pressure, the loss in weight will not be appreciable until the temperature of 178° is reached. At this point ±2° the compound breaks down to form the diammonate. Analyses of the products obtained by heating copper selenate tetrammonate to a temperature of 185° in an atmosphere of ammonia gas at atmospheric pressure are in close agreement with the calculated values.

Anal. Calcd. for $CuSeO_4 \cdot 2NH_3$: CuO, 33.04; Se, 32.88; NH_3, 14.14. Found: CuO, 33.03; Se. 32.56; NH_3, 14.14 (all av. of 3 detns.).

The diammonate is a light blue powder. It corresponds somewhat to the BG normal tone of Mulliken's standards[12] and is insoluble in water but soluble in dilute mineral acids and ammonia solution. The compound is stable if preserved in a closed container. Below 178° the material absorbs ammonia to form either the tetrammonate or the pentammonate depending upon the temperature and pressure. Heated above 192° the diammonate is decomposed with the production of ammonia and a black residue which consists of a mixture of copper oxide and copper selenide. Selenium dioxide has been noticed in the cooler parts of the reaction tube when the temperature exceeds 200°.

Summary

1. Copper selenate pentammonate and copper selenate diammonate have been prepared and identified.

2. A new and satisfactory method for the preparation of copper selenate tetrammonate has been described.

3. No evidence was found for the existence of the tetrammonate dihydrate of copper selenate reported by Lange.

4. Copper selenate tetrammonate monohydrate, copper selenate tetraammonate and copper selenate triammonate monohydrate have been prepared according to the methods of Dennis and Koller. Analysis of the products indicates composition in accord with ascribed formulas.

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[Contribution from the Chemical Laboratory of the University of Illinois]

MOLECULAR RAY EXPERIMENTS. THE CHEMICAL ACTIVITY OF MOLECULAR AND ATOMIC OXYGEN[1]

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The initial purpose of this investigation was to find some chemical reaction by which the image of a beam of oxygen molecules could be formed on a target for a Stern–Gerlach experiment. The first attempts in this direction in this Laboratory were made at the time that the magnetic moment of atomic hydrogen was measured. It became evident[1c,d] at that

[1] Previous publications on molecular rays from this Laboratory are as follows: (a) Kunz, Taylor and Rodebush, *Science*, **63**, 550 (1926); (b) Taylor, *Phys. Rev.*, **28**, 576 (1926); (c) Phipps and Taylor, *Science*, **64**, 480 (1926); (d) Phipps and Taylor, *Phys. Rev.*, **29**, 309 (1927); (e) Rodebush, *Proc. Nat. Acad. Sci.*, **13**, 50 (1927); (f) Rodebush and Copley, *Phys. Rev.*, **33**, 1083 (1929); (g) Kurt and Phipps, *ibid.*, **34**, 1357 (1929); (h) Rodebush and Nichols, *ibid.*, **35**, 649 (1930); (i) Shaw, Phipps and Rodebush, *ibid.*, **35**, 1126 (1930).

time that there were certain interesting chemical problems in connection with the reactions of molecular rays and that, furthermore, molecular rays constitute an especially powerful method of studying heterogeneous reactions because it is possible with an inhomogeneous magnetic field to determine not only the molecular species that is reacting but the actual state of excitation as expressed by the spectroscopic term. For instance, the only absolute test for atomic hydrogen is the Stern–Gerlach experiment. The main purpose of this paper has been the investigation of the chemical activity of the various molecular species that can be produced in oxygen.

Molecular Oxygen.—Molecular oxygen reacts readily with the polished surfaces of certain metals, *e. g.*, copper, at slightly elevated temperatures and the film of oxide formed is readily visible. One interesting question which arises at once is: will the reaction take place between a beam of cold molecules and a hot surface or between a beam of hot molecules and a cold surface? In this connection it should be noted that the average temperature of a molecule beam is higher than the temperature of the gas in front of the source slit. The average kinetic energy normal to the surface of the molecules striking a surface is kT. If we interpose a slit system we select only the faster molecules, so that the average kinetic energy in the direction of the beam is now $2kT$. This process of selection lowers the effective pressure of the beam enormously, so that it is difficult to obtain beams with effective pressures greater than 10^{-6} mm. This pressure is often considerably less than the pressure obtainable with the best pumping conditions in the apparatus beyond the slit system and constitutes a serious limitation to the chemical activity.

The reactivities of cold surfaces of metallic silver, copper and sodium, phosphorus, indigo and a number of lower oxides, including those of lead and molybdenum, were tried without any observed result. In a number of trials the oxygen molecules were heated to temperatures of several hundred degrees centigrade. No reaction was observed in any case. It was thought that the oxide film might be difficult to observe and a copper target which had been exposed to a beam of oxygen molecules was exposed to mercury vapor. If a similar experiment is made with electrons, the spot which has been bombarded does not amalgamate[2] but complete amalgamation was always obtained with targets bombarded by oxygen molecules. It seems probable that the temperature of the surface itself must be raised in order to bring about a reaction with oxygen molecules. The part played by water in oxidation must not be overlooked. In the high vacuum the surfaces must be very dry and it is well known that in the case of sodium, for example, the presence of moisture catalyzes the oxidation of the surfaces. It could be predicted in advance that no reaction would be obtained between a beam of oxygen molecules and a hot copper

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[2] Carr, *Phys. Rev.*, **33**, 1068 (1929).

or silver surface because the dissociation pressure of the oxide is greater than the partial pressure of oxygen in the beam.

Atomic Oxygen.—Langmuir's[3] method of thermal dissociation was tried. An iridium filament was used at first. Iridium has a high melting point and its oxide is reported to dissociate at high temperatures, so that furnaces wound with iridium wire can be operated in contact with the atmosphere. At low pressures of oxygen, however, the glass walls near the filament were soon coated with a black deposit of what was presumably iridium oxide so that the use of iridium was abandoned in favor of platinum. With a platinum filament heated near its melting point in an oxygen pressure of a few tenths of a millimeter marked oxidizing action was obtained on a large number of substances which were introduced into the chamber within a few centimeters of the filament. It was not possible to say whether the active species was atoms or activated molecules, and it was not possible to obtain any activation in a beam formed with the hot filament directly in front of the source slit. The lack of activity in the beam is probably accounted for by the very small concentration of active species existing in the neighborhood of the filament.

In all further experiments upon atomic oxygen the electrodeless discharge was used. This arrangement eliminates the disturbing action of the electrodes and the frequent replacement of electrodes necessary with a gas such as oxygen. Details of such an apparatus have been described by Kurt and Phipps.[1g]

The reaction of oxygen in the electrodeless discharge at a partial pressure of 0.1 mm. is strongly oxidizing upon any substance placed in the discharge tube. Lead oxide is oxidized to the dioxide, the blue reduced oxide of molybdenum is converted to the yellow trioxide and numerous other substances were tested in a similar way. No exceptions were found to this generalization and the reaction was extremely rapid.

Reducing Action of Atomic Oxygen.—The only reaction hitherto recorded for molecular beams from the oxygen discharge is the conversion of lead oxide to the dioxide, which was used by Kurt and Phipps. They showed by the magnetic moment that this reaction was due to the atom.

It is well known in chemistry that molecular oxygen is evolved by hydrogen peroxide in the presence of many metallic oxides and the reaction is usually described as reduction. A satisfactory mechanism is provided if it is assumed that the hydrogen peroxide liberates atomic oxygen. This suggested to the authors that a similar reducing action might be anticipated with atomic oxygen. Silver oxide was tried first and afterward a number of other metallic oxides, including the trioxides of tungsten and molybdenum. A surface coated with the oxide was exposed to the beam from the electrodeless discharge in oxygen for some hours. The beam was formed by two

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[3] Langmuir, THIS JOURNAL, 37, 417 (1915).

slits 0.1 mm. in width by 1.4 mm. length placed six cm. apart. No reaction was obtained with any oxide except molybdenum trioxide. In the case of molybdenum trioxide a slate-blue image was produced on the target which appeared like the image produced by atomic hydrogen. The slate blue color is generally accepted as characteristic of one of the lower oxides of molybdenum, probably Mo_3O_8. The image could be obtained with atomic hydrogen in about fifteen minutes. With atomic oxygen a somewhat longer time was required but the image always appeared in less than an hour.

Pure oxygen was prepared from various sources and passed over heated copper oxide to remove traces of hydrogen. The oxygen was always passed through a liquid-air trap. In every case the reaction was obtained, so that it was shown conclusively that the reaction was produced by pure oxygen containing only the traces of water vapor that might be given off by the walls of the discharge bulb. As the discharge bulb was often operated continuously for hours and in some cases a second liquid-air trap was connected directly to the discharge bulb, the amount of moisture in the oxygen must have been very small indeed in some runs, but the reaction was not noticeably affected. Copeland[4] has reported that an appreciable amount of water vapor must be present in order to obtain a good line spectrum with the electrodeless discharge in oxygen. We are not able to confirm this. The discharge was not quite so steady when the second liquid-air trap was connected directly to the bulb but in all cases the line spectrum of oxygen was obtained and the reaction with the trioxide. It is our opinion that water vapor is not necessary to bring about the dissociation of oxygen, but that its presence is necessary to prevent the recombination of the atoms on the walls of the tube is shown conclusively by the work of Rodebush and Troxel on the heat of dissociation.[5]

The molybdenum trioxide was "smoked" on the target in a finely divided condition by burning a molybdenum wire under it. It was not possible to produce enough of the "reduced" oxide to make any sort of a chemical analysis but when beams of atomic oxygen and atomic hydrogen were alternately impinged on the target no change in the appearance of the blue image was observed. It was not possible to produce the blue coloration with atomic oxygen unless the target was separated from the discharge tube by two slits. When a single pinhole slit was used, no action was obtained on the target.

In order to identify the active species the oxygen beam was passed through an inhomogeneous magnetic field using the arrangement described by Kurt and Phipps. The central undeviated line was obtained but the fainter side lines characteristic of atomic oxygen were not obtained although the run was continued for more than twenty-four hours.

[4] Private communication to the authors.

[5] To be published shortly.

The reaction which takes place between a beam of atomic oxygen and molybdenum trioxide is believed to be

$$3MoO_3 + O = Mo_3O_8 + O_2$$

It has not been proved of course that the reaction is the same for atomic oxygen as for atomic hydrogen. It seems very doubtful, however, if a higher oxide of molybdenum than MoO_3 would have an appearance identical with the partially reduced oxide and none is known to exist. This conclusion is strengthened by the fact that the blue oxide is quickly changed to the yellow trioxide on direct contact with the discharge in oxygen, which has been shown to have a strongly oxidizing action on most substances.

The Stern–Gerlach experiment shows that the reducing action cannot be due to *hydrogen*, traces of which might be produced from the water evolved from the glass surfaces. Since the side lines characteristic of the oxygen atom were not obtained, it does not prove conclusively that atomic oxygen is the reducing agent. The central undeviated line might be due to the OH molecule or to an activated oxygen molecule in the $^1\Sigma$ state for example. Since the hydroxyl molecule must be present in vanishingly small amounts and it is difficult to formulate a reaction for either hydroxyl or the oxygen molecule, there seems to be no reason to doubt that the reaction is due to the oxygen atoms.

There remains to be considered the question of why the side lines were not obtained in the Stern–Gerlach experiment. These side lines are characteristic of the $^3P_1$ and $^3P_2$ states of the oxygen atom. It might be assumed that only the $^3P_0$ state reacts with the molybdenum trioxide but this would appear a fanciful hypothesis. The more reasonable explanation is to be found in the fact that the reduction can only be brought about when the active species is passed through a double slit system. Evidently the reducing action can only take place in the presence of a very low pressure of molecular oxygen. The partial pressure in the deflected beam of the atoms in the $^3P_1$ and $^3P_2$ states is very small indeed and we may suspect that there is a critical value for the ratio of the partial pressure of atoms to the partial pressure of molecules below which the reduction does not take place.

Summary

An exhaustive search failed to discover any surface with which a beam of oxygen molecules will react to give a visible image.

A beam of oxygen atoms appears to give the same reaction with molybdenum trioxide as a beam of atomic hydrogen. This reaction is believed to be represented by the equation

$$3MoO_3 + O = Mo_3O_8 + O_2$$

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