

2. The active gas seems to consist of atomic hydrogen and NH or NH<sub>2</sub>.
3. Catalytic effects of certain substances and characteristic luminescences at various surfaces have been observed.

<sup>1</sup> Bonhoeffer and Haber, *Z. physik. Chem.*, **A137**, 263 (1928); Bonhoeffer and Har-teck, *ibid.*, **139**, 64 (1928); Von Wartenburg and Schulze, *ibid.*, **B2**, 1 (1929); Paneth, *Ber.*, **62B**, 1335 (1929); Taylor and Jones, *J. Am. Chem. Soc.*, **52**, 1111 (1930); Taylor and Lavin, *ibid.*, **52**, 1910 (1930); Steiner, *Z. Elektrochem.*, **36**, 807 (1930).

<sup>2</sup> Wood, *Proc. Roy. Soc.*, **102A**, 1 (1922).

<sup>3</sup> Bonhoeffer, *Z. physik. Chem.*, **113**, 199 (1924).

<sup>4</sup> Lavin and Stewart, *Proc. Nat. Acad. Sci.*, **15**, 829 (1929).

<sup>5</sup> Gaviola and Wood, *Phil. Mag.*, [7] **6**, 1191 (1928).

<sup>6</sup> Lavin and Bates, *Nature*, **125**, 709 (1930).

<sup>7</sup> Hulthen and Nakamura, *Nature*, **119**, 235 (1927).

<sup>8</sup> Rideal and Taylor, *Catalysis in Theory and Practice*, 2nd edition, p. 177 (1926).

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## THE SEPARATION OF THE TWO TYPES OF IODINE MOLECULE AND THE PHOTOCHEMICAL REACTION OF GASEOUS IODINE WITH HEXENE

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Soon after Dennison had deduced from the specific-heat curve that ordinary hydrogen gas consists of a mixture of two types of molecule, the so-called *ortho* and *para* hydrogen, a similar state of affairs in the case of iodine gas was demonstrated by direct experiment by R. W. Wood and F. W. Loomis.<sup>1</sup> In brief, these experimenters found that the iodine bands observed in fluorescence stimulated by white light differ from those in the fluorescence excited by the green mercury line  $\lambda$  5461, which happens to coincide with one of the iodine absorption lines. Half of the lines are missing in the latter case, only those being present which are due to transitions in which the rotational quantum number of the upper state is an even integer. In other words, in the fluorescence spectrum excited by  $\lambda$  5461 only those lines appear which are due to what we may provisionally call the "ortho" type of iodine molecule.

It is evident that by irradiating iodine gas with the green mercury line it is possible to selectively activate molecules of the "ortho" type. Furthermore, as shown by these experiments, a molecule of the "ortho" type has an average life time in this form longer than the time it remains in the activated condition before emitting radiation.

It occurred to one of us that these facts might be made use of in effecting

a separation of the two molecular types. If some substance is added to the iodine gas with which only the activated molecules will react, one should be able to get rid of them, leaving only the other type of molecule which does not absorb the mercury line.

Since very little is known about photochemical reactions of gaseous iodine, numerous preliminary experiments had to be made to discover a

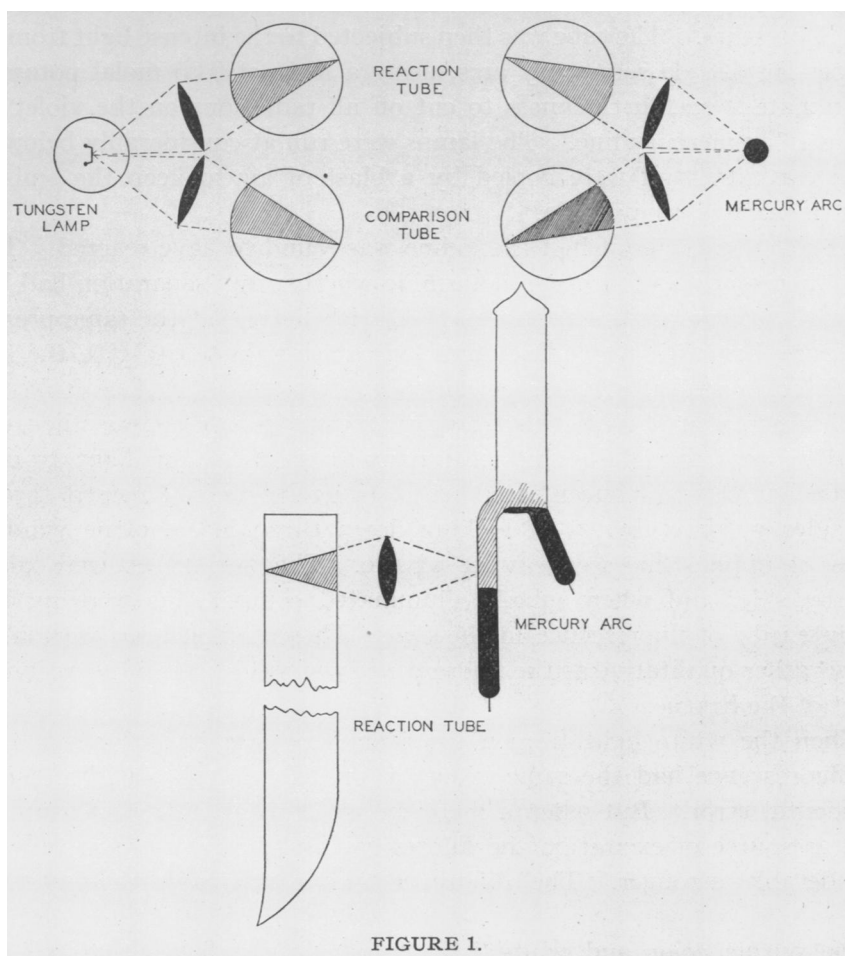


Diagram of the arrangement used in making the fluorescence comparisons

suitable iodine acceptor. It was desired if possible to find a reaction which involved only the direct addition of an activated iodine molecule onto a double bond. We finally found that iodine activated by green light combines with hexene at a reasonable rate, while the thermal reaction is not troublesome since at low pressures the equilibrium is in the direction of almost complete dissociation. The hexene used was prepared by the dehydration of hexyl alcohol with 80 per cent phosphoric acid. It had a

boiling point of 68–70°C. and probably consisted principally of the straight-chain form having the double bond between the second and third carbon atoms.

The experiments on the iodine separation were conducted as follows. A tubular vessel of pyrex glass, having at one end a plane window and at the other end a conical "light-trap," was evacuated and then filled with iodine at about 0.17 mm. pressure, and then with hexene at about 6 mm. partial pressure. The tube was then subjected to the intense light from two Cooper-Hewitt glass mercury arcs, using a filter of 0.05 molal potassium dichromate 2 cm. in thickness to cut off all radiations on the violet side of the green mercury line. The lamps were run at considerably below the rated capacity, and were cooled by a blast of air to keep the emission lines as narrow as possible.

After 24 hours about half the iodine was found to have reacted. Tests were then made as follows to determine whether any separation had been effected. A comparison tube was filled with hexene at the same pressure as before, but with the iodine partial pressure adjusted to give the same purple color as that of the reaction tube.

The fluorescence in the reaction and comparison tubes was then compared as represented in the accompanying figure. The light from an intense source was concentrated with strong lenses and passed through the sides of the tubes. On looking down through the plane windows, cones of orange fluorescence were visible. The two tubes were placed side by side, and when equally illuminated comparisons were made of the intensity of fluorescence in the two. These comparisons were necessarily rather qualitative as the fluorescence was weak due to the quenching effect of the hexene.

When the white light from a tungsten lamp was used for excitation, the fluorescence had the same intensity in the two tubes within the experimental error. But when a mercury arc burning at low pressure was used as source of excitation the fluorescence in the comparison tube was considerably stronger. The difference was not great, but quite definite.

The purple color and white-light fluorescence indicate that we have about the same amount of iodine in the two tubes; but evidently there is a difference in certain properties. We believe that we are justified in concluding that in the reaction tube the equilibrium existing in ordinary iodine gas has been materially disturbed, and that an iodine has been produced which contains a higher percentage of the type of molecule which cannot absorb the mercury green line than in the normal mixture.

As to why a more complete separation was not obtained there may be several answers. In the first place it is possible that the rate at which equilibrium between the two forms of iodine is restored is not negligibly

small in comparison with the rate of the photochemical reaction. Secondly, the photochemical reaction may not be as simple as one might hope and may involve the production of iodine atoms at some stage. We hope later to investigate the rate and nature of the reaction, as the possibility of distinguishing between two kinds of molecule gives a new tool for this purpose, especially useful in the case of chain reactions.

However, a final experiment, using a more concentrated dichromate filter, indicated that we may be able to improve our results considerably. In this event it is expected to compare the properties of the two types of iodine and to measure the rate at which equilibrium between the two is restored. Some qualitative experiments along this line, which need to be confirmed, indicate that equilibrium is restored rather slowly and several days at least are required. Condensation and re-evaporation of the iodine does not seem to hasten the attainment of equilibrium appreciably, indicating the persistence of the two molecular forms in the solid state.

<sup>1</sup> Wood and Loomis, *J. Frank. Inst.*, 205, 481 (1928).

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### NOTE ON THE EQUATION OF STATE EXPLICIT IN THE VOLUME

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Kinetic considerations always lead to an equation of state giving the pressure as a function of the concentration and temperature, but for many purposes it is more convenient to know the molal volume as a function of the pressure and temperature. Beattie<sup>1</sup> has indicated how the constants of an equation, similar in form to the Beattie-Bridgeman equation,<sup>2</sup> may be obtained from  $p, V, T$  data. Often, however, the labor of this determination is not compensated by the added convenience.

Beattie<sup>1</sup> has also shown how an approximation sufficient for many purposes may be obtained making use of the constants already obtained for the Beattie-Bridgeman equation. The treatment is the same for any equation which may be expressed in the virial form. So expressed the Beattie-Bridgeman equation has four terms:

$$p = RT(n/V) + \beta(n/V)^2 + \gamma(n/V)^3 + \delta(n/V)^4 \quad (1)$$

$p$  is the pressure,  $R$  the gas constant,  $T$  the absolute temperature,  $n$  the