

does not function as a "mixed halogen," but as a salt of hydrocyanic acid with the weak base iodine hydroxide.⁷ The salt-like behavior of the iodine-halogen compounds is emphasized by several investigators.⁸ In conclusion it may be said that according to the results which have been obtained the hypothesis that the structure of the iodine cyanide molecule is different from that of the iodine molecule is confirmed, and that it is to the different chemical nature of iodine cyanide that we may attribute its divergent reactivity.

Summary

The reactivity of iodine cyanide toward silver saccharate in various solvents has been investigated. It is shown that contrary to the behavior of iodine the reactivity of iodine cyanide is independent of the nature of the solvent. From this fact the conclusion may be drawn that iodine cyanide represents a heteropolar compound and does not function as a "mixed halogen." The yield of iodine cyanide has been increased by modifying the purification methods.

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THE DENSITIES OF COEXISTING LIQUID AND GASEOUS NITROUS OXIDE

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During an investigation of the internal pressure of liquid nitrous oxide by the measurement of its surface tension, the authors found that no data existed on the densities of the liquid and its saturated vapor at temperatures below zero. As these data were necessary for calculating the surface tension, it became necessary to interrupt the investigation and to attempt a set of measurements for supplying these values. This paper describes the method of making these determinations and the results obtained over a temperature range from 30 to -50° .

The densities of liquid nitrous oxide and its saturated vapor were determined between the temperatures of 30 and 0° by Villard¹ in the year 1894. While the reliability of these determinations has never been questioned, the temperature range covered is not great enough for the work at hand. The advisability of extrapolating these values to the lower temperatures was carefully considered but it seemed best under the circumstances to make direct measurements.

⁷ Cf. Abegg, "Handbuch der anorganischen Chemie," 1913, Vol. IV, 2, pp. 455 ff.

⁸ P. Walden, *Z. physik. Chem.*, **43**, 385 (1903); R. Abegg, *Z. anorg. Chem.*, **39**, 330 (1904).

¹ Villard, *Compt. rend.*, **118**, 1096 (1894).

As it was necessary to make measurements below the freezing point of mercury the usual method in which mercury is used as a confining liquid could not be used. The method of Young² seemed to be the only one applicable under these conditions and after slight modification was found to give quite satisfactory results. Several glass tubes of different lengths were filled to about two-thirds of their capacity with liquid nitrous oxide; the volumes of the liquid and saturated vapor were determined at different temperatures and the weight of the compound in each tube was measured. From these values by means of simultaneous equations it was possible to calculate the densities of the two phases at each temperature at which measurements were made.

Experimental Method

The five pycnometers used in this work were simple straight "soda-glass" tubes having an outside diameter of 12 mm. and a wall thickness of 2 mm. These tubes varied in length from 10 to 20 cm. and were graduated on the outside in mm. divisions. The greatest care was necessary in their manufacture as it was necessary for them to withstand at times a gas pressure as high as 68 atmospheres. It was found that proper annealing after working in the gas flame was much more important than the thickness of the tube wall, provided, of course, that it had a reasonable thickness. The two-thirds capacity filling of the tubes was also important because tubes having very much less than this amount could not be used over the whole temperature range. Stewart³ showed in the case of carbon dioxide, which behaves much the same as nitrous oxide, that the liquid in a tube filled to less than about two-thirds of its volume contracts on cooling until some temperature is eventually reached where the liquid condensed from the gaseous phase, due to the lowering of the temperature, is equal to the contraction of the liquid phase. It is quite obvious that measurements made under such conditions would be of no value for density determinations.

The nitrous oxide used in this investigation was taken from a commercial cylinder of the liquefied gas manufactured by the Ohio Chemical and Manufacturing Company. The gas was carefully analyzed qualitatively using the tests suggested by Hackh⁴ and found to be free from other oxides of nitrogen, halogens, carbon dioxide, sulfur compounds and ammonia. A small quantity of air was present but the most troublesome impurity was water vapor. In order to remove these impurities as well as any other substance that might be present in small amounts the liquid was fractionally distilled several times in an apparatus represented by the drawing in Fig. 1. The pycnometer, e, was cemented to the exit tube with de Khotinsky cement and the whole apparatus evacuated with an oil pump until the pressure was less than 3 mm., as indicated by a mercury manometer. During the evacuation the pycnometer was heated with a hand blast lamp until it was much too hot to permit touching with the bare hand. Nitrous oxide was then admitted to the apparatus and when the pressure reached that of the atmosphere the vacuum pump was stopped, the valve on the safety line closed and the safety valve adjusted. Then after a slight pressure had been put on the system, the valve to the safety line was opened and the pressure increased until the safety valve operated. While in this condition a Dewar flask containing solid carbon dioxide and ether, the temperature of which had been lowered to -100° by means of a vacuum

² Young, *Trans. Chem. Soc.*, **59**, 37, 126, 929 (1891); *Proc. Phys. Soc.*, **13**, 617 (1895).

³ Stewart, *Trans. Am. Soc. Mech. Eng.*, **30**, 1111 (1908).

⁴ Hackh, *J. Am. Pharm. Assocn.*, **13**, No. 3, March (1924).

pump, was pushed up over Tube a. Gaseous nitrous oxide was admitted from the cylinder fast enough to keep the safety valve close to the opening point until a sufficient quantity of the liquid had collected in Tube a. The supply of nitrous oxide was then cut off and the valve to the safety line closed. The freezing mixture was then transferred to Tube b and the liquid in a was permitted to distil into b, after which a Dewar flask containing liquid oxygen was substituted for the carbon dioxide freezing mixture. As soon as the nitrous oxide was frozen the vacuum pump was connected and the system evacuated to 3 mm. or less. As Tube b was cooled with liquid oxygen before all of the liquid in a had evaporated, a residue of liquid nitrous oxide was left in a which usually changed to a solid as soon as vapor pressure was decreased by lowering the temperature of Tube b. This residue was removed by heating after the vacuum pump had been operating for a few minutes. The residual gases were able to pass to the pump without coming in contact with the solid nitrous oxide. This procedure was repeated by distilling to a liquid in c and freezing to a solid and pumping in d and finally distilling the proper amount into the pycnometer e, freezing and evacuating. The pycnometer

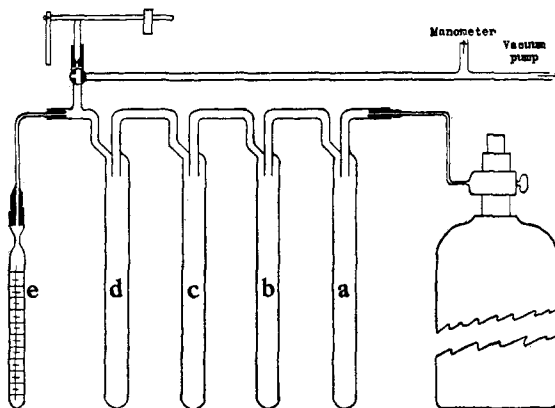


Fig. 1.

containing the proper amount of solid nitrous oxide was sealed while the vacuum pump held the pressure to less than 3 mm. and after the heated end of the tube had cooled it was removed from the liquid oxygen and the whole tube warmed slowly to room temperature. That this process was effective in removing the water from the gas is indicated by the fact that in preliminary experiments in which the gas was dried by passing it through a 50-cm. tower of calcium chloride, crystals of some impurity, supposedly water, separated from the liquid nitrous oxide on cooling to about -20° . Liquid nitrous oxide distilled in this apparatus failed to show such an impurity at any temperature. Weighing the tubes was delayed for several days so as to permit them to stand at room temperature long enough to give some assurance that they would not explode in the balance case. Several tubes exploded during this period, usually very soon after filling but none caused any trouble after starting the measurements, some even being heated to the critical temperature.

After weighing, the pycnometers were placed in long glass tubes having one end closed. A wad of cotton prevented the pycnometers from touching the bottom and a roll of paper held the top end securely in place. These tubes made it easy to handle the pycnometers and to clamp them in position in the thermostat. The thermostat used has already been described.⁵ The temperature was kept constant by expanding

⁵ Quinn, THIS JOURNAL, 49, 2704 (1927).

liquid carbon dioxide through a cooling coil submerged in an alcohol-bath. Some improvement was made when a so-called "siphon cylinder" was substituted for the inverted carbon dioxide cylinder. This made handling easier and prevented water and oil from being forced through the coils. The temperature was adjusted every thirty seconds during the period of measuring and it was not difficult to hold it within $\pm 0.25^\circ$ of the desired temperature down to -60° . Temperature measurements were made with a pentane thermometer which had been calibrated twice by the U. S. Bureau of Standards. The last calibration was made during the summer of 1928.

The routine procedure of reading the volumes of liquid in the several tubes was as follows. The tubes were submerged in the alcohol-bath at the desired temperature for ten minutes. They were then removed and quickly shaken thoroughly and returned to the bath. At the end of six to seven minutes a reading was taken of the position of the meniscus on the tube graduations and it was again removed, quickly inverted and returned to the bath. In three to four minutes or as soon as the liquid nitrous oxide had drained from the sides of the tubes a second reading was made and if the two readings checked this value was used as the volume of the liquid at that temperature. The time necessary to reach equilibrium in the tube was determined several times by taking readings every twenty seconds until they became constant. It never took over seven minutes to reach this point.

After the readings had been completed the temperature of the tube was lowered in a solid carbon dioxide and ether bath and a small hole made in the tip of the pycnometer with a hand blast lamp. The tubes were then removed and the nitrous oxide permitted to escape. The last of this compound was removed with a vacuum pump and its place taken by air, the weight of which was easily determined. The weight of the tube was then determined, after which it was filled to the top with freshly boiled distilled water and again weighed. From these weighings and the temperature of the water the total volume of the pycnometer was determined. The top of the tube was then removed and the lower portion calibrated by filling with water to the marks reached by the liquid nitrous oxide at the various temperatures. The curvature of the meniscus in the case of water was, of course, different from that of the nitrous oxide and a correction for this difference had to be applied at each temperature.

The weight of the water in the meniscus was found in the following manner. A tube of the same size as that used for the pycnometers partly was filled with mercury and a little water placed on top. It was then put in a projection lantern and its image, enlarged 23 times, was projected on a white piece of paper. A drawing was made of the two menisci which is represented by Fig. 2, abcd being the meniscus of the water and efgh that of the mercury. These areas

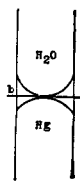


Fig. 3.

were then cut from the paper and weighed. The weight of abcd divided by the weight of abcd + efgh times 100 gave the percentage of the total area due to water above the line bc which was found in three determinations to be 62, 61 and 61%, respectively.

The same tube was dried and weighed with mercury, after which water was added and sucked out until the meniscus of the water just touched the meniscus of the mercury as in Fig. 3. The weight of the water was then determined and 61% of this was taken as the weight above the line bc. A tube containing liquid nitrous oxide was then warmed to 30° and a drawing made of its meniscus. The surface came so near to being flat that it was assumed that no appreciable error would be introduced by so considering it. An attempt was made to get a drawing of the nitrous oxide meniscus at a low temperature. This was unsuccessful and it was therefore necessary to be content with the apparent similarity of the meniscus of the liquefied gas at -60° and that of water at $+30^\circ$. It was quite evident that if any correction was needed at this point it was very small. The correction

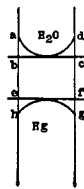


Fig. 2.

at 30° was 0.05 g. This was the weight of the water in the curved meniscus above the comparatively flat surface of the liquid nitrous oxide. The correction at -60° was 0. By interpolation the correction to be subtracted at each temperature was determined.

The thermal expansion of the tube from -60° to the temperature at which the calibration was made was calculated and it was found that this made a difference in the volume of the tube of about 1 part in 500. As this correction was less than the probable error in the readings, it was not applied.

The dilation of a glass tube under a pressure practically the same as in this case was measured experimentally with liquid carbon dioxide⁶ and was found to be less than 0.1%. This correction could, therefore, be neglected in these calculations.

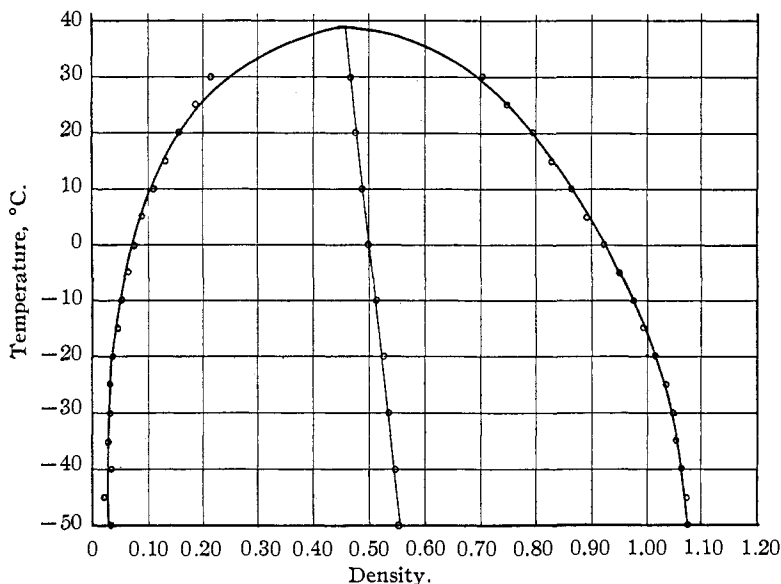


Fig. 4.

In order to eliminate as far as possible the experimental errors involved in determining the volume of the liquid nitrous oxide at the various temperatures, the volumes obtained by calibrating the tubes were plotted on coordinate paper 50 × 80 cm. and a curve was constructed for each set of readings. The agreement between the points on each curve was very satisfactory, only a few points failing to fall in the proper position. The values used for the calculations of the density of the liquid and the density of the gas were read from these curves. Tube No. 1 was discarded at the outset as it was quite evident that the volume of the liquid was too great to give reliable results for the gaseous density. Readings from Tube No. 3 also had to be discarded although the curve seemed to be quite regular. Apparently the trouble was due to an error in the total weight of the nitrous oxide or its total volume. As the tube had been cut it was quite

⁶ Quinn, *THIS JOURNAL*, 50, 675 (1928).

impossible to check back on either of these points. The densities were determined by setting up simultaneous equations between different sets of volume readings. Five calculations were thus made at each temperature and the values plotted in Fig. 4 were the averages between these results. In constructing this curve the value obtained by Villard for the critical temperature was used, that is, 38.8°. It is quite evident from an inspection of the curve that the values reported at times around 35° could not be used. The critical density was determined by the method of Cailletet and Mathias⁷ in which the values for $(D + d)/2$ were plotted against the temperature and the straight line thus produced was extrapolated to the critical temperature. This gave a value of 0.459 for the critical density, while the value reported by Villard was 0.456.

Experimental Results

The results of these measurements are tabulated in Table I. Villard's results were plotted and values read from his curve at corresponding temperatures are given in the table for comparison. It will be noted that the agreement is, in general, very satisfactory. Lowry and Erickson⁸ de-

TABLE I
THE DENSITIES OF COEXISTING LIQUID AND GASEOUS NITROUS OXIDE

Temp., °C.	Quinn and Wernimont				Villard	
	Obs. <i>D</i>	Calcd.	Obs. <i>d</i>	Calcd.	<i>D</i>	<i>d</i>
38.8	0.451	0.459	0.459	0.459	0.456	0.456
30	.704	.721	.217	.216	.680	.240
25	.750	.780	.181	.166	.740	.196
20	.793	.805	.153	.155	.784	.160
15	.826	.837	.133	.133	.820	.135
10	.861	.866	.111	.116	.856	.114
5	.894	.892	.090	.102	.886	.099
0	.925	.916	.073	.088	.912	.087
- 5	.952	.939	.062	.077		
-10	.975	.960	.051	.066		
-15	.995	.980	.042	.058		
-20	1.013	.999	.038	.049		
-25	1.033	1.018	.030	.042		
-30	1.044	1.036	.029	.034		
-35	1.053	1.054	.028	.028		
-40	1.062	1.070	.031	.022		
-45	1.071	1.087	.020	.017		
-50	1.079	1.103	.032	.013		

The experimental error for the liquid densities is estimated as about $\pm 0.25\%$. The error of measurement of the gaseous phase is much greater. Neglecting the two highest and two lowest values, which are obviously much in error, the average deviation will run about $\pm 2.0\%$.

⁷ Cailletet and Mathias, *Compt. rend.*, **102**, 1202 (1886); **104**, 1563 (1887).

⁸ Lowry and Erickson, *THIS JOURNAL*, **49**, 2731 (1927).

veloped equations for the relation between the values for $(D + d)/2$ and the densities of the gaseous and liquid phases of carbon dioxide. These equations when applied to nitrous oxide take the following form

$$\begin{aligned} D &= 0.459 + 0.00111 (t_k - t) + 0.1222 \sqrt[3]{t_k - t} \\ d &= 0.459 + 0.00111 (t_k - t) - 0.1222 \sqrt[3]{t_k - t} \quad \text{and} \\ (D + d)/2 &= 0.459 + 0.00111 (t_k - t) \end{aligned}$$

In these equations D is the density of the liquid phase and d the density of the gaseous phase. The values of D and d calculated by means of these equations have also been tabulated and it will be noted that the agreement is not especially good and this disagreement is more pronounced at the higher temperatures. Lowry and Erickson, in the case of carbon dioxide, obtained excellent agreement between the calculated and observed values.

It is of some interest to use these results for calculating the molecular volume at absolute zero, using for this purpose the equation proposed by Sugden.⁹ If the equation is written in the form $D - d = D_0 (1 - T/T_K)^{3/10}$ D_0 being a constant which in the case of nitrous oxide has a value of 1.566, then the molecular volume at absolute zero would be $44/1.566$ or 28.1 cc. The actual volume occupied by each molecule could be calculated easily from this value by the use of Avogadro's number.

Summary

The densities of the coexisting gaseous and liquid phases of nitrous oxide have been determined over a temperature range of 80°. The critical density was found to be 0.459 and the molecular volume at absolute zero to be 28.1 cc. when calculated from Sugden's equation. The values for the density of the liquid and its saturated vapor show a very good agreement with those obtained over part of the temperature range by Villard.

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⁹ Sugden, *J. Chem. Soc.*, **130**, 1780 (1927).