EISE-BJ 32-0018



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.

MELBOURNE, VICTORIA, AUSTRALIA

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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 METHANE[1]

BY B. J. EISEMAN, JR.

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 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.

[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.



**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.

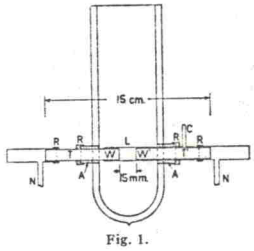

Fig. 1.

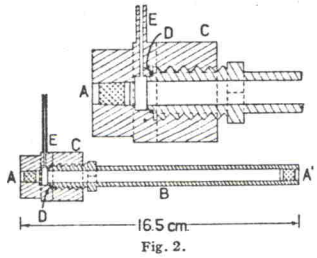

Fig. 2.

Steel absorption tubes with fused-quartz windows were used for the examination of gases at high pressures. In Fig. 2 the tube II was of high tensile strength machine steel. It consisted of two parts (B and C) which could be screwed together. The longer section (B) had an outer diameter of 11 millimeters and a bore of 7.3 millimeters. The bore was tapered at one end to take one of the windows (A′). The other window (A) was in a hexagonal cap (C). An aluminum washer, D, the cross section of which was 1 millimeter square, rendered the tube tight when compressed 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