action under the same conditions and with iodide at concentrations used in obtaining the maximum induction factors. This would seem to exclude the possibility that trivalent vanadium is involved in the induced catalysis, and would do so if the trivalent vanadium initially formed in the pentavalent vanadium–iodide reaction were in the same state as that present in solutions of trivalent vanadium of equal acidity. It seems more probable that the trivalent vanadium initially formed is temporarily in a highly hydrolyzed state, since the pentavalent vanadium exists over a wide range of acid concentration principally as the vanadol ion, $V(OH)_4^+$.[2] It seems probable from our results that in this highly hydrolyzed state the trivalent vanadium may be very rapidly oxidized by oxygen, and could therefore be involved in the induced catalysis. This possibility may be formulated as follows

$$V(OH)_4^+ + I^- \longrightarrow V(OH)_3 + HIO \qquad (11)$$

followed either by

$$V(OH)_3 + O_2 \longrightarrow VO(OH)_2 + HO_2 \qquad (12a)$$

or by

$$V(OH)_3 + H_3O^+ + O_2 \longrightarrow V(OH)_4^+ + H_2O_2 \qquad (12b)$$

If an appreciable fraction of the trivalent vanadium is oxidized in either of these ways, the induced catalysis becomes a case of "true catalysis." The hydrogen peroxide formed in either case is very rapidly reduced by iodide, in the presence of pentavalent vanadium, and also by tetravalent vanadium (eq. 12a). A decision regarding the most probable mechanism of this induced catalysis cannot be made on the basis of the results available.

Summary and Conclusions

The rate laws of the trivalent vanadium–oxygen reaction have been established in absence of copper and when catalyzed by copper. Probable mechanisms have been proposed.

Variation in the "dust particle" content of the different stock solutions of trivalent vanadium is suggested as a possible reason for the different values of the rate constants obtained for the uncatalyzed reaction.

The critical increments have been determined and found to have the relative values expected for a catalyzed and an uncatalyzed reaction.

The rate of the uncatalyzed reaction is independent of the salt concentration, while that of the copper-catalyzed reaction has a positive salt effect over the range of ionic strength, 0.1 to 1.0. The latter has been interpreted in terms of the Brönsted theory.

On the basis of the results of this investigation a mechanism of the induced catalysis of the oxygen–iodide reaction has been suggested.

It is considered significant that the two "nonoxide" containing oxidants, oxygen and cupric copper, like iodine, react at a measurable rate solely with hydrolyzed trivalent vanadium, even though it constitutes but a very small fraction of the total trivalent vanadium present in the acid solutions used.

LOS ANGELES, CALIFORNIA

RECEIVED SEPTEMBER 26, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY]

Molecular Surface Energy of Sulfur Dioxide Addition Compounds. I[1]

BY J. RUSSELL BRIGHT AND JOSEPH J. JASPER

Gaseous sulfur dioxide dissolves in dimethylaniline to form a red-colored oily liquid.[2] A recent investigation[3] has shown the existence of a single 1:1 addition compound in the binary system sulfur dioxide–dimethylaniline. This compound melts at 12°,[3] but it is very easily supercooled.[2] The density and surface tension of pure dimethylaniline at 20°, for example, are 0.9562 g./ml. and 36.56 dynes/cm., respectively[4]; the Eötvös constant is 2.4.[4]

The purpose of the present investigation was to measure certain important physical constants of this sulfur dioxide molecular addition compound over the temperature range 0 to 30°.

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[1] Presented before the Division of Physical and Inorganic Chemistry at the Atlantic City meeting of the American Chemical Society, September, 1941.

[2] Hill and Fitzgerald, THIS JOURNAL, **57**, 250 (1935). These workers found no solid formation at temperatures as low as −10°.

[3] Unpublished results by Bright and Fernelius, presented before the Division of Physical and Inorganic Chemistry at the Detroit meeting of the American Chemical Society, September, 1940.

[4] "Int. Crit. Tables," Vol. IV, McGraw-Hill Book Co., Inc., New York, N. Y., 1929, p. 458.

Experimental

Preparation of the Liquid Molecular Addition Compound.—Two moles of Eastman Kodak Co. grade dimethylaniline, purified in the usual manner by distillation and drying over freshly cut sodium, was placed in a Florence flask. Two moles of gaseous sulfur dioxide, which was distilled from a small commercial tank and dried by passage through concentrated sulfuric acid and over phosphoric oxide, was added slowly at room temperature; melting point of product, 12°. It is interesting to note that addition of either too little or too much sulfur dioxide causes the product to have a melting point less than 12°. The compound is easily kept in a stoppered flask for an indefinite period.

Procedure.—Density measurements on the anhydrous material were made in a pycnometer of 20-ml. capacity, fitted with an expansion bulb and a ground glass stopper. Measurements above 30° were impossible, due to evident loss of sulfur dioxide. Water was used to calibrate the pycnometer.

Since the capillary height method lends itself most readily to experimental procedure, this method was adopted for the surface tension measurements. It was necessary to carefully protect the liquid from moisture during the measurements. The apparatus used, therefore, was a slight modification of that designed and described by Richards and Coombs.[5] The constancy of the capillary bore was determined with the aid of a measuring microscope and a filar micrometer. The variation in the length of a column of mercury about two centimeters long was observed as it was drawn through the capillary tube in successive steps.

The portion selected for the apparatus had a radius of 0.01807 cm. and showed but negligible variation in the length of the mercury column over a distance of about 18 cm. The measurements were taken at temperature intervals of 5° over a range of 0 to 30° with a precision of 0.02°. Each recorded measurement is the average of ten to fifteen readings. Between the separate readings the capillary was thoroughly wetted by drawing the liquid to the full length of the bore, and allowing it to recede spontaneously to its static equilibrium position. To ensure the system reaching thermal equilibrium with the water-bath, at least thirty minutes were allowed at the different temperature intervals. To equalize the pressure within the system and that of the prevailing atmosphere, the single stopcock with which the apparatus was equipped was opened for a few seconds from time to time.

Results

Experimental data are presented in Table I. It is evident that in the range 0 to 30° there is a straight line relation in each case. The equation of the best curve for the effect of temperature on density (d) is: $d = -0.001253t + 1.1746$; that for the effect on surface tension (γ) is: $\gamma = -0.1799t + 43.874$. Thus, both the density and surface tension of this compound are substantially greater than for dimethylaniline.

TABLE I

DENSITY AND SURFACE TENSION DATA FOR THE ADDITION COMPOUND OF SULFUR DIOXIDE WITH DIMETHYLANILINE

Temp., °C.	Density, g./ml.	Capillary rise, cm.	Surface tension, dynes/cm.	Eötvös constant
0	1.1764	4.216	43.87	..
1	1.1734	4.205	43.71	..
5	1.1681	4.150	42.97	4.32
10	1.1620	4.081	42.02	4.71
15	1.1558	4.030	41.26	3.61
20	1.1493	3.952	40.23	5.18
25	1.1424	3.890	39.37	4.15
30	1.1370	3.822	38.49	4.51

The presence of some sort of complicated molecules is shown by the high values of the Eötvös constant, which has an average value of 2.12 for non-polar liquids.

The data in Table II indicate a molecular volume of 11 or 12 units less than values obtained by adding the molecular volume of liquid sulfur dioxide and dimethylaniline. This decrease is due, perhaps, to the highly probable polar nature of the addition compound.

TABLE II

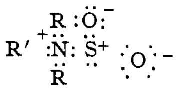
MOLECULAR VOLUME OF $C_6H_5(CH_3)_2N{\cdot}SO_2$

Temp., °C.	Mol. vol. liq. SO_2[a]	Mol. vol. C_6H_5-$(CH_3)_2N$[a]	Mol. vol. of addn. compd. Calcd.	Found
0	44.67	124.5	169.1	157.6
10	45.46	125.5	170.9	159.3
20	46.32	126.6	172.9	161.1
30	47.24	127.7	174.9	162.8

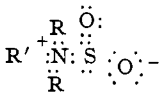
[a] Calculated from data in "Int. Crit. Tables."

The parachor of the addition compound is readily obtained from the data of Table I. This observed value of 405.4 is within about 2% of 396.8, the value obtained from the sum of the atomic and structural parachors[6] for structures I and IV. For a 1:1 addition compound, several electronic structures may be written.[7]

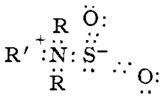
($R' = C_6H_5$, $R = CH_3$)



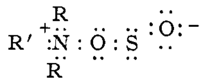
I



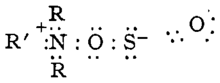
II



III



IV



V

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[5] Richards and Coombs, THIS JOURNAL, **37**, 1656 (1915).

[6] Sugden, "The Parachor and Valency," Alfred A. Knopf, New York, N. Y., 1930, p. 38.

[7] Bright, Dissertation, The Ohio State University, June, 1940.

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.