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STUDIES ON THE RATE OF OXIDATION OF NITRIC OXIDE

I. A NEW METHOD OF MEASURING THE VELOCITY OF A RAPID GASEOUS REACTION

BY MAX LATSHAW[1] AND WALTER A. PATRICK

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A search of the literature shows the need of an improved method for the study of the kinetics of rapid gas reactions. Investigators in this field have confined their attention largely to reactions that proceed at moderate rates. In fact, practically all of the reliable data that we have are for this class of comparatively slow reactions. We have been interested in measuring the velocity of the reaction of nitric oxide and oxygen; it is very rapid, especially at the lower temperatures, 0–30°, since it possesses a marked negative temperature coefficient. Bodenstein[2] developed an apparatus for the study of this reaction, following its course by direct reading of the pressure changes as indicated by an α-bromonaphthalene manometer. He realized that his results at 0° were subject to considerable error. It is very desirable to study the reaction at short time intervals in the beginning when it is progressing very rapidly. This was not possible in Bodenstein's work due to (1) the uncertainty of zero time and (2) his inability to make direct readings of the rapidly moving manometer meniscus. In many cases, the reaction had proceeded 20–30% to completion before the first reliable reading was taken. A careful study of the reaction in the first few seconds should help us to settle the question as to the occurrence of autocatalysis.

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[1] The apparatus described in this paper is the result of the joint work of Drs. Latshaw and Hasche. Dr. Latshaw built the first form of the apparatus with which the measurements reported at the meeting of the American Institute of Chemical Engineers, Dec. 11, 1924, were made. Dr. Hasche then reconstructed the apparatus, making a number of important improvements.

[2] Bodenstein, *Z. Elektrochem.*, **24,** 183 (1918).

It occurred to us that an apparatus could be devised to record the pressure changes (as indicated by a liquid manometer) on a photographic film at much shorter time intervals than would be possible by direct reading of the manometer. After much experimenting, the apparatus was developed which is described in this article; the results given in the second article indicate the possibilities of the apparatus and technique in the study of rapid gaseous reactions accompanied by a change in the number of molecules. The apparatus is somewhat similar to that employed by Bodenstein,[2] being modified so as to allow of a rapid flow of the reacting gases into the reaction chamber.

Apparatus

The experimental method used was the manometric-volumetric; the volume was kept constant and the pressure change followed by photographing an α-bromonaphthalene manometer. The apparatus, exclusive of the timing mechanism and camera, is shown in Fig. 1.

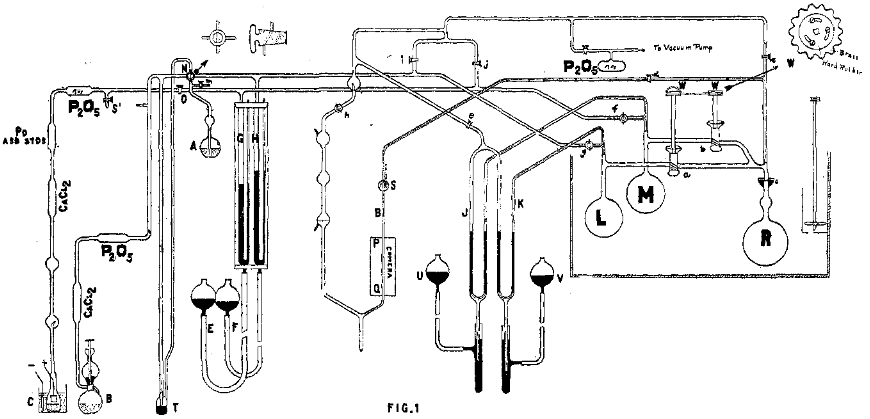

FIG. 1

The oxygen was generated electrolytically in the cell (C) with platinum electrodes and dil. sulfuric acid as the electrolyte. The gas passed over freshly prepared palladium asbestos to remove traces of hydrogen and was dried by phosphorus pentoxide. It was delivered at Stopcock O. Previous to using the oxygen for an experiment, it was generated for several days and liberated through Stopcock S. The generator worked on the Kipp principle, automatically cutting off the current when the pressure in the anode compartment became slightly more than atmospheric.

The nitric oxide was generated slowly and continuously in (B) from the interaction of mercury on lead chamber crystals dissolved in sulfuric acid. The nitrosyl sulfuric acid was made by passing sulfur dioxide gas through fuming nitric acid cooled by ice water. The crystals were filtered by suction through an alundum crucible, washed with a little glacial acetic acid and then freely with carbon tetrachloride. They were dried in a vacuum desiccator over sulfuric acid. The nitric oxide generator was first evacuated through Stopcock N; then by turning the ground glass stopper of the generator, mercury could be introduced into the nitrosyl sulfuric acid solution. A few drops of mercury added every few days insured the continuous flow of a stream of nitric oxide. The gas was dried over calcium chloride and phosphorus pentoxide. When nitric oxide was not being used, the 4-way Stopcock N was closed to the rest of the apparatus and the nitric oxide bubbled through the mercury trap (T) and out through the sulfuric acid bottle at (A). The latter served as a trap allowing an exit for excess of nitric oxide and preventing entrance of air. The mercury trap (T) protected (A) during evacuation.

The purity of the nitric oxide was tested by drawing off samples at the 3-way Stopcock M. The gas was analyzed by the method of Moser,[3] using a strong solution of potassium permanganate acidified with sulfuric acid as the oxidizing and absorbing liquid. The residual gaseous impurities amounted to less than 0.5%.

The leveling burets (G) and (H) were used to regulate the pressure of oxygen and nitric oxide in their respective storage bulbs (M) and (L). The burets could be evacuated through Stopcocks j and i and were connected to the storage bulbs through Stopcocks f and g.

The nitric oxide and oxygen storage bulbs (L) and (M) and the reaction chamber (R) were immersed in a thermostat kept constant to ±0.01°. The water line extended up to the mercury seals of the large Stopcocks a and b; the glass tubing above the water line was all capillary. Gas pressures in the storage bulbs were read by a cathetometer from the Y-shaped manometers (J) and (K). The right limb of each manometer was capillary over a part of its length as shown in the figure; the left limbs were open to the vacuum through Stopcock e. When a pressure reading was made on either manometer, the mercury in the right limb was always brought to the same mark just below the capillary by means of the leveling bulbs (U) and (V). Thus a constant, known volume was always maintained. The storage bulbs could be evacuated either through Stopcocks f, g, i and j or through a, b and c. The bulbs were connected directly to the reaction chamber (R) by specially designed mercury-sealed vacuum stopcocks of 6 mm. bore; the ends of the keys were square to accommodate brass sprocket wheels, the design of which is shown in detail at (W). The sprockets were adjustable to one-half the width of a tooth and were connected by a brass ladder chain. The whole mechanism made it possible to open and close the two stopcocks synchronously, and the tubing of 6 mm. bore permitted a very rapid flow of the gases into the reaction chamber.

The large and small surface reaction chambers could be connected with

[3] Moser, *Z. anorg. Chem.*, 121, 313 (1922).

the apparatus by the mercury-sealed normal grindings at (n). They were of approximately the same capacity, the large surface vessel being filled with very fine glass wool. Pressure in the reaction chamber was followed by the α-bromonaphthalene manometer (B) through Stopcock d. The recording part of the manometer on the right limb was thin-walled, 3 mm. tubing calibrated in millimeters on a dividing engine. Every tenth division was omitted so as to aid in reading the scale from the film. The camera is not shown in Fig. 1; it was a light-tight box enclosing the manometer between (P) and (Q). The difference in height of the left limb of the manometer was negligible because of the large volume of α-bromonaphthalene in the bulb. The other bulbs could be used for work at higher pressures and also served as very effective traps, in case the pressure on the right side of the manometer was excessive due to accidental opening of Stopcock d to atmospheric pressure while Stopcock h was closed. Since the coefficient of expansion of α-bromonaphthalene is very large (0.0015 per degree), its temperature at the time the measurements were made must be known. Its temperature was read on the thermometer (S) dipping into a plaster of paris well, filled with mercury.

The oxygen storage bulb was calibrated by mercury before sealing into the apparatus. The nitric oxide bulb and two reaction chambers were calibrated from the oxygen bulb by expansion of gas from the latter into the others, and the pressure changes recorded by the mercury manometers gave all the data required to calculate the unknown volumes by making use of the gas laws. The α-bromonaphthalene served as check on the mercury manometers.

The timing mechanism and camera are shown in Fig. 2. Exposures of the manometer were made on a circuit film which was mounted on the drum of a kymograph. The kymograph was enclosed in a box, light-tight with the exception of a narrow slit formed by two wooden strips holding the manometer. The shutter (S) was an aluminum tube open at the opposite ends of the diameter. This was free to rotate on shafts fitting into bearings at either end. At the top of the shutter, a clock-spring movement produced a spinning tension on the cylinder when the escapement (R) was released by a current through the electromagnet (e). The double-dog escapement lever allowed the cylindrical shutter to rotate through only an angle of 180° for each impulse through the electromagnet. By this arrangement the wide aperture of a focal plane shutter was obtained. The time of exposure was about $^1/_{25}$ of a second.

An Eastman timer served as the movement for the interval timer. Around the dial of the clock was a Bakelite plate turned on a lathe to the form shown in the diagram in Fig. 2. Thirty holes 2.5 mm. in diameter were drilled for a distance into the inner rim of the plate; opposite these on the outer, raised rim thirty holes 5 mm. in diameter were drilled to the same depth as the first set. Each pair of holes was connected by a third drilled at right angles and the outer opening closed with a set screw. In the diagram of (T) in Fig. 2, a cross section through a mercury well shows the construction.

Electrical connection was made through the induction coil (C), actuating the camera shutter, when the hand of the clock (itself connected to one pole of the battery) passed through a mercury drop on the inner rim of the timer plate. The current flowed through the mercury trough to the resistance box type plug which dipped into the mercury. The plug made connection with the brass ring (B) which was connected to the other pole of the battery. By inserting plugs at the time intervals desired, exposures were made automatically on the rotating film. The plugs were drilled at the ends and piano wire contacts driven into them. The piano wire insured good contact and prevented amalgamation of the brass. The other contact with the mercury was made by the platinum tip soldered to the second hand of the clock. The amount of mercury in the wells could be so regulated that the tip of the second hand passed through the globule only when a plug had been inserted, thus raising the level of the mercury by a very small amount. Three cells of an Edison storage battery worked the timer circuit, and the electromagnet operated on the 110-volt d. c. line through the lamp bank (L).

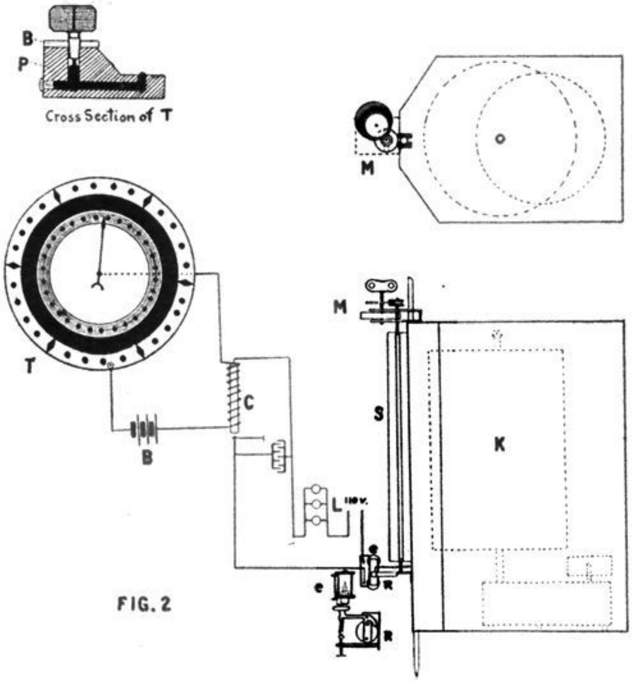

FIG. 2

An arc lamp operating on the 110-volt d. c. line and using 5 amperes furnished the illumination for the α-bromonaphthalene manometer. A mirror reflected a narrow beam of light of even intensity on the shutter.

Method of Measurement

The apparatus exclusive of the gas generating systems was evacuated to 0.003 mm. preliminary to making a run. Great care was necessary to evacuate both sides of the manometers at the same rate, otherwise the manometer liquid might be thrown into the storage bulbs or reaction chamber. After evacuation, all stopcocks except (f) and (g) were closed. Oxygen was admitted to the storage bulb by carefully opening Stopcock O. When approximately the desired pressure was obtained, Stopcock O was closed and a finer adjustment was made by raising or lowering the leveling bulb (E). Stockcock f was then closed, and after bringing the mercury to the calibration mark on the right limb by means of the leveling bulb, the pressure was read by the cathetometer. The same procedure was followed with the nitric oxide, admitting it through the 4-way Stopcock N. After the pressures of the oxygen and nitric oxide had been read and recorded, the zero of the α-bromonaphthalene manometer was read and also a reference mark which was etched on the graduated manometer scale within the range of pressure change as recorded on the film. The temperature of the α-bromonaphthalene was also read.

The room was darkened and the film 20 cm. in width mounted on the kymograph, the end of the film being fastened with adhesive tape. The kymograph was placed in the camera box with the drum at the proper focal distance from the manometer. It was started rotating by throwing the release lever, the camera closed and the arc lamp and clock started. At one second before zero time, the mechanism for the turning of Stopcocks a and b was set in motion. It required about three seconds for the whole operation of opening and closing, although the actual period during which the keys were open to the reaction chamber was never more than one second. No back diffusion occurred in any of the experiments and in the majority of the cases equilibrium was attained. No attention to the apparatus was required during a run unless the time intervals were lengthened, when plugs were removed from the timer. Exposures on the film could be made as close together as 3 mm. which gave a continuous picture of the manometer with no intervening spaces. The length of the runs varied from four minutes to fifteen, depending on the frequency of exposures and the temperature at which we were working.

When the run was completed, the film was developed immediately and the pressures of the residual gases in the storage chambers read on the mercury manometers. The difference between the initial and final readings gave a means of calculation of the initial pressures of oxygen and nitric oxide, since the volumes of the storage bulbs and reaction chamber were known. The system was immediately evacuated.

Several possible sources of error which we have considered as negligible should be mentioned. In the first place, we have assumed that there is no change of volume of the reaction chamber due to the manometer. This assumption is justifiable since the maximum change in volume due to the manometer was about 0.9 cc. which is less than the experimental error in the calibration of the reaction chamber by the gaseous expansion method. We have assumed that the heat of the reaction was not sufficient to affect the temperature of the reaction mixture and hence alter the observed velocity. This was verified by sealing a thermometer into a reaction chamber and introducing the reacting gases under actual experimental conditions. The maximum rise in temperature occurred in the first minute and was only 0.3°, which is negligible. Finally, the α-bromonaphthalene manometer was almost instantaneous in its response to pressure changes within the system. None of the photographs obtained in the investigation given in the second paper shows any evidence of a lag.

Summary

An apparatus has been described which is capable of measuring accurately the velocity of a rapid gaseous reaction.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

STUDIES ON THE RATE OF OXIDATION OF NITRIC OXIDE[1]

II. THE VELOCITY OF THE REACTION BETWEEN NITRIC OXIDE AND OXYGEN AT 0° AND 30°

BY R. LEONARD HASCHE AND WALTER A. PATRICK

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A number of investigators have studied the kinetics of the reaction between nitric oxide and oxygen. It was the subject of a long controversy between Raschig and Lunge. They used similar experimental methods, absorbing the reacting gaseous mixture in sodium hydroxide or sulfuric acid and titrating the amount of nitrogen dioxide formed with potassium permanganate. Raschig claimed experimental evidence pointing to the formation of nitrogen trioxide as an intermediate product; while Lunge's results indicated that nitrogen dioxide was formed directly, strictly in accordance with the law of a third-order reaction. Raschig's view regarding the intermediate, nitrogen trioxide, is also held by Briner and co-workers,[2] and by Jolibois and Sanfourche.[3] That the reaction possesses a small, but marked, negative temperature coefficient was first noted by Foerster and Blich.[4] Recently, Briner, Pfeiffer and Malet[5] have studied the reaction at low temperatures, down to —193°; Bodenstein,[6] in 1918, worked at the temperatures 0°, 30°, 60° and 90°; later, Bodenstein and Linder[7] con-

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[1] The material in this article is taken from a dissertation submitted by R. Leonard Hasche in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Johns Hopkins University.

[2] Briner and Fridori, *J. chim. phys.*, **16**, 279 (1918). Briner and Fridori, *Helvetica Chim. Acta*, **16**, 181 (1918). Briner, Niewiazski and Wiswald, *J. chim. phys.*, **19**, 290 (1921).

[3] Jolibois and Sanfourche, *Compt. rend.*, **168**, 235 (1919). Sanfourche, Bl, **25**, 533, 646 (1919).

[4] Foerster and Blich, *Z. angew. Chem.*, **23**, 2017 (1910).

[5] Briner, Pfeiffer and Malet, *J. chim. phys.*, **28**, 25 (1924).

[6] Bodenstein, *Z. Elektrochem.*, **24**, 183 (1918).

[7] Bodenstein and Linder, *Z. physik. Chem.*, **100**, 87 (1922).