity, Entropy, and Heats of Transition, Fusion, and Vaporization of Dimethylacetylene. Free Rotation in the Dimethylacetylene Molecule

BY DON M. YOST, DARRELL W. OSBORNE, AND CLIFFORD S. GARNER[1]

Introduction

As a result of the work of Kemp and Pitzer,[2] the existence of a barrier restricting the rotation of the methyl groups in ethane and similar molecules is now generally accepted. In ethane the barrier amounts to about 3000 cal./mole. It was the purpose of the research described in this paper to determine the extent of any barrier restricting the rotation of the methyl groups in dimethylacetylene, $H_3C{-}C{\equiv}C{-}CH_3$. If the barrier in ethane is due to interactions of the methyl groups, one would expect that the increased separation of the methyl groups in dimethylacetylene would lead to a small barrier. On the other hand, if the barrier is due to double-bond character of the C–C bond, then one might expect to find a large restricting potential, because the C—C bond distance in dimethylacetylene,[3] as in methylacetylene,[3,4] is 0.07 Å. shorter than the normal value; such a shortening is usually interpreted as due to considerable double bond character. Comparison of the entropy from our thermal data extending to low temperatures, a preliminary value for which has already been published,[5] with that from molecular data indicates, as is shown below, that the methyl groups in dimethylacetylene are subject to little or no restriction in their rotation.

Dimethylacetylene is of further interest because of an anomaly in the heat capacity of the solid at about 154°K.

Experimental

Preparation of the Dimethylacetylene Sample.—Dimethylacetylene was prepared by Mr. Thurston Skei by slowly adding 2,3-dibromobutane to a solution of potassium hydroxide in diethylene glycol heated to 180°C. The crude product was passed through a cuprous chloride-50% ethanolamine solution to remove ethylacetylene, and after being dried over sodium it was twice fractionated in a three-foot column packed with glass helices by Mr. Russell Doescher. The middle fraction was distilled *in vacuo* through phosphorus pentoxide into the weighing bulb and then into the calorimeter.

Heat Capacity Measurements.—The heat capacity of dimethylacetylene was determined with the adiabatic calorimeter (Gold-plated Copper Calorimeter I, and strain-free platinum resistance thermometer CT-26) described elsewhere.[6]

The data of Heisig and Davis[7] on the density of the liquid and on the vapor pressures of the liquid and solid were used to correct for vaporization into the gas space, which was about 60 cc. or about half the volume of the calorimeter. The volume of the solid was estimated. The correction amounted to approximately 0.05% at 210°K. and 1.1% at 285°K.

A small pressure of helium was present in the calorimeter to improve thermal conductivity at low temperatures, and a somewhat higher pressure was used to prevent diffusion of dimethylacetylene to cold spots in the 1-mm. monel metal filling tube when the vapor pressure became appreciable.

The results of the heat capacity measurements are presented in Table I and in Fig. 1. They are

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[1] This work was performed while C. S. Garner and D. W. Osborne were A. A. Noyes Fellows in Chemistry.

[2] J. D. Kemp and K. S. Pitzer, THIS JOURNAL, **59**, 276 (1937).

[3] L. Pauling, H. D. Springall and K. J. Palmer, *ibid.*, **61**, 927 (1939).

[4] G. Herzberg, F. Patat and H. Verleger, *J. Phys. Chem.*, **41**, 123 (1937); R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 599 (1937).

[5] D. W. Osborne, C. S. Garner and Don M. Yost, *J. Chem. Phys.*, **8** 131 (1940).

[6] Yost, Garner, Osborne, Rubin and Russell, THIS JOURNAL, **63**, 3488 (1941).

[7] G. B. Heisig and H. M. Davis, *ibid.*, **57**, 339 (1935).