methods. A sample of drinking water supplied to Cleveland gave results that indicate less than 0.002 mg. of iodine in 10 liters.

Table I

Samples Containing Potassium Iodide and Iodate Expressed as Equivalent to Mg. of Potassium Iodide per Cc.

Observed			Present		
Total	KI	KIO_3	Total	KI	KIO_3
0.08	0.08	0	0.08	0.08	0
.10	.06	0.04	.10	.06	0.04
.10	.10	0	.10	.10	0
.03	0	.03	.03	0	.03
.01	0	.01	.01	0	.01
.02	.01	.01	.02	.01	.01

Table II

Samples Containing Potassium Iodide Expressed as Mg. of Potassium Iodide per Cc.

									Brine
Found	0.0125	0.007	0.0015	0	0	0.05	1.00	0.0012	6 p.p.m.
Present	.0130	.0075	.0025	0	0	.05	1.00	.00125	6 p.p.m.

Summary

A method is described for the determination of iodine as iodides and iodates which gives accurate results when the concentration of iodine is between 0.01 and 0.10 mg. per 15cc. sample and in which a variation of 0.01 mg. is readily distinguished. The lower limit of the test is 6 to 7 parts per million. The method is made applicable to solutions which contain interfering substances by the introduction of a preliminary steam distillation in acid solution with ferric chloride.

Cleveland, Ohio

[Contribution from the Kent Chemical Laboratory of the University of Chicago]

PHOTOCHEMICAL STUDIES. III. THE REACTION BETWEEN NITROGEN AND HYDROGEN IN THE PRESENCE OF MERCURY VAPOR, AND THE RESONANCE RADIATION OF MERCURY

By W. Albert Noyes, Jr.

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For certain reactions, even for those which involve a decrease in free energy, a catalyst seems necessary in order that the reaction may take place; that is, the action of the catalyst may be such as to increase the rate of a reaction which otherwise is immeasurably slow, or a catalyst may be necessary in order that a reaction may take place appreciably even during a long period of time. When the rate of a reaction is so small that only a few molecules react in unit time, then the ordinary laws of kinetic theory probably cease to be valid. This sort of reasoning has led to the formulation of radiation hypotheses by Trautz,[1] W. C. M. Lewis[2] and Perrin.[3]

While the radiation hypothesis must still be considered open to serious objection, it would seem that some of the attempts to test this hypothesis experimentally are not entirely free from criticism. It is not the purpose of the present article to discuss this hypothesis, but it will be necessary in the course of the discussion to use the terms "activation" and "energy of activation." We shall understand by the latter term the amount of energy which must be added to a given molecular species to put it in such a metastable state that it may decompose or react with another molecular species. There may be, therefore, several different energies and states of activation, depending upon the different possible modes of decomposition or reaction. Indeed, if we bring over the idea of stationary states into this subject, the probability that a given reaction will take place may depend upon the amount of energy added, so that the so-called energy of activation may not be a perfectly definite quantity. There may be, however, a definite minimum energy of activation.[4] The heat of activation apparently bears no direct relation to the free energy of the reaction under consideration. Neither does the frequency of the radiation necessary to activate a given substance necessarily bear any direct relation to the absorption spectrum of the substance involved. Recently, Volmar[5] by postulating a given activated state for certain organic compounds has been able to calculate with some degree of success the wave length of light which should make them decompose.

In photochemical reactions, as in ordinary reactions, a substance which does not appear directly in the chemical equation may play an important role. This has been clearly brought out in the experiments of Daniels and Johnston[6] on the decomposition of nitrogen pentoxide, and by the effect of mercury vapor on the dissociation of hydrogen, in the experiments of Cario and Franck[7] and of Franck.[8] Recently, Dickinson[9] has added further evidence in favor of the assumption of Cario and Franck by causing oxygen and hydrogen to combine at 45°.

It is conceivable that these foreign substances might act in at least two

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[1] Trautz, "Sitzungsber. Heidelberger Akad. Wissenschaft," **1917.**

[2] Lewis, *Trans. Faraday Soc.*, **17**, 573 (1922). This article presents a brief statement of Lewis' viewpoint. Other articles were published previously in *J. Chem. Soc.*

[3] Perrin, *Annales de physique*, **11**, 5 (1919).

[4] Noyes, *Compt. rend.*, **176**, 1468 (1923).

[5] Volmar, *ibid.*, **178**, 698 (1924).

[6] Daniels and Johnston, THIS JOURNAL, **43**, 72 (1921).

[7] Cario and Franck, *Z. Physik*, **11**, 161 (1922).

[8] Franck, *ibid.*, **24**, 450 (1923).

[9] Dickinson, *Proc. Nat. Acad. Sci.*, **10**, 409 (1924).

distinct ways: (1) by absorption of incident radiation and subsequent emission of light of the proper wave length to activate the molecules in question; (2) by absorption of the incident radiation, and on collision of these molecules in a metastable state with other molecules the energy might be transferred *without radiation* in such a manner as to activate the molecules in question. It seems that the activated state in the case discussed in the present paper consists of monatomic hydrogen. Since the mercury vapor absorbs more energy than is necessary to activate the hydrogen, the remaining energy must either appear as kinetic energy or as radiation.

This type of phenomenon is doubtless much more common in photochemistry than has hitherto been supposed, and it was thought that a further study of a few simple cases might lead to more definite ideas upon the general laws governing photochemical reactions.

Experimental Part

For the reaction, $^1/_2N_2(g) + {}^3/_2H_2(g) = NH_3\ (g)$; $\Delta F^\circ_{298} = -3910$. However, at the boiling point of mercury (630.4°K.) the free energy of the above reaction becomes[10] +4620.

The first experiments were tried by passing a mixture of nitrogen and hydrogen over boiling mercury in a tube fitted with a quartz window. The source of light was a quartz mercury-arc lamp of the type used by Moore and Noyes.[11] A quartz lens was used to focus the light, and flowmeters were used to measure the rate of flow of each gas. The gases were bubbled through dil. sulfuric acid of known strength and the latter titrated at the end of the experiment, using sodium alizarin sulfonate as the indicator. The results were entirely negative when oxygen and water vapor were carefully removed from the nitrogen and hydrogen.

In the next experiments a quartz reaction vessel was attached to the line by means of sealing wax and nitrogen and hydrogen were admitted to a total pressure of about two-thirds of an atmosphere. Slight pressure decreases were noted, so that it was decided to work at higher pressures, about 1.1 atmospheres. Kuhn[12] has shown that ammonia is readily decomposed by radiation of wave length 2063 Å. It was found that better yields of ammonia could be obtained by interposing a color filter of ethyl alcohol. The absorption spectrum of the latter was photographed and it was found that practically no radiation of wave length shorter than 2150 Å. was transmitted. Kuhn's results were qualitatively verified by allowing ammonia gas to be exposed to the lamp without color filter. A pressure increase of about 8 mm. an hour was noted when the initial pressure of the ammonia was about 200 mm.

In these experiments on ammonia synthesis, positive tests were always obtained for ammonia but the pressure decrease was considerably greater

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[10] Calculated from the formula given in Lewis and Randall's "Thermodynamics," McGraw-Hill Book Company, **1923**, p. 557.

[11] Moore and Noyes, THIS JOURNAL, **46**, 1369 (1924).

[12] Kuhn, *Compt. rend.*, **177**, 956 (1923); **178**, 708 (1924).

than could be accounted for by the ammonia obtained. However, when mercury traps were placed in the line in such a way that the gases were not in contact with the stopcock grease, the amount of ammonia obtained corresponded roughly to the pressure decrease noted. There still remained the possibility of hydrazine formation. Since no satisfactory qualitative test for hydrazine was found in the literature, a quantitative test seemed necessary. The gases from the reaction vessel were swept out into a Piccard absorption bulb containing approximately 0.5 *N* hydrogen chloride by means of nitrogen from which oxygen had been removed by passing over heated copper turnings and dried by calcium chloride and concd. sulfuric acid. The absorption bulb was thoroughly washed out and the solution made basic with sodium hydroxide. Hydrazine was determined by the iodine method carefully investigated by Bray and Cuy.[13] The amount of hydrazine present did not exceed 4×10^{-5} g., which was about the limit of experimental error of the method as carried out.

Table I gives some of the results obtained in several different runs. The amount of ammonia was determined in two ways: (1) by the Nessler reagent; (2) by sweeping the gases through concd. sulfuric acid contained in a Piccard absorption bulb and weighing.

TABLE I

RESULTS

Run	Initial press. of nitrogen Mm.	Initial press. of hydrogen Mm.	Time Min.	Amt. of ammonia G.	Method of detn.
1	345	481	80	0.00004	(1)
2	513	352	200	.00008	(1)
3	349	477	90		(1)[a]
4	277	486	100	.0043	(2)[a]
5	287	496	79	.0008	(2)
6	348	528	86	.0002	(2)
7	239	622	92		(1)[a]
8	296	601	89	.0002	(1)
9	365	484	60	.0004	(2)
10[b]	304	510	120	.00002	(1)
11[c]	372	504	127	.00000	(1)
12[c]	463	424	96	.00000	(1)

[a] Qualitative test only.

[b] Without ethyl alcohol light filter.

[c] In the presence of mercury vapor but without the light. Traces of ammonia were sometimes obtained without the light.

Values by Method 1, are good to about 0.0001 g., except for Run 4 in which a larger error may have entered. By Method 2 the error may be as much as 20%. During the first five runs the gases were in contact with the stopcock grease so that these runs should not be compared directly with the others. The data are scarcely accurate enough to

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[13] Bray and Cuy, THIS JOURNAL, **46**, 1786 (1924).

give much meaning to determinations of the order of the reaction. The light intensity varied from one run to another, but during a given run the first-order equation with respect to hydrogen seems to fit the data better than other possibilities. Second order with respect to nitrogen and hydrogen, second order with respect to hydrogen, and first order with respect to nitrogen seemed to give definite trends with increased time.

Discussion of Results

The dissociation of hydrogen by mercury atoms which are in the $2p_2$ state noted by Cario and Franck[7] has been further investigated by Duffendack and Compton[14] and by Compton and Turner.[15] Duffendack and Compton also studied the effect in nitrogen. They found the effect in nitrogen to be about one-tenth as great as in hydrogen and ascribed it to the presence of mercury atoms in the $2P$ state. Recently Saha and Sur[16] have studied the question of active nitrogen from the same viewpoint.

The first resonance potential of mercury is 4.9 volts, whereas the heat of dissociation of hydrogen apparently corresponds to about 3.16 volts.[17] Mercury atoms in the first resonance state are capable, therefore, of giving up enough energy to dissociate hydrogen upon collision with hydrogen molecules.

If we take the heat capacity of nitrogen[18] as being given by the equation, $c_p = 6.50 + 0.0010\ T$, and the entropy of nitrogen gas at 298°K. as 45.6,[19] then by means of the entropy equation for a monatomic gas, $s = 5/2R\ ln\ T + 3/2R\ ln\ w - R\ ln\ p - 2.63$, for the reaction $N_2\ (g) = 2N\ (g)$; $\Delta S^{\circ}_{3500} = 26.8$.

Langmuir[20] has found that nitrogen is not appreciably dissociated even at 3500°K. If this is due to the fact that equilibrium lies far on the side of the diatomic molecules at this temperature and not to a very slow rate of attaining equilibrium, then since $-\Delta F = RT\ ln\ K$, ΔF must be large at this temperature and we see from the fundamental free-energy equation, $\Delta F = \Delta H - T\Delta S$ that $\Delta H > T\Delta S$. Since $T\Delta S$ at this temperature is 93,800 cal., ΔH is probably considerably larger than this figure. Indeed, if the gas is 1% dissociated at this temperature, ΔH would be more than 140,000 calories. Mercury atoms in the first resonance state would not be able to dissociate nitrogen. If Duffendack and Compton[14] are right in assuming that mercury in the $2P$ state is capable of "activating" or dissociating nitrogen, then since the $1S-2P$ transition corresponds to an energy of 6.67 volts, the "active" nitrogen formed probably does not

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[14] Duffendack and Compton, *Phys. Rev.*, **23,** 583 (1924).

[15] Compton and Turner, *Phil. Mag.*, **48,** 360 (1924).

[16] Saha and Sur, *ibid.*, **48,** 421 (1924).

[17] Olson and Glockler, *Proc. Nat. Acad. Sci.*, **9,** 122 (1923).

[18] Ref. 10, p. 80.

[19] Lewis, Gibson and Latimer, THIS JOURNAL, **44,** 1008 (1922).

[20] Langmuir, *ibid.*, **34,** 860 (1912).

correspond to the "active" nitrogen discussed by Saha and Sur,[16] since the latter presumably necessitates an energy corresponding to about 8 volts. Mercury vapor may be placed in the $2P$ state either by direct absorption of light of wave length 1849.6 Å. which would not be present in the light used in the present experiments, or perhaps by successive absorption of light of wave lengths 2537 Å. and 6820 Å. Since the length of time that an atom will remain in the first resonance state is presumably of the order of 10^{-8} second, the intensity of the radiation of wave length 6820 Å. would have to be relatively large in order to give many atoms in the $2P$ state. This would probably not be the case in the experiments herein described.[21] No record of this line could be found in the literature.

The evidence would seem to indicate that the dissociation of the hydrogen is the important step in the formation of ammonia by this method. The free energy of formation of ammonia at 25°C. is —3910 calories, while for the reaction $H(g) + H_2(g) + {}^1/_2N_2(g) = NH_3(g)$, $\Delta F^{\circ}_{298} = -41{,}640$. The tendency to form ammonia is considerably greater if monatomic hydrogen is present. Compton and Turner[15] consider it probable that mercury atoms in the first resonance state react with hydrogen to give an unstable mercury hydride and monatomic hydrogen. Either the monatomic hydrogen or the mercury hydride could then react with nitrogen in the first step of ammonia formation.

Storch and Olson[22] in studying the formation of ammonia from the elements in the low-voltage arc, found that sufficient ammonia is formed to give a test with the Nessler reagent only when the arc is present. Since it is difficult to conceive of any ionization of the nitrogen or hydrogen in the present experiments, it would seem probable that dissociation of the hydrogen only takes place under electron bombardment at potentials above the ionization potential. This is in accord with the results of Smyth[23] which showed that monatomic hydrogen ions were formed only at voltages higher than the theoretical value of about 17 volts.

From the free-energy value for the formation of ammonia at the boiling point of mercury the equilibrium constant is found to be 0.023. In the present experiments if the volume of the apparatus is taken as 100 cc., it is found that the reaction has nearly attained equilibrium in most of the runs and slightly exceeded it in others. Since the temperature of the apparatus was not constant throughout, it is probably not fair to assume that all of the reaction took place at the boiling point of mercury.

A rough calculation of the number of quanta showed the number of molecules of ammonia formed to be of the same order of magnitude as

[21] The spectrum of the lamp shows no trace of this line when photographed by means of a quartz prism spectrograph. The spectrograph is scarcely good in this region of the spectrum, although the lamp used by Moore and Noyes showed a line at about 6720.

[22] Storch and Olson, THIS JOURNAL, **45,** 1605 (1923).

[23] Smyth, *Proc. Roy. Soc.*, **102A,** 283 (1922); **104A,** 121 (1923).

the number of quanta of 2537 radiation incident on the vessel. This, at least, does not indicate any effect of the nature of that found by Moore and Noyes[11] in which the number of molecules reacting was roughly 10^8 times as great as the number of incident quanta.

Summary

1. Gaseous hydrogen and nitrogen combine to form ammonia in the presence of mercury vapor and the first resonance radiation of mercury at the boiling point of mercury, 630.4°K.
2. Hydrazine, if formed at all, is formed only in traces.
3. It is considered probable that the dissociation of hydrogen is the important factor in the reaction as here carried out, since the nitrogen would be little if at all affected by mercury vapor under the conditions of the experiments described.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 170]

THE MOVING-BOUNDARY METHOD FOR DETERMINING TRANSFERENCE NUMBERS. IV. THE TRANSFERENCE NUMBERS OF SOME CHLORIDE SOLUTIONS

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In the earlier articles of this series[1] two forms of apparatus for measuring transference numbers by the method of moving boundaries were described, neither of which was entirely satisfactory. In the first form the electrodes were apparently too near the calibrated tube through which the boundary sweeps. The second form, which was otherwise properly designed, was constructed on too large a scale, and gave difficulty due to the heating effects of the current passing through the apparatus. In this article an apparatus is described which is satisfactory both in design and dimensions. Also, results are given of measurements, made with the new apparatus, of the transference numbers of solutions of potassium chloride, sodium chloride and of hydrochloric acid.

The equation for the transference number from the movement of a single boundary[1] and the correction, first pointed out by G. N. Lewis,[2] can be conveniently combined into the formula

$$T = \frac{1}{\Phi}\left(\frac{VF}{Q} \pm \Delta v\right) \qquad (1)$$

In this expression Φ is the volume of solution which contains one equivalent of solute, F is equal to 96,500 coulombs, Q is the number of coulombs

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[1] (a) MacInnes and Smith, THIS JOURNAL, **45**, 2246 (1923). (b) Smith and MacInnes, *ibid.*, **46**, 1398 (1924).

[2] Lewis, *ibid.*, **32**, 862 (1910).