It was not found possible to prepare samples of Bi_2O_4 or Bi_2O_5 of sufficient purity to determine their specific heats. However, by comparison of the entropies of arsenic and antimony it is suggested that until the entropies are actually determined, the value 35.0 ± 2 E. U. may be used for each, with reasonable assurance.

Related Thermal Data.—The heat of formation of Bi_2O_3 has been determined by Mixter[7] and Ditte and Metzner.[8] Mixter gives $-136,000$ cal., and Ditte and Metzner gives $-137,800$ cal.

Using Mixter's values of $-136,000$ cal. with the measured entropies of Bi and Bi_2O_3 and the accepted entropy of O_2, the free energy of Bi_2O_3 is calculated as $-118,000$ cal.

In conclusion the author wishes to thank K. K. Kelley for his assistance in making the new temperature scale and in checking the calculations in the determinations of the entropies.

Summary

The heat capacities of bismuth and bismuth trioxide from about 60 to 300°K. have been determined and their corresponding entropies calculated. The free energy of Bi_2O_3 has been calculated.

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[Contribution from the Chemical Laboratory of the University of Utah]

THE SURFACE TENSION OF LIQUID NITROUS OXIDE

By Elton L. Quinn and Grant Wernimont

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Many investigators find carbon dioxide and nitrous oxide an interesting pair of compounds largely because of the similarity of their physical properties. The close agreement between the densities, vapor pressures, critical temperatures, molecular weights, etc., is very remarkable, and it is not uncommon to group them together when considering questions pertaining to their physical make-up. The fact that such an agreement does not extend to the chemical behavior of these two substances, enhances this interest as it indicates that the physical properties are related more to the arrangement of the atoms in the molecules than to the ultimate constitution of the atoms.

Niven[1] gives reasons quite sufficient for concluding that carbon dioxide and nitrous oxide have the same electronic arrangement. Rankine[2] shows from crystal structure data and viscosity data, the similarity in structure of molecules of the two compounds. Many other investigators have dealt

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[7] Mixter, *Am. J. Sci.*, [4] **28**, 103 (1909).

[8] Ditte and Metzner, *Compt. rend.*, **115**, 1303 (1892).

[1] Niven, *Phil. Mag.*, [7] **3**, 1314–1334 (1927).

[2] Rankine, *Proc. Roy. Soc.* (London), **A98**, 369–374 (1921).

with this problem in various ways, and in all cases their results indicate a remarkable similarity in the structure of the two kinds of molecules.

It seemed to the authors that any data on the forces acting between the molecules of carbon dioxide and nitrous oxide might be of interest, not only as affecting these compounds, but also from the general point of view of surface tension and solubility. This paper will be devoted to the study of the surface tension of liquid nitrous oxide, from which an attempt to estimate its internal pressure will be made, while a later publication will deal with the internal pressure from a determination of the solubility of various solutes in liquid nitrous oxide. Carbon dioxide has already been studied from this point of view.

The surface tension of liquid nitrous oxide was first determined by Verschaffelt[3] over a temperature range from 25 to $-25°$, and later by Grunmach,[4] who made four determinations over a temperature range from 20 to $-90°$. Verschaffelt used the capillary tube method while Grunmach used the so-called capillary wave method. The original paper of Verschaffelt was not available to the authors, so it was not possible to determine just what was done about the density of the saturated vapor over the liquid nitrous oxide. As far as the authors are aware, no reliable determinations of the densities of the gaseous and liquid phases of nitrous oxide below 0° have ever been made previous to those recently published.[5]

Preparation of Tubes

The capillary tubes used in these measurements were drawn from soft "soda glass" tubing. Before drawing, the larger tubes were carefully cleaned and dried. A large number of such tubes were made and pieces from these were carefully selected in order to insure a circular cross section and a uniform bore. The ends of these capillaries were measured with a microscope and the variation in the length of a thread of mercury, moved along the tube, was used to indicate uniformity of bore. The exact diameter of each tube selected was determined, at a point to which it was estimated the liquid would reach, during the capillary measurements, by the usual method of weighing a thread of mercury of known length. These measurements were checked after the measurements of capillary rise by cutting the capillaries at the average height reached by the liquid, and measuring the internal diameter of the cut ends with a microscope. The agreement between the results of these two methods of measurement was quite satisfactory. Before the capillary tubes were placed in the jackets in which the liquid nitrous oxide was to be condensed, they were boiled with a cleaning solution of chromic acid, washed many times with distilled water and finally dried in a current of dry, dust-free air. Each capillary was supported in the center of a larger outer jacket by means of platinum wires. The outside tubes were very carefully made from thick-walled pyrex glass tubing having an internal diameter of about 16 mm. and a wall thickness of 3 mm. It was desirable to have the diameter of these tubes large in order to keep any correction occasioned by them as low as possible. These tubes proved to be very satisfactory and none of them failed during the period of this investigation.

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[3] Verschaffelt, Comm. Phys. Lab. Univ. Leiden, No. 18, 640 (1895).

[4] Grunmach, *Ann. Physik*, [4] 15, 401 (1904).

[5] Quinn and Wernimont, THIS JOURNAL, 51, 2002 (1929).

The nitrous oxide was obtained from a commercial cylinder of the liquid manufactured by the Ohio Chemical Company. A very careful qualitative analysis showed that it was free from other oxides of nitrogen, halogens, carbon dioxide, sulfur compounds and ammonia. In some preliminary tests the gas was distilled into the pyrex tubes from the liquid through a calcium chloride tower 55 cm. long. When the temperature of this liquid was lowered to about 10 or 20° below zero, a few very fine crystals separated. It was assumed that this impurity was water so a glass trap filled with short pieces of aluminum wire was placed in the line. Into this trap the nitrous oxide was distilled after passing through the calcium chloride. It was condensed to a liquid, at a temperature close to the freezing point of the nitrous oxide, and vaporized again at a temperature of about $-50°$. This vapor was conducted to the pyrex tube containing the capillary and again condensed to a liquid, then frozen to a solid and while in this state the tube was sealed. After this treatment, no solids ever separated at any temperature from the liquid nitrous oxide and this was considered evidence that the water had been successfully removed. The distillation method of purification, which has already been described,[5] is considered by the authors to be superior to this, but the work on surface tension had already been completed before this distillation process was developed. There are many reasons for believing, however, that the liquid nitrous oxide used in this investigation was very pure.

To facilitate the handling of the pyrex tube containing the liquid nitrous oxide, it was placed in a larger tube sealed at one end and about 65 cm. (2 feet) long. A ring of paper at the top and a wad of cotton on the bottom held this tube firmly in position.

The thermostat used and the method of measuring the capillary rise has already been described by one of us[6] and this procedure was modified only slightly in the present investigation.

Calculations

Calculation of surface tension from the liquid rise in a capillary tube placed in the center of a larger tube makes several corrections necessary and some of these are difficult to evaluate. The effect of the weight of the liquid in the small meniscus above the point of measurement has been pretty well worked out and in a small tube of capillary size the measured height is usually corrected by the addition of $r/3$, where r is the radius of the capillary. The effect of the outer jacket on the rise of the liquid in the capillary tube is somewhat more difficult to determine. This question has received considerable attention from Richards and his co-workers at Harvard University but the apparatus used by these workers could not be adapted easily to this investigation because of the high pressures used. The method and apparatus used by Sugden[7] could have been employed but certain difficulties, especially those of obtaining accurate readings of the very small capillary rise near the critical temperature, made it seem unwise. It was believed, however, that Sugden's method of calculation could be used to calculate the effect of the outer jacket on the capillary rise, especially as it seemed very likely that any such effect would be much below the experimental error. It was found that the meniscus of the liquid in the outer jacket was sufficiently flat even at the lowest temperatures to be read easily

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[6] Quinn, THIS JOURNAL, 49, 2704 (1927).

[7] Sugden, *J. Chem. Soc.*, 119, 1483 (1921).

and that the capillary tube, standing in the center, caused no serious distortion of the surface.

It should be noted that Sugden's method of calculating the effect of the larger tube on the capillary rise in the smaller one is based on two tubes standing parallel to each other and connected at the bottom. The system used in this work is somewhat different and the capillary tube itself is bound to have some effect on the action of the larger tube, but, as will be shown later, this effect must be so small that it need not be considered here. Verschaffelt[8] has worked out a graphical method of treating a system such as was used in this work but as his original paper was not available to the authors, no attempt was made to use it.

Table I gives the values for the capillary constant a^2 in mm.^{2} for tube No. 7 at nine temperatures. The first values of a^2 were calculated from the equation $a^2 = r(h_0 + r/3)$, in which r is the radius of the capillary, h_0 is the measured height in mm. above the meniscus in the outer jacket and $r/3$ is the correction for the liquid in the small meniscus in the capillary tube. In this calculation the effect of the outer jacket on the height of the liquid in the capillary is not taken into consideration. In the third column the values for a^2 are calculated by means of Sugden's method, which takes this effect into consideration. It will be noted that the agreement between the two sets of values is quite remarkable and indicates that no correction is necessary when dealing with tubes of the sizes used in this investigation, and when using liquids with such low surface tensions. As there might be some question about neglecting the effect of the capillary tube in reducing the effective diameter of the larger tube, one calculation was made on the same tube at the lowest temperature, where any such effect would be greatest, and the absurd assumption was made that the capillary decreased the effective diameter of the tube by one-half. This calculation gave a value for a^2 which was only 1% above that actually obtained.

TABLE I

SHOWING THE EFFECT OF THE OUTER JACKET ON THE CAPILLARY RISE

Measurements on Tube No. 7 were used for these calculations

Temp., °C.	$a^2 = r(h_0 + r/3)$	a^2 (Sugden's method)	Difference, %
30	0.2443	0.2437	−0.20
20	0.6495	0.6490	− .10
10	1.0123	1.0126	+ .03
0	1.334	1.335	+ .10
−10	1.635	1.635	.00
−20	1.983	1.983	.00
−30	2.255	2.256	+ .05
−40	2.508	2.508	.00
−50	2.847	2.848	+ .03

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[8] Verschaffelt, *Bull. acad. roy. méd. Belg. Cl. Sci.*, 574 (1921).

In Table II the values of a^2 were calculated from $r(h_0 + r/3)$ for each reading. The average of these values at each temperature was taken and the surface tension γ was calculated from the equation $\gamma = 0.5\,a^2g(D - d)$ in which g is the acceleration due to gravity, D is the density of the liquid

TABLE II

SURFACE TENSION MEASUREMENTS OF LIQUID NITROUS OXIDE

Temp., °C.	Tube no.	h_0, cm.	h, cm.	a^2, mm.^{2}	a^2, average	$D-d$	Surface tension γ, dynes/cm.
30	3	0.1127	0.1191	0.2296			
	4	.1912	.1955	.2506			
	6	.1448	.1506	.2640			
	7	.1334	.1392	.2443	0.2471	0.456	0.552
20	3	.3398	.3462	.6675			
	4	.4713	.4756	.6097			
	6	.3637	.3695	.6477			
	7	.3643	.3701	.6495	.6436	.638	2.012
10	3	.5019	.5083	.9800			
	4	.7163	.7206	.9238			
	6	.5730	.5788	1.0146			
	7	.5710	.5768	1.0123	.9827	.755	3.636
0	3	.6730	.6794	1.310			
	4	.9385	.9428	1.209			
	6	.7511	.7569	1.327			
	7	.7545	.7603	1.334	1.295	.851	5.400
−10	3	.8231	.8295	1.599			
	6	.9310	.9368	1.642			
	7	.9261	.9319	1.635			
	8	.6857	.6934	1.616	1.623	.926	7.364
−20	4	1.4182	1.4225	1.824			
	6	1.1080	1.1138	1.952			
	7	1.1240	1.1298	1.983			
	8	0.7902	0.7979	1.858	1.904	.979	9.134
−30	4	1.6522	1.6565	2.124			
	6	1.2705	1.2763	2.237			
	7	1.2793	1.2851	2.255			
	8	0.9128	0.9205	2.145	2.190	1.014	10.88
−40	3	1.2880	1.2944	2.496			
	6	1.3919	1.3977	2.450			
	7	1.4230	1.4288	2.508			
	8	1.0600	1.0677	2.488	2.485	1.037	12.63
−50	3	1.4060	1.4124	2.723			
	6	1.5908	1.5966	2.799			
	7	1.6164	1.6222	2.847			
	8	1.1881	1.1958	2.787	2.789	1.053	14.39

INTERNAL RADIUS OF CAPILLARY TUBES

Tube No........	3	4	6	7	8
Radius, cm......	0.01928	0.01282	0.01753	0.01755	0.02330

and d the density of its saturated vapor. The values for these densities were obtained by plotting on large-scale cross-section paper the results obtained by the authors in a previous investigation,[9] and from the curve thus obtained, the density values for both liquid and vapor were read.

Discussion of Results

Much interest has been shown in recent years in the relations between surface tension, liquid and gaseous densities and internal pressures. Some years ago van der Waals,[10] by a theoretical consideration of the forces acting between the molecules of a liquid, developed the equation $\gamma = K(1 - T/T_c)^n$. In this equation γ is the surface tension at the absolute temperature T, n is an exponent having a value of about 1.2 for all non-polar liquids and T_c is the critical temperature of the liquid. The constant K is supposed to hold over a large temperature range and is characteristic of the liquid. As in most equations involving the surface tension, it fits the experimental values much better at temperatures well removed from the critical temperature.

Recently, Macleod[11] developed an empirical equation for the relation between the surface tension and the densities of a liquid and its saturated vapor. This equation, when put in the form $\gamma/(D - d)^4 = C$, represents the experimental results very well in most cases. Here D is the density of the liquid and d the density of its saturated vapor, while C is a constant characteristic of the liquid in question.

Another interesting equation is that proposed by Sugden,[12] which he writes in the form $D - d = D_0(1 - T/T_c)^{0.3}$. D_0 in this equation represents the density of the supercooled liquid at absolute zero.

By combining the equations of Macleod and Sugden, the following equation is obtained: $\gamma = C \times D_0^4(1 - T/T_c)^{1.2}$. This is evidently van der Waals' equation in such cases as the exponent n may be 1.2. It is perhaps interesting to note that van der Waals' constant K is equal to $C \times D_0^4$ and as C is equal to the ratio of the surface tension to the fourth power of the difference in density of the liquid and vapor, it is quite possible to make use of it in calculating the volume occupied by a molecule of the liquid.

From the surface tension measurements made during this investigation, it seems that van der Waals' equation gives the highest degree of accuracy when written in the form $\gamma = 72.8\ (1 - T/311.8)^{1.26}$. The exponent n was calculated from the readings at fifteen pairs of temperatures and the average was found to be 1.26. The value of K was determined at all temperatures at which surface tension measurements had been made, using

[9] Quinn and Wernimont, THIS JOURNAL, **51**, 2007 (1929).

[10] Van der Waals, *Z. physik. Chem.*, **13**, 716 (1894).

[11] Macleod, *Trans. Faraday Soc.*, **19**, 38 (1923).

[12] Sugden, *J. Chem. Soc.*, **130**, [Part 2] 1780 (1927).

the exponent 1.26. The average of these values, excluding the one obtained at 30°, was 72.8. The agreement between the observed values obtained in this investigation for the surface tension of liquid nitrous oxide and those calculated from the above equation is shown in Table III, while the observed and calculated values obtained from Verschaffelt's[13] work are given in Table IV for comparison.

TABLE III

OBSERVED AND CALCULATED VALUES FOR THE SURFACE TENSION OF NITROUS OXIDE OBTAINED IN THIS INVESTIGATION

Temp., °C.	K	Observed	Calculated	Diff.	% diff.
30	49.3	0.552	0.816	+0.26	+47.8
20	69.3	2.01	2.11	+ .10	+ 4.9
10	73.0	3.64	3.63	− .01	− 0.3
0	74.6	5.40	5.27	− .13	− 2.4
−10	76.2	7.36	7.03	− .33	− 4.4
−20	74.7	9.13	8.90	− .23	− 2.5
−30	73.0	10.88	10.84	− .04	− 0.4
−40	71.5	12.63	12.86	+ .23	+ 1.8
−50	70.0	14.39	14.95	+ .56	+ 3.9

Average percentage difference (disregarding sign) 2.6

NOTE.—Values obtained at 30° are not used in averages because this temperature is so near the critical temperature.

TABLE IV

OBSERVED AND CALCULATED VALUES FOR THE SURFACE TENSION OF LIQUID NITROUS OXIDE OBTAINED BY VERSCHAFFELT

Temp., °C.	Observed	Calculated	Diff.	% Diff.
25	1.07	1.36	+0.29	+27.1
20	1.75	2.05	+ .30	+17.1
15	2.50	2.81	+ .31	+12.4
10	3.30	3.62	+ .32	+10.0
−25	10.10	10.40	+ .30	+ 3.0

Average percentage difference 13.8

NOTE.—These results seem to indicate that the constants as given by Verschaffelt could be changed so as to greatly improve the agreement between the calculated and observed values.

The Internal Pressure of Nitrous Oxide

No very satisfactory method for calculating internal pressure from surface tension measurements exists, in spite of the fact that one would expect this to be one of the best ways of dealing with the question. According to Hildebrand[14] the values of $\gamma/v^{1/3}$ are useful for indicating the relative internal pressures where v is the molal volume of the liquid. Calculating

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[13] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, Vol. IV, p. 447.

[14] Hildebrand, "Solubility," The Chemical Catalog Co., Inc., New York, 1924, p. 111.

the values for $\gamma/v^{1/3}$ at 20° for carbon dioxide and nitrous oxide, we get 0.355 and 0.528, respectively. Now if we arrange these compounds in the Hildebrand series according to the decreasing order here indicated, we find that carbon dioxide is the first member, then nitrous oxide, and after a big gap we come to nickel carbonyl. According to the theory of solubility this can only mean that carbon dioxide and nitrous oxide in the liquid state are poor solvents for the common solutes and that of the two compounds we would expect nitrous oxide to be the better.

Summary

1. Surface tension measurements of liquid nitrous oxide have been made over a temperature range of 30 to $-50°$.

2. The equation of van der Waals for the change of surface tension with a change of temperature, when put in the form of $\gamma = 72.8\ (1 - T/311.8)^{1.26}$ gave values for γ which were in fairly good agreement with those determined experimentally.

3. From the position of nitrous oxide in the internal pressure series of Hildebrand, it was predicted that it would be a poor solvent for the common solutes but that it was somewhat better than liquid carbon dioxide.

SALT LAKE CITY, UTAH

[CONTRIBUTION FROM THE LABORATORIES OF GENERAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE COAGULATION OF FERRIC OXIDE SOLS BY GAS BUBBLES[1]

BY HENRY M. STARK

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A ferric oxide sol of great purity has been prepared by C. H. Sorum[2] in this Laboratory. Due to its extremely low chloride content this sol has rather special properties. While making conductivity measurements on this sol Sorum observed that if streams of air bubbles were used as a stirring agent coagulation took place. Other gases were tried and the phenomenon seemed to be general. Since no mention had been made anywhere in the literature concerning the coagulation of colloid systems by gas bubbles, this phenomenon presented an interesting problem for investigation.

Coagulation of colloids such as ferric oxide is usually considered to be due either to destruction or neutralization of the charge on the particle by the

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[1] An extract from a thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, University of Wisconsin. The problem was suggested by Dr. C. H. Sorum and carried out under the supervision of Professor J. H. Walton. The author wishes to express his indebtedness to Mr. A. G. Jacques for many valuable suggestions.

[2] Sorum, THIS JOURNAL, 50, 1263 (1928).