15,680 calories; change in free energy per degree, or entropy change, 4.8; heat of formation at 25°, 14,354 calories.

8. The bearing of these data on some earlier attempts to verify the Third Law of Thermodynamics is discussed.

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

NOTE ON MEASUREMENTS OF THE RATE OF DECOMPOSITION OF NITROGEN PENTOXIDE AT VERY LOW PRESSURES[1]

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Introduction

The decomposition of nitrogen pentoxide is one of the most interesting and most extensively studied of the few known unimolecular reactions. Data on the rate of its decomposition are of great importance to the advancement of our knowledge of the mechanism of chemical reaction.

Although the decomposition of nitrogen pentoxide has finally been shown to be strictly unimolecular over a considerable pressure range,[3] the measurements of Hirst and Rideal[4] would seem to indicate a quite unexpected increase in the specific rate of decomposition at very low pressures. These authors state that, after a critical consideration of their data, they are of the opinion that the increase is real and outside of the experimental uncertainty. Just preceding the presentation of our data, Hibben,[5] by a method similar to Hirst and Rideal's, the details of which are not given, fails to agree with Hirst and Rideal and concludes that the normal rate obtains down to very low pressures.

Since Hirst and Rideal's result is totally unexpected and requires a unique theoretical treatment,[6] it was thought advisable to repeat these measurements by the method which would avoid or at least detect the presence or absence of what seemed to us some objectionable features in Hirst and Rideal's experiments. Especially does this seem desirable since another investigator, using a method similar to Hirst and Rideal's, has obtained a totally different result.

The possible objections to Hirst and Rideal's method that occurred to us were the following. First, unless the apparatus were of proper design,

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[3] Daniels and Johnston, THIS JOURNAL, **43**, 53 (1921); Lueck, *ibid.*, **44**, 757 (1922); Hunt and Daniels, *ibid.*, **47**, 1602 (1925); White and Johnson, *ibid.*, **47**, 1240 (1925).

[4] Hirst and Rideal, *Proc. Roy. Soc. London*, **109A**, 526 (1925).

[5] Hibben, *Proc. Nat. Acad. Sci.*, **13** (8), 626 (1927).

[6] See Thomson, *Phil. Mag.*, **269**, (7), 241 (1927).

the condensation of a heavy gas in the presence of a noncondensable gas might be a relatively slow and incomplete process even at low pressure. Second, condensation of the heavy gas might involve a considerable amount of occlusion of the lighter gas. Third, adsorption effects, which would be inappreciable at high pressures, might at low pressures be relatively large compared to the total amount of gas present.

Experimental Method

The authors' apparatus and experimental procedure may be understood by reference to Fig. 1. The nitrogen pentoxide prepared in the usual way by dehydrating pure nitric acid with phosphorus pentoxide, was first distilled into a receiver (not shown in the figure) cooled by ice and salt. A small part of this, as needed, was distilled in a stream of dry ozone into the tube *a*, which was kept cold. The purified crystals in *a* were then pumped off at 0 and −20° by means of an oil pump connected through a liquid-air trap. They were then pumped off at −100° with a mercury diffusion pump. After the whole apparatus had been thoroughly baked and pumped out with the diffusion pump until a spark discharge gap showed perfectly dark (pressure $< 10^{-5}$ mm.), the tube *a* was brought to 0° and the pipet *c* kept at about 1° while the latter was filled with nitrogen pentoxide at its vapor pressure at 0° (50 mm.). The volume of the pipet *c* was such as to give the required pressure when its contents were admitted to the 5-liter flask *g*. The nitrogen pentoxide from the pipet was allowed to pass over and condense in the U-tube *f*, which was cooled by liquid air. After sufficient time had elapsed to allow complete condensation in the U-tube, the apparatus was evacuated again through the stopcock *d* while the tube was sealed off at *e*. At no time did the spark gap show the presence of any oxygen at this point.

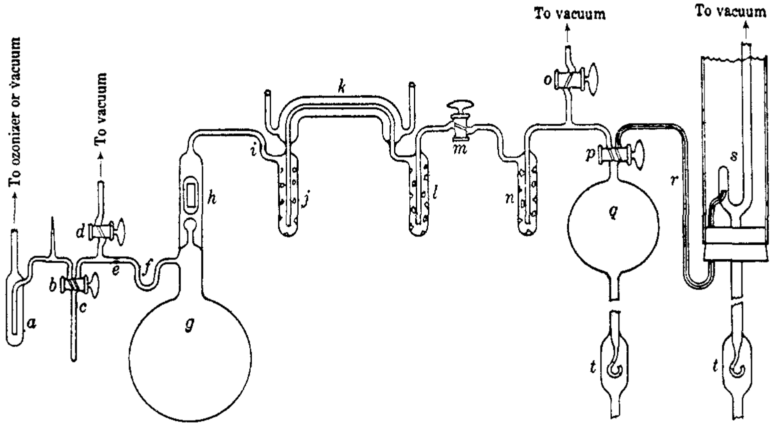

Fig. 1.—Diagram of apparatus.

The 5-liter flask *g* was provided with a thin glass bulb by means of which communication could be established with the rest of the apparatus by applying a magnet to raise and lower the piece of iron enclosed in a glass tube at *h*, thus breaking the thin bulb. The flask *g*, after removal of the liquid air from the U-tube, was placed in a thermostat at 30.00°, at which temperature nitrogen pentoxide decomposes at a convenient rate. During the time the decomposition of the nitrogen pentoxide was taking place, the flask was sealed onto the rest of the apparatus, and the connecting tubes were baked out and thoroughly evacuated with the diffusion pump. The small glass tubes *j*, *l* and *n* are filled with glass beads to serve as condensers; *k* is a jacket through which cold air could be passed to prevent decomposition of nitrogen pentoxide if it was desired to distil the nitrogen pentoxide back and forth between *j* and *l*.

After an experiment the oxygen was pumped out of *g* by means of a large (2-liter) Toepler pump *q*, the heavy gases being retained in the liquid-air condensers *j* and *l*. The oxygen was delivered from the Toepler pump into the calibrated pipet *s* containing mercury and surrounded by a jacket filled with water at a uniform temperature. Pressures and volumes were measured in the pipet by means of a high-grade cathetometer. Air traps were provided, as at *t*, wherever there was danger that air might be carried into the apparatus by the mercury. Great care was taken to pump out thoroughly every part of the apparatus and to avoid subsequent entrance of traces of air. Points on the apparatus where seals were later to be made were always previously heated to the softening temperature and pumped off in order to avoid driving out gas from the glass during sealing.

After the flask *g* was pumped out, it could be sealed off at *i*. The total nitrogen pentoxide present was determined by closing the stopcock *m* and heating the condensers to decompose all the nitrogen pentoxide. The resulting oxygen was then pumped over into the pipet *s* as before, a third liquid-air trap at *n* assuring that no heavy gases escaped into the Toepler pump.

Adsorbed gas in *g* could be obtained by heating and further pumping. Occluded gas in the traps *j* and *l* could be obtained, after sealing off at *i*, by distilling the condensate back and forth between *j* and *l* and pumping off the gas so liberated.

Experimental Results

Experiment 1.—As a check on our method, an experiment was made first at moderate pressure. The oxygen from the decomposition that took place in seventy minutes at a temperature of 30.00° occupied a volume of 3.2909 cc. at a pressure of 104.22 mm. and a temperature of 26.59°. The oxygen from complete decomposition had a pressure of 366.81 mm. at the same volume and temperature. The reaction rate constant for the decomposition of nitrogen pentoxide is thus calculated from these data to be $k = 4.7 \times 10^{-3}$. Calculated from the experiments of Daniels and Johnston, the constant at high pressures is 4.1×10^{-3}. We considered this agreement to be as close as could be expected. The original pressure of nitrogen pentoxide in the 5-liter flask in this experiment was thus about 0.25 mm.—the pressure below which Hirst and Rideal state that the constant begins to increase. The total oxygen obtained is roughly that which we expected from the amount of nitrogen pentoxide injected into the reaction flask.

Experiment 2.—An experiment was next made at a pressure which, judging from Hirst and Rideal's results, would be low enough to effect a marked increase in the rate of decomposition. Approximately 1.4 cc. of nitrogen pentoxide at a pressure of about 50 mm. was put into the reaction flask. The results are as follows: time of reaction at 30°, 105 min.; oxygen from reaction, 0.7580 cc. at p = 12.90 mm. and t = 24.50°; oxygen from complete decomposition, 0.7580 cc. at p = 17.99 mm. and t = 24.50°. From the oxygen recovered, the pressure in the reaction flask is calculated to be 0.0055 mm. The rate constant from these data is 12×10^{-3}, which would seem to confirm Hirst and Rideal's results. However, the amount of nitrogen pentoxide calculated from the oxygen recovered is but about 40% of that actually put into the apparatus. This fact suggested the existence of adsorption or occlusion effects.

Experiment 3.—Experiment 3 was designed to determine the extent to which the heavy gases condensed in the two liquid-air traps had occluded oxygen. Approximately 1.0 cc. of nitrogen pentoxide at 50 mm. was injected into the 5-liter reaction flask: time of reaction at 30°, 102 min.; oxygen from the decomposition taking place in this time, 0.4908 cc. at p = 11.13 mm. and t = 26.33°; oxygen from complete decomposition of the nitrogen pentoxide, 0.4908 cc. at p = 13.53 mm. and t = 26.33° (includes preceding amount of oxygen); oxygen after repeatedly redistilling and pumping condensate, 0.4908 cc. at p = 16.73 mm. and t = 26.33° (includes both preceding amounts of oxygen). The oxygen occluded is thus about 24% of the oxygen which would otherwise be obtained. The total oxygen recovered would correspond to a pressure of nitrogen pentoxide in the 5-liter flask of 0.0033 mm. This is but 30% of the nitrogen pentoxide actually used.

Experiment 4.—An attempt was made to determine the amount of adsorption of nitrogen pentoxide in the 5-liter reaction flask. One cc. of nitrogen pentoxide at approximately 50 mm. was injected into the reaction flask. To show further that no nitrogen pentoxide had decomposed during its injection into the reaction flask, the apparatus was pumped out with the Toepler pump at this stage of the experiment, with the liquid air still in the U-tube f of Fig. 1. No oxygen was obtained. The liquid air was then removed from the U-tube, the apparatus having been provided with a stopcock at e in place of the seal at h. The flask was allowed to stand at room temperature for ten minutes. The stopcock was then opened to the liquid-air-cooled condensers j and l and the flask pumped out with the Toepler pump. The amount of oxygen obtained was 0.6100 cc. at p = 6.00 mm. and t = 27.04°. (At this point the reaction flask was heated with a flame and pumped out several times.) The oxygen obtained, including the previous amount, was 0.6100 cc. at p = 10.64 mm. and t = 27.04°. The stopcock at e was then closed and the remaining nitrogen pentoxide decomposed. The oxygen obtained, including both previous amounts, was 0.6100 cc. at p = 16.41 mm. and t = 27.04°. The nitrogen pentoxide adsorbed in the 5-liter reaction flask was thus 25% of the total accounted for nitrogen pentoxide.

Experiment 5.—Although it was not thought that oxygen would be appreciably adsorbed on the glass in the presence of the heavier gases, an experiment was made to determine the magnitude of adsorption effects with pure oxygen. Accordingly about 1.5 cc. of oxygen at 40 mm. was injected into the 5-liter flask, provided with a stopcock as before. After a few minutes' standing at room temperature, the oxygen was pumped out with the Toepler pump. The amount of oxygen obtained was 0.7300 cc. at p = 71.63 mm. and t = 26.41°. The additional amount of oxygen obtained by heating the 5-liter flask was v = 0.7300 cc. at p = 2.54 mm. and t = 26.41°. The stopcock at e

was then closed, the liquid air was removed from the condensers j and l, and the condensers were heated with a flame while the adsorbed oxygen was pumped out. An additional amount of oxygen was obtained from the condensers of 0.7300 cc. at p = 6.71 mm. and t = 26.41°. The oxygen adsorptions might be still smaller in the presence of the heavier gases.

Experiment 6.—In order to furnish a more conclusive demonstration that surface effects were causing the discrepancy, an experiment was made in the same reaction flask in which had been placed, after careful cleaning and drying, about 24 meters of tubing (of Pyrex glass the same as that of the reaction flask) of 3 mm. internal and 5 mm. external diameter, cut into 3.5-cm. lengths. This tubing increased the ratio of surface to volume in the reaction flask from 0.28 to 1.52 or about 5.4-fold.

The nitrogen pentoxide injected into the flask was 1.4 cc. at about 50 mm. The oxygen obtained after seventy-four minutes' decomposition at 30.00° was 0.5217 cc. at p = 1.55 mm. and t = 25.72°. The oxygen from complete decomposition of the nitrogen pentoxide caught in the condensers j and l was 0.5217 cc. at p = 3.19 mm. and t = 25.72° (including the previous amount of oxygen). The reaction velocity constant calculated directly from these data is 9×10^{-3}. The total oxygen recovered, however, corresponds to but 4.6% of the amount of nitrogen pentoxide injected into the reaction flask.

Discussion of the Results

Our data show that adsorption and occlusion effects involve a large fraction of the gas present at low pressures. It is likely that surface conditions changed during the course of the experiments and, since they were not well defined, the quantitative reproducibility of surface effects could not be expected. Experiment 6, however, aside from any quantitative data, conclusively shows the large part played by surface effects. Thus, with an increase of roughly 5-fold in the ratio of surface to volume, the amount of nitrogen pentoxide accounted for in our ordinary procedure was at most only about 15% of the usual recovery. We believe that the effect in this experiment is entirely outside of any possible experimental uncertainty.

Because of the conditions mentioned, we considered it inadvisable to attempt further work by this method on the reaction in glass apparatus at very low pressures. Some of the complications involved are the following: the reproduction of surface conditions and the necessary uniform treatment of the surfaces involved, in regard to heating and pumping off adsorbed gases, would be troublesome if not impossible; the measurement of oxygen adsorptions in the presence of nitrogen pentoxide at these temperatures could not well be accomplished; the amount of occlusion doubtless depends not only upon the quantities of gases present, but also on the rate of condensation of the heavy gas; the rate of decomposition of the nitrogen pentoxide which is attached to the walls of the apparatus is not known; and during the time taken to pump out the reaction flask the adsorbed nitrogen pentoxide would be decomposing and contributing an indeterminate amount of oxygen. We have therefore been content to demonstrate the existence of these effects without attempting to estimate quantitatively the true homogeneous rate of the reaction. However, although the application of corrections to the rate on the basis of our data is somewhat arbitrary, it seems likely that a reasonable account of these effects would tend toward giving about the normal rate of decomposition.

Although we do not know how different, if at all, these adsorption and occlusion effects were in the apparatus used by Hirst and Rideal and by Hibben, the presumption is that these effects were present to some degree in their experiments also. Results at these low pressures which do not take account of adsorption and occlusion effects when present we feel are fictitious, and we believe that the information previously obtained on the rate of decomposition of nitrogen pentoxide at very low pressures is open to serious question. Without knowing more of the details of the apparatus and procedure used by the other investigators, we are, of course unable to say in what way, if in any, their results may have been influenced by effects such as we found.

In the light of previous knowledge of adsorption phenomena, it is readily seen why adsorption does not appreciably affect experiments in which comparatively large quantities of gas are used. The nitrogen pentoxide adsorption is evidently that type which, at very low pressures, increases with increasing pressure only up to the point at which the surface becomes completely covered with adsorbed gas. Occlusion effects in any method involving condensation of the heavier gases might be appreciable, even at higher pressures; in fact, our first experiment seems to indicate this.

Summary

1. Objectionable features in previous methods for the study of the decomposition of nitrogen pentoxide at very low pressures have been pointed out and the reaction has been studied by a new method.

2. At very low pressures the adsorption of nitrogen pentoxide on the walls of our Pyrex glass apparatus and the occlusion of oxygen as the heavier gases are condensed have been shown to involve a large fraction of the total amount of gas present.

3. It is believed that experiments formerly thought to indicate an increased rate of decomposition of nitrogen pentoxide at low pressures are open to serious question, and that any experiments by the method hitherto used would yield fictitious results when adsorption and occlusion effects are present and not taken into account.

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