

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,  
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## THE TRANSMISSION OF LIQUID CARBON DIOXIDE

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RECEIVED NOVEMBER 24, 1931

PUBLISHED MAY 7, 1932

Preliminary measurements by one of us<sup>1</sup> 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.<sup>2</sup> The double steel tube,<sup>2</sup> 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 (CO<sub>2</sub>)<sub>n</sub>, 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 Harig<sup>3</sup> appeared on the ultraviolet absorption of liquid carbon dioxide. His results were similar to our early experience except that he found

<sup>1</sup> B. J. Eiseman, Jr., Ph.D. Thesis, M. I. T., 1927.

<sup>2</sup> B. J. Eiseman, Jr., THIS JOURNAL, 54, 1778 (1932).

<sup>3</sup> 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  $(\text{CO}_2)_x$  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 tube<sup>2</sup> 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  $-50^\circ$  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 ( $-56.6^\circ$ ) 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  $-51^\circ$ . 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

of light. The plates were photometered with the aid of microphotometer lent by Professor G. R. Harrison. The accuracy of the final measurements was within a few per cent. No absorption was observed from 6000 to 2150 Å.

**Note.**—The last filling of the double steel tube with carbon dioxide was in December, 1928. It was left in January, 1929, with liquid carbon dioxide in the shorter arm. In January, 1931, the amount of liquid was still the same as when it was left two years earlier.

### Conclusions

Liquid carbon dioxide (1.5 cm. layer) at  $-51^{\circ}$  has been found to be transparent to the visible and quartz ultraviolet. A 16.35-cm. layer of liquid carbon dioxide at room temperature was also found to be transparent except perhaps for a slight continuous absorption below 2500 Å.

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[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES AT PITTSBURGH]

## THE KINETICS OF GAS EXPLOSIONS. II. THE THERMAL REACTION BETWEEN OZONE AND HYDROGEN BROMIDE<sup>1</sup>

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RECEIVED NOVEMBER 30, 1931

PUBLISHED MAY 7, 1932

It was suggested<sup>4</sup> that the oxygen atom and an active oxygen molecule are the carriers in the reaction chains involved in the thermal decomposition and explosion of ozone sensitized by bromine vapor.<sup>4,5</sup> In an attempt to detect the presence of free oxygen atoms during this reaction, hydrogen bromide<sup>6</sup> was added to the mixture, since it is known to react easily with the former.<sup>7</sup> It was found, however, that ozone reacts with pure hydrogen bromide so rapidly that the chains in the ozone-bromine reaction are dwarfed in comparison with the fast and long chains in this new ozone-hydrogen bromide reaction.

<sup>1</sup> Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.) Read before the American Chemical Society, Buffalo, Sept., 1931.

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<sup>4</sup> Part I. Lewis and Feitknecht, *THIS JOURNAL*, **53**, 2910 (1931).

<sup>5</sup> Lewis and Feitknecht, *Z. physik. Chem. Bodenstein-Festband*, 113 (1931). See also Lewis and Schumacher, *ibid.*, **138A**, 462 (1928); **6B**, 423 (1930); *Z. anorg. Chem.*, **182**, 182 (1929); *Z. Electrochem.*, **35**, 651 (1929).

<sup>6</sup> Lewis and Feitknecht, *THIS JOURNAL*, **53**, 3565 (1931). The effect of hydrogen will be described elsewhere.

<sup>7</sup> Harteck and Kopsch, *Z. physik. Chem.*, **12B**, 327 (1931).