

THE ACTIVATION OF HYDROGEN BY EXCITED MERCURY
ATOMS

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Introduction.—That mercury atoms excited by absorption of the line 2537Å are able to activate various kinds of atoms by collisions of the second kind has been shown in several different ways. Using pressure measurements to follow the reaction, Cario and Franck¹ showed that hydrogen, in the presence of excited mercury vapor, can be activated and made to reduce copper oxide or tungsten oxide, while Dickinson² repeated the experiment using gaseous oxygen instead of solid oxide. Employing spectroscopic methods of detection, Cario³ activated thallium vapor by collisions with excited mercury atoms and observed the radiation of the green thallium line 5351Å and indeed all the thallium lines which would theoretically be expected.

Donat,⁴ and later Stuart,⁵ investigated the decrease of resonance-radiation of mercury in the $2p_2$ state on the addition of certain gases, including hydrogen, oxygen and argon; and found that the resonance-radiation of mercury was greatly decreased by the addition of quantities of hydrogen up to 5 mm., somewhat less by the addition of the same quantities of oxygen, and very slightly by the addition of argon. This decrease in the case of hydrogen is due to the fact that the mercury in the $2p_2$ state activates the hydrogen and falls back to its normal (1S) state without emitting radiation. Donat, following up the work of Cario on the emission of the green thallium line showed that on the addition of argon or nitrogen the intensity of the thallium line was greatly increased, which result has been confirmed in this Institute by Loria.⁶

Donat explains this increase in the intensity of the thallium line in the following manner. By collisions with argon, the mercury atoms in the $2p_2$ state are forced into the $2p_3$ state, which has a slightly lower amount of energy. The mercury atoms in this lower energy state are forbidden by the quantum theory to lose energy by radiation, and furthermore in accordance with the hypothesis of Donat can endure many collisions with argon without losing energy. Hence they have a very long life, and the only way they can give up their energy is by collisions with thallium atoms. This they do, activating the thallium atoms thus causing them to emit the green line, 5351Å. This would also account for the slight decrease in the resonance-radiation of mercury on addition of argon, as observed by Stuart and by Donat.

The purpose of this research was to extend Dickinson's experiments, in

order to determine the effect of varying the pressures of hydrogen and oxygen and of adding argon on the rate of the reaction between the hydrogen and oxygen.

Experimental Procedure.—Light from a quartz-mercury arc lamp was passed through a quartz lens into a reaction tube of quartz contained in a cylindrical electrically heated furnace. The furnace was kept at about 45° as in the experiments of Dickinson. The quartz reaction tube, 2 cm. in diameter and 16 cm. long, had a clear quartz window fused to one end and a small quartz tube joined to the other. A sealing-wax joint connected the latter to a glass trap which was kept immersed in liquid air. A side bulb containing mercury which could be drawn out permitted the gas to be expanded and recompressed, thus facilitating the removal of condensible material by the use of liquid air. By means of stopcocks the gas space could be put in communication either with a mercury diffusion pump or a gas mixing chamber containing the desired reaction mixture. Hydrogen and oxygen, generated electrolytically from a barium hydroxide solution could be introduced by means of stopcocks. Argon could also be let into the gas mixing chamber at suitable pressures. In order to keep the line 2537\AA from being reversed, the anode of the mercury arc lamp was cooled by a blast of air, kept constant with the aid of a Pitot tube. The rate of reaction was measured by means of the decrease in pressure as read on a MacLeod gauge.

The experimental procedure was as follows. After pumping out the whole system, a known mixture of hydrogen and oxygen was admitted and the pressure read on the MacLeod gauge, so that the partial pressures of oxygen and hydrogen could be calculated. The reaction tube was now illuminated with the light from the mercury arc, the intensity being kept constant with the help of an ammeter, voltmeter, and slide-wire resistance. After a definite time of illumination, usually ten minutes, the condensible matter was removed and the pressure read. This process was repeated six times, giving a total time of illumination of about an hour. About 2 cc. of mercury were placed in the reaction tube at the beginning of the series of experiments and were replenished once in the latter part of the series.

In the cases where argon was added the procedure was modified as follows. An approximately equal mixture of hydrogen and oxygen was admitted to the mixing chamber and thence to the reaction tube, and the pressure read. The gas-mixing chamber was then shut off and the reaction-tube system pumped out. In the meantime a definite amount of argon was let into the gas-mixing chamber. The mixture of hydrogen, oxygen, and argon was then admitted to the reaction tube and allowed to come to equilibrium. The pressure was again read. The ratio of the volume of the mixing chamber to that of the reaction tube having been determined, the ratio of argon to hydrogen and oxygen could now be calculated.

The Experimental Results.—The experiments of Dickinson were repeated with similar results, and in addition experiments were carried out to show the dependence of the rate of reaction on the pressures of hydrogen and oxygen.

When the concentration of oxygen was kept constant at about 0.036 to 0.04 mm., the rate was found to increase as the pressure of hydrogen was increased, but seemed to reach a saturation value as in the experiment with Cario and Franck. It was, however, difficult to get reproducible results with pressures of hydrogen much above the usual of about 0.04 mm. The important fact, nevertheless, was demonstrated that at pressures of hydrogen as high as 0.6 to 0.7 mm., there was a large rate of reaction as great as $11-12 \times 10^{-4}$ mm./min. This result will be referred to again in connection with our discussion of the effect of large additions of argon.

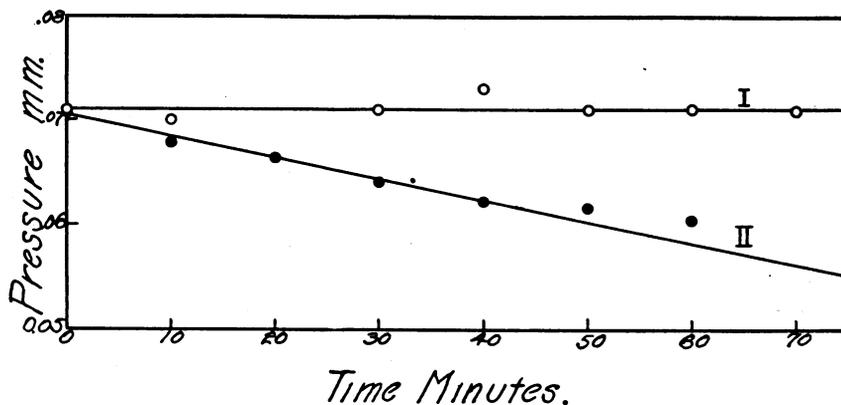
Experiments were also made keeping the pressure of hydrogen constant and varying the amount of oxygen. When no oxygen was present the rate was found to be zero. On addition of small quantities of oxygen the rate increased very rapidly (almost linearly) until it reached a maximum at 0.01 mm. of oxygen, then decreased until a small but measurable rate was reached. Table 1 shows the rate of reaction as a function of the pressure of oxygen, the pressure of hydrogen being kept constant at 0.041 mm.

TABLE I
EFFECT OF OXYGEN ON THE RATE OF REACTION

OXYGEN PRESSURE IN MM.	PRESSURE OF HYDROGEN CONSTANT AT 0.041 MM.		RATE MM./MIN.
	RATE MM./MIN.	OXYGEN PRESSURE IN MM.	
0.002	0.7×10^{-4}	0.081	3.0×10^{-4}
0.003	0.7	0.117	2.0
0.004	2.4	0.120	2.0
0.004	2.2	0.194	1.8
0.009	6.7	0.305	1.7
0.01	5.5	0.343	1.2
0.027	3.7	0.345	1.4
0.041	3.2	0.351	1.5
0.080	2.5	0.355	1.5

The addition of relatively large quantities of argon was found to stop the reaction completely. Two sets of experiments were carried out with two different samples of argon. In the first set argon made by the General Electric Company was taken from a tank under pressure. It was thought to be pure, but no guarantee was given. In the second set compressed argon, guaranteed by the General Electric Company to be 99.8% pure, was used. The results in the two cases were found to be the same. The results of a typical experiment are shown in the figure. The pressure of hydrogen and oxygen are plotted against the time of illumination. Curve I gives the rate when the ratio of argon to hydrogen is about twelve to one. Curve II gives the rate when there is no argon present.

Further experiments were made in which the pressure of hydrogen and oxygen were kept constant (within five per cent) and the pressure of argon



was varied. The rate of reaction was found to decrease as the pressure of argon increased. Table 2 shows this effect for both sets of experiments.

TABLE 2
EFFECT OF ADDITION OF ARGON ON THE RATE OF REACTION
PRESSURE OF HYDROGEN CONSTANT AT 0.036 MM.; PRESSURE OF OXYGEN CONSTANT AT 0.036 MM.

FIRST GROUP		SECOND GROUP	
PRESSURE OF ARGON IN MM.	RATE MM./MIN.	PRESSURE OF ARGON IN MM.	RATE MM./MIN.
0.0	2.2×10^{-4}	0.00	3.2×10^{-4}
0.067	1.67	0.190	2.0
0.180	1.50	0.358	1.3
0.216	1.41	0.372	1.2
0.219	1.25	0.379	1.5
0.299	0.67	0.380	1.4
0.431	0.00	0.458	0.7
0.455	0.00	0.458	1.0
		0.478	0.8
		0.571	0.0
		0.575	0.0

Discussion of the Results.—The dependence of the rate of reaction on the pressure of oxygen may be explained as follows. Below the optimum pressure of oxygen (0.01 mm.) many of the hydrogen molecules which are activated by collisions with mercury atoms in the $2p_2$ state lose their activation before they have made contact with an oxygen molecule. On the other hand, when the oxygen is above the optimum pressure many of the excited mercury atoms are killed off by collision with oxygen molecules, as is also shown by the work of Stuart, thus leaving fewer excited mercury atoms to activate the hydrogen. Collisions between excited mercury atoms and oxygen molecules seem not to activate the latter sufficiently to allow them to form water by collisions with hydrogen molecules.

The experiments showing the decrease of rate of formation of water on the addition of argon seem not to be in agreement with what might have been expected on the basis of the results reported by Donat; nor are they to be fully explained by the experiments of Stuart, which show that the addition of argon cuts down the resonance radiation of mercury but slightly.

That no increase in the rate of reaction was observed on addition of argon due to collisions with mercury atoms which have been put into the $2p_3$ state by collisions with argon may be explained by one of the following hypotheses:

(a) That mercury atoms in the $2p_3$ state, while able to give up their energy to thallium, are not able to interact with hydrogen molecules.

(b) That mercury atoms in the $2p_3$ state, while able to endure many collisions with argon atoms without losing energy, are immediately deactivated by collisions with oxygen atoms.

That such a large decrease in the rate of formation of water was observed on addition of argon might be explained by the assumption that hydrogen is dissociated by excited mercury atoms and that addition of argon furnishes a means whereby two hydrogen atoms may combine through a triple collision with an argon atom, thereby decreasing the rate of reaction. An attempt to test this hypothesis was made by measuring the rate when a large amount of hydrogen was present, since the excess of hydrogen should also furnish molecules for the triple collisions. The rate, nevertheless, did not decrease as might have been expected, as will be seen from the large rate which was observed when the pressure was 0.6 to 0.7 mm. This is not conclusive proof, however, that hydrogen atoms are not combining through triple collision with hydrogen molecules, since the large rate observed might be due to the increased chance of forming a greater amount of activated hydrogen which masks the effect of triple collisions.

An alternative hypothesis is that activated hydrogen is not atomic, as assumed by Cario and Franck, but is molecular hydrogen in a higher quantum state, having for example one or more quanta of energy of oscillation, with a definite life-time and capable of being deactivated by collisions with argon. This assumption as to the nature of activated hydrogen affords an even simpler explanation of the Dickinson experiment than does the hypothesis of monatomic hydrogen, and is in accord with the speculations of Compton and Turner⁷ concerning equilibrium in a region containing hydrogen and mercury. Since, however, it has been shown by Cario and Franck that activated hydrogen can diffuse through high pressure hydrogen gas and still remain activated, the above assumption would necessitate the further hypothesis that this higher quantum state of hydrogen is metastable towards collisions with hydrogen molecules.

The above hypotheses do not exhaust the possibilities of explanation,

and further work will be necessary to elucidate the exact mechanism of all the processes occurring.

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¹ G. Cario and J. Franck, *Zt. Physik.*, **11**, 161 (1922).

² Dickinson, *Proc. Nat. Acad. Sci.*, **10**, 409 (1924).

³ Cario, *Zt. Physik.*, **10**, 185 (1922).

⁴ K. Donat, *Zt. Physik.*, **29**, 345 (1924).

⁵ Herbert Stuart, *Zt. f. Physik.*, **32**, 262 (1925).

⁶ Loria, *Phys. Rev.*, **25**, 212 (1925).

⁷ Compton and Turner, *Phil. Mag.*, **48**, 360 (1924).

WHAT IS HUMUS?¹

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Several theories have been proposed at various times to explain the origin of the black-colored organic substances, which go to make up the bulk of the soil organic matter and which are commonly known as "humus." None of these theories, however, sufficiently explained processes involved in the formation of the complex mass of soil organic matter, to be universally accepted. The very nature of the chemical constituents of this "humus" is little understood, although an extensive literature concerning some of these constituents, namely the "humic acids," is available. A number of methods have been suggested for determining quantitatively this soil "humus" and "humic acid," since this was usually considered to be the available portion of the soil organic matter. However, none of the methods proved satisfactory; the results obtained for the same soil by different methods varied greatly, and we are still in the dark concerning the nature of the soil organic matter, its formation, and physical and chemical properties. Schreiner and Shorey, in summing up in 1909 the survey of the literature on this subject, came to the conclusion that "the most conspicuous feature is the lack of specific knowledge concerning the organic matter of the soil." Since then, new theories and new methods have been proposed, but even at present "the complete lack of knowledge concerning the nature of soil organic matter, the indefinite limit between