

3. When the rate of evolution of oxygen is measured, the reaction is strictly unimolecular after a very short period of acceleration which is ascribed to supersaturation.

4. The temperature coefficient of the reaction is about 3.1.

5. A method of weight titration of hydrogen peroxide by permanganate is described which enabled reaction velocity measurements to be carried out in the very early stages of the reaction.

6. A graphical method is described which enables unimolecular velocity coefficients to be calculated from measurements of the rate of evolution of gas without any knowledge of the total volume of gas evolved or the exact concentration of the peroxide.

It is believed that both these methods are new.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 279]

ABSORPTION SPECTRA AT HIGH PRESSURES AND AT LOW TEMPERATURES. THE TRANSPARENCY OF ARGON AND METHANE¹

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RECEIVED NOVEMBER 24, 1931

PUBLISHED MAY 7, 1932

The purpose of this investigation was to study the absorption spectra of a number of substances whose pressure, volume, and temperature relations suggested the possibility of molecular aggregation as a factor in the attempt to account for the physical properties at high concentration and at low temperature. Since it was not possible to predict the spectral region of the absorption of the supposed associated or aggregated molecular species, the spectral region selected was the visible and the quartz ultraviolet, where absorption may be most readily studied. In this paper we shall describe the design of apparatus found satisfactory for the purpose and the results of the studies with argon and methane.

Method.—The light absorption was determined by the method of photographic spectrophotometry. The relative blackening of the photographic plate served as a measure of the light transmission through the empty absorption tube and through the tube filled with fluid.

An Adam Hilger E 1 spectrograph with glass and quartz optical system was used for photographing the spectra. Exposures were twenty minutes to one hour for slit widths of 0.01 to 0.02 millimeter.

An under-water spark served as a source of continuous light. However, the usual aluminum and copper electrodes were replaced advantageously by magnesium electrodes for the shorter wave lengths. In later work we have used the hydrogen discharge tube as

¹ The results presented here are to be found in greater detail in the Ph.D. Thesis of B. J. Eiseman, Jr., Massachusetts Institute of Technology, 1927.

a source of continuous ultraviolet radiation. For the visible region, a tungsten ribbon heated with 18 amperes at 6 volts in a nitrogen filled glass bulb was very satisfactory.

The iron spark and iron arc spectra were used for obtaining reference lines for determining the wave lengths.

It is doubtful whether a continuous absorption amounting to less than 10% would have been detected with the procedure described.

Absorption Tubes.—A fused quartz Dewar tube of special design was used to contain the refrigerant and absorption tube during loading and for the low temperature absorption measurements. Two tubulations, opposite each other, in the double walls of the Dewar tube permitted the insertion of an absorption tube through the body of the Dewar tube. Figure 1 shows the Dewar tube with the quartz absorption tube (I), used for the low-temperature measurements. Two quartz tubes (T and T'), each with a plane window (W and W') fused on at one end, and the other end open, were fused into another quartz tube (L) of slightly larger diameter to complete the absorption tube, in which all three tubes (T, T' and L) are coaxial. A side tube (C) on the larger tube connected to the vacuum line and loading system by means of a quartz-Pyrex graded seal. The windows (W and W') were 15 millimeters apart and the bore of the larger tube (L) was 10 millimeters. The refrigerant was prevented from escaping through the small clearance space between the tubulations and the absorption tube by packing moistened asbestos fiber (A) in this space. After the asbestos had dried, rubber tape (R) was wound around the ends of the tubulations and the projecting arms of the absorption tube. A stream of dry nitrogen was passed through N at each end of the absorption tube. In an earlier design tubes T and T' were replaced by quartz rods. However, the ultraviolet transmission was not so satisfactory as in the arrangement described above.

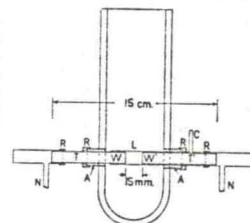


Fig. 1.

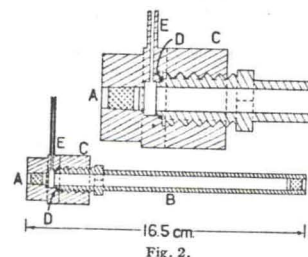


Fig. 2.

between B and C. The assembled tube had a light path of 14.4 centimeters. Connection to the vacuum and loading system was made through E, which was silver soldered to C. The truncated cones (A and A') were of transparent fused quartz, the end faces being polished plane, parallel to each other and perpendicular to the axis of symmetry of the

steel tube. A and A' were carefully ground into their respective tapers in the steel tube by carrying out the preliminary grinding in several replicas of the tapers of the steel tube. The final light grinding was done in the steel tube tapers. The larger faces of the quartz cones were about 8 millimeters in diameter, the taper was about 3° and the height of the truncated cone about 1 centimeter. A number of unsuccessful attempts to produce a tube of this design capable of withstanding a pressure of 500 atmospheres resulted from non-uniform contact between the steel and quartz. In these cases the windows were shattered or so pulverized internally as to become practically opaque upon application of pressure. Inasmuch as the windows are displaced about 0.5 mm. as the pressure is raised to 500 atmospheres, it is very essential that the peripheries of the faces be round chamfered to prevent chipping. The windows were pressed firmly into the steel tapers covered with molten "piccin," and tested with an oil injector. During the testing most of the "piccin" was extruded, leaving a bright metallic contact surface. The tubes were vacuum tight and could be evacuated so that the pressure rose to only 0.001 millimeter of mercury on standing overnight. The steel absorption tube was of sufficiently small outside diameter to fit into the tubulation of the quartz Dewar tube mentioned above.

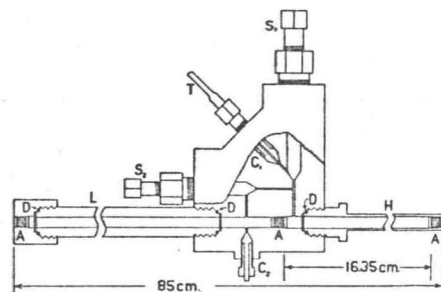


Fig. 3.

A special tube (III) was built for studying Beer's law at high pressures. The general construction was as described for steel tube II. Figure 3 shows a steel absorption tube with three quartz windows (A) affording two absorption chambers of the same internal diameter in tandem. Connection to the vacuum and loading system was made through T, with steel stopcock S₁. The fluid contained in the shorter tube (H) could be expanded to fill both chambers (H and L) with opening stopcock S₂. This afforded a considerable change in density of the fluid accompanied by only a slight change in the amount of matter in the light path. The sum of the internal lengths of the absorption chambers was 81.97 centimeters and the internal length of the short absorption chamber was 16.35 centimeters. The ratio of these lengths was 5.013 and the ratio of the corresponding volumes about 3% less. This tube will be referred to as the double steel tube.

Argon

Shaver² found that a column of gas at 140 atmospheres' pressure and 35 centimeters long containing 80% argon and 20% nitrogen was transparent

² W. W. Shaver, *Trans. Roy. Soc. Canada*, 16, III, 135 (1922).

from 7000 to 2150 Å. E. Meyer³ believed that his measurements showed a slight absorption in the ultraviolet due to gaseous argon at low pressure. Dolezalek,⁴ from a study of the vapor pressures of mixtures of argon and nitrogen, concluded that liquid argon contained a considerable proportion of A₂.

Liquid argon was examined, since any absorption that might be found would be that of an aggregate and thus of considerable interest.

Procedure.—The argon, supplied in a glass bulb, by the Research Laboratory of the General Electric Company, was specified to be of a high purity. It was manipulated in a glass vacuum line by the use of liquid air at reduced pressure and distilled into the quartz absorption tube (I) in the tubulated Dewar flask containing liquid air.

Results and Discussion.—Liquid argon at about -180° and 135 centimeters of mercury pressure was examined from 6780 to 2450 Å. Argon, as a glassy solid at about -190° and 20 centimeters of mercury pressure, was examined from 2490 to 2130 Å. No absorption was found. Accordingly, argon exercises no sensible selective absorption in the region examined, and if there is a general absorption it must be very small. If aggregates form in appreciable quantity, their absorption does not lie within this spectral region.

Methane

Glockler⁵ found a length of 54 centimeters at atmospheric pressure of methane to be transparent to 2400 Å. Dennison and Ingram⁶ found a length of 10 meters of methane at 70 centimeters pressure of mercury to have one absorption band (8800 to 9000 Å.) in the region from 6500 to 9500 Å.

For this investigation the methane was prepared by the method of Keyes, Smith and Joubert⁷ and loaded into the short steel tube (II). The methane was examined at a pressure of 400 atmospheres at 20° from 6900 to 2150 Å. It was also examined at this concentration, but at a temperature just above that of the disappearance of the liquid phase, from 4500 to 3240 Å. No absorption was found and the conclusions are identical with those for argon.

Acknowledgment.—I wish to thank Professor F. G. Keyes under whose guidance this work was carried out, Dr. R. H. Gerke who suggested the problem, and Professor Louis Harris for his assistance.

Summary

Apparatus for the examination of the absorption spectra of liquefied

³ E. Meyer, *Verhandl. deut. physik. Ges.*, 2, 362 (1904).

⁴ F. Dolezalek, *Z. physik. Chem.*, 93, 585 (1918-1919).

⁵ G. Glockler, *Proc. Nat. Acad. Sci.*, 11, 71 (1925).

⁶ D. D. Dennison and S. B. Ingram, *Phys. Rev.*, 36, 1451 (1930).

⁷ Keyes, Smith and Joubert, *J. Math. Phys., Mass. Inst. Tech.*, 1, 192 (1922).

gases at low temperatures and of fluids up to 500 atmospheres in the visible and quartz ultraviolet has been described.

Argon and methane have been found to be transparent at high concentration in that spectral range.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 280]

THE TRANSMISSION OF LIQUID CARBON DIOXIDE

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RECEIVED NOVEMBER 24, 1931

PUBLISHED MAY 7, 1932

Preliminary measurements by one of us¹ seemed to indicate a continuous absorption of ultraviolet light by liquid carbon dioxide at room temperature. These measurements were made with the short steel absorption tube.² The double steel tube,³ in which the product of length times density was the same through the liquid and gaseous carbon dioxide, gave the same results. When liquid carbon dioxide filled the short arm (16.35 cm.), there was absorption below 3000 Å.; when this liquid was expanded to a gas so that the original mass was distributed over a length of 81.97 cm., no absorption was observed. Upon recondensing this carbon dioxide to a liquid in the short arm, the absorption reappeared. The conclusion seemed inevitable that some molecular species, probably $(\text{CO}_2)_n$, was present in large quantity in the liquid carbon dioxide and absorbed in the ultraviolet. However, after the short arm of the double steel tube had been flushed with liquid carbon dioxide a number of times and the carbon dioxide given more careful purification, the results could not be duplicated. The absorption in the liquid carbon dioxide seemed to be a strange function of the density and eventually disappeared abruptly except perhaps for a slight continuous absorption below 2500 Å. Liquid carbon dioxide containing water (introduced intentionally) showed a slight absorption (beginning around 2650 Å.) which disappeared on vaporizing. (The accuracy of these early measurements was not better than about 10%.) It was necessary to conclude that the absorption in the liquid was due to some dissolved impurity. Whether the impurity causing the absorption was picked up in the absorption tube or was present in the gas originally introduced has not been settled by this work.

Shortly after this phase of the work had been completed, an article by Harig³ appeared on the ultraviolet absorption of liquid carbon dioxide. His results were similar to our early experience except that he found

¹ B. J. Eiseman, Jr., Ph.D. Thesis, M. I. T., 1927.

² B. J. Eiseman, Jr., THIS JOURNAL, 54, 1778 (1932).

³ Harig, *Physik. Z.*, 30, 8 (1929).

even more absorption in liquid carbon dioxide. A two-millimeter length of liquid carbon dioxide was sufficient to absorb nearly all radiation below 2600 Å. He found no absorption in a 110-cm. layer of gaseous carbon dioxide at 60 atmospheres. No matter what the conditions of temperature or pressure might be, he found absorption as long as liquid carbon dioxide was present and none through the gaseous carbon dioxide. He concluded that a polymer $(\text{CO}_2)_n$ was present in the liquid carbon dioxide. In the light of our later experience it seemed very certain that Harig was measuring the absorption of some impurity soluble in liquid carbon dioxide. We decided to repeat our measurements in such a way as to avoid all contact of carbon dioxide with grease, oil or any other substances likely to be dissolved by carbon dioxide and thus try to check our later measurements independently.

Preparation of Carbon Dioxide.—Carbon dioxide was prepared by heating sodium bicarbonate. Most of the water was removed by cooling and the last traces of water removed with phosphorus pentoxide. The carbon dioxide was sublimed very slowly three times, first and last portions being discarded each time. The carbon dioxide was stored in large glass bulbs connected to a quartz spiral manometer. Carbon dioxide was introduced from the bulbs into the absorption tube by breaking a tip in a glass valve. (All valves were of this type.) The carbon dioxide was never in contact with grease, cements, or metal.

Apparatus and Manipulation.—The "low temperature" absorption tube² was used for these measurements. Instead of blowing nitrogen on the windows to prevent frost, it was found much more advantageous to add two extra quartz windows to the absorption tube after it had been assembled in the tubulated Dewar tube. The spaces between these extra windows and the windows of the absorption tube were evacuated. There was never any tendency for frost to form on the windows although the body of the absorption tube was kept at -50° for hours. In order to determine the transmission of the absorption tube empty, the lead from the absorption tube was connected to a trap in which the carbon dioxide could be frozen. The absorption tube with this trap attached was sealed off from the pumping system and carbon dioxide reservoir after sufficient (calculated from the known volumes and the change in pressure) carbon dioxide had been loaded into the trap. This arrangement permitted many observations of the transmission, with the tube full or empty, to be made with one sample of carbon dioxide without changing the position of the absorption tube. Solid carbon dioxide-alcohol was the refrigerant used in the tubulated Dewar surrounding the absorption tube, while liquid air was used for freezing out the carbon dioxide in the adjoining trap. At the carbon dioxide triple point (-56.6°) the pressure is 5.2 atmospheres and since it was necessary to make measurements at more elevated temperatures, it was gratifying to find that the absorption tube would withstand pressures up to 10 atmospheres.

The absorption of liquid carbon dioxide was determined at -51° . Although the length of this absorption tube (1.5 cm.) was about one-tenth the length we used previously (ten times the length of the tube used by Harig) the increased density and the lower temperature would certainly favor the formation of carbon dioxide aggregates.

Spectrograms were made with the tube empty and the tube full using a Hilger E 315 spectrograph. A hydrogen discharge tube served as a source