[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Thermal Decomposition of Deuterium Iodide

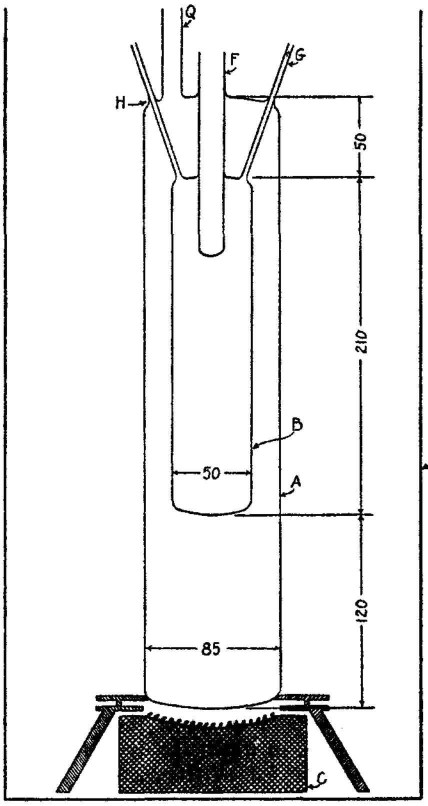
BY D. RITTENBERG AND HAROLD C. UREY

Shortly after the discovery of the hydrogen isotope of atomic weight 2, we calculated[1] the equilibrium constants of the hydrogen–chlorine–hydrogen chloride and the hydrogen–iodine–hydrogen iodide reactions as a function of the isotopic composition of the hydrogen. These calculations showed that a marked dependence of the values of these constants on isotopic composition should exist. In the case of the first reaction, the percentage dissociation of deuterium chloride should be less than that of protium chloride, while in the case of the second reaction, the equilibrium is shifted in the opposite direction with increasing deuterium concentration in the reaction substances. The theoretical predictions based on well-established theory indicated such marked differences in chemical properties that we were led to conclude that marked variations in the properties of the hydrogens and their compounds were certainly to be expected. It is the purpose of this paper to report the experimental confirmation of the theory in the case of the hydrogen–iodine–hydrogen iodide reaction.[2]

The thermal dissociation of hydrogen iodide was extensively studied by M. Bodenstein[3] from 302–516°. He found that the dissociation in this range was reversible and equal to about 20–25%. We have repeated two of his values, and are able to check his results within the limits of both his and our experimental error.

Experimental Materials.—Deuterium rich hydrogen was prepared either by the reaction of water with a magnesium amalgam or by the electrolysis of water containing a high concentration of deuterium oxide. Hydrogen iodide was prepared from its elements: 35 g. of iodine was placed in a five-liter flask containing a platinum catalyst. The vessel was evacuated until all air had been displaced by iodine vapor. Hydrogen was pumped in with a Toepler pump to a pressure of 12 cm. of mercury, and the flask sealed off. It was heated in an air bath at 370° for six hours. More than 90% of the hydrogen reacted. This was purified by distillation before use as will be described below.

Thermostat and Reaction Vessel.—A diagram of the thermostat and reaction vessel is shown in Fig. 1. The reaction vessel was kept at constant temperature by immersion in the vapor of a liquid boiling at constant pressure. Two liquids, mercury and sulfur, were used to obtain a wide temperature range. A device to hold the pressure constant over the boiling liquid was developed in this Laboratory and independently described by C. C. Coffin.[4] It consists of a 100-watt heater placed in a five-liter bulb connected to the thermostat. The heater current is controlled by a relay actuated by a pair of contacts on a mercury manometer. When the pressure falls below the predetermined value, the heater is turned on and increases the pressure. When the pressure rises, the heater is shut off, the gas in the five-liter flask cools and the pressure in the system falls. The fluctuations in pressures were about 0.2 mm. In the range of temperatures used, the fluctuations correspond to about 0.008° for mercury and to about 0.014° for sulfur. The pressure fluctuations have a period of about two to three seconds and since it is scarcely possible for the temperature of the thermostat to follow such rapid changes, the fluctuation in the temperature of the reaction vessel was probably considerably less than the above figures.



All measurements in millimeters

Fig. 1.

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(1) H. C. Urey and D. Rittenberg, *J. Chem. Phys.*, **1**, 137 (1933).

(2) A preliminary note reporting these results has been published in the *J. Chem. Phys.*, **2**, 106 (1934).

(3) M. Bodenstein, *Z. physik. Chem.*, **13**, 56 (1894); **22**, 1 (1897); **29**, 295 (1899).

(4) C. C. Coffin, THIS JOURNAL, **55**, 3646 (1933).

A is the outer jacket of the thermostat in which the liquid is boiled by the 250-watt heater, C. B is the reaction vessel. The entire thermostat was placed in the iron can, D, and then packed with diatomaceous earth. The diatomaceous earth packing served the double function of a thermal insulator and of a rigid support for the thermostat. The refluxing liquid was condensed by the air condenser, Q, which leads to the pressure control device. F is a thermometer well. G and H are 1-mm. capillary tubes through which the reaction vessel is filled and emptied.

The temperatures were measured by a chromel–alumel thermocouple which had been standardized[5] against boiling water, mercury and sulfur. A vertical section of the thermostat outside the reaction vessel was explored with the thermocouple for temperature uniformity. The thermocouple was read by means of a Leeds and Northrup type K potentiometer. The maximum difference between the readings was 0.015 mv., corresponding to 0.35°. The fluctuations were random and did not indicate any superheating of the vapor. Further, the temperature in the thermometer well was observed and found to agree closely with the temperature outside the reaction vessel.

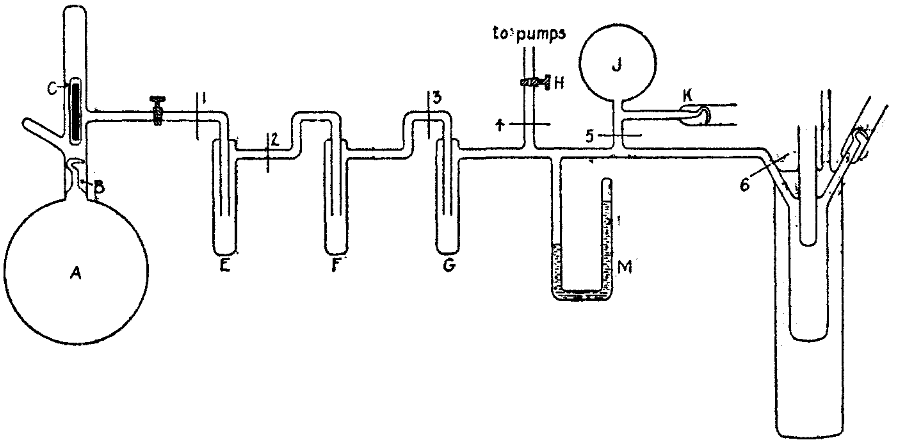

Fig. 2.

Experimental Procedure

Figure 2 is a diagram of the apparatus used in purifying the hydrogen iodide and in filling the reaction vessel. The five-liter flask, A, in which the hydrogen iodide had been prepared was sealed to stopcock D. The entire system was then evacuated. Stopcock D was closed and the break seal, B, crushed with the magnetic hammer C. E was immersed in liquid air, after which A was slowly pumped out. When the hydrogen iodide had all been condensed in E, the system was sealed off at 1, and evacuated through H. After H was closed, F was immersed in liquid air and E in solid carbon dioxide–alcohol mixture. The vapor pressure of hydrogen iodide is about 7 cm. at −79° and it therefore rapidly distils over into F. The hydrogen iodide after this distillation was pure white. The system was sealed off at 2 and pumped out through H. To determine the concentration of deuterium iodide in the hydrogen iodide, a sample of hydrogen iodide was secured at this point by sealing off the one-liter flask J at about 40 cm. pressure. The hydrogen iodide was again condensed in F. In sealing off J, the hydrogen iodide in the capillary between J and the main line was decomposed, but due to the small volume of the capillary, the amount decomposed was small. The hydrogen was pumped out and the iodine sublimed back into F. Following the same procedure as above, the hydrogen iodide was sublimed into the trap G. The system was sealed off at 3, pumped for thirty minutes and sealed off at 4. The hydrogen iodide in G at this stage was pure white, showing no signs of iodine. To admit the hydrogen iodide to the reaction vessel, the liquid air was removed from trap G and the pressure allowed to rise to about 60 cm. The capillary tube leading to the reaction vessel was then sealed off at 6. The seal was made as close to the thermostat as possible.

The thermostat was set into operation and run until equilibrium had been attained. In general, the time of heating was from 3 to 40 times more than that required by ordinary hydrogen iodide to come within 1 part in 2000 of equilibrium. The kinetic data of M. Bodenstein[8] were used in these calculations.

When equilibrium had been established, the reaction vessel was pumped out through the system shown in Fig. 3; 40 cc. of a 5% solution of potassium iodide was deaerated and frozen in H by a solid carbon dioxide–alcohol bath. The function of the trap, L, was to prevent mercury vapor from the Toepler pump M from diffusing back into the traps, F, G, H and J. The entire system was evacuated through K. F, G and J were immersed in liquid air. Stopcock K was closed, the automatic Toepler pump[6] M started, and the break seal B was crushed by the magnetic hammer. The rate of flow of the gases was slowed down by the capillary leak, C, which under a pressure drop of one atmosphere passed about 2 cc. of gas per second. The hydrogen iodide and iodine were frozen out in the traps F, G and J, and the hydrogen pumped into the bulb N. When the rate of flow of the gases had slowed down (as shown by the amount of hydrogen pumped during a stroke of the Toepler pump), the break seal D was crushed. D was a large break seal with an opening of 4 mm. which when crushed allowed the system to be pumped out easily. When most of the hydrogen had been pumped into N, the system was sealed off at 1 and 2. The remainder of the hydrogen was removed through K by the high vacuum pumps. The system was allowed to stand overnight to permit all iodine which had condensed in the tubes leading from B to F to sublime over to F. The traps, G and J, were used for protection against loss of iodine or hydrogen iodide in the first surge of gas when B was crushed. No condensate, however, was ever seen in

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(5) P. D. Foote, C. O. Fairchild and T. R. Harrison, "Pyrometric Practice," U. S. Bureau of Standards, Technologic Paper No. 170.

(6) D. MacGillavry, "Dissertation," Columbia University, 193[illegible].

them. Neither the mercury in the Toepler pump nor the droplets of mercury which were put into N showed any signs of reaction with hydrogen iodide.

After standing overnight, the system was sealed off at 3 and 4 and the iodine and hydrogen iodide distilled into J. It was then sealed at 5. The water in H was allowed to melt and the hydrogen iodide and iodine dissolved in it. The solution was washed back and forth in H and J until it was of uniform composition.

The equilibrium was not shifted during the process of pumping out the reaction vessel; since it is not affected by pressure. The rate of reaction at 300° is very small[3] and since the time required for the gases to cool to 300° is also very small, it is highly improbable that the equilibrium proportions changed while the gas was being pumped out.

Analytical Method.—The quantity which we seek to evaluate from our analytical data is ζ, the fraction of hydrogen iodide decomposed at equilibrium, namely

$$\zeta = 2(I_2)/2(I_2) + (HI)$$

where (I_2) is moles of I_2 present at equilibrium, and (HI) is moles of HI present at equilibrium. Two different analytical methods were used.

Method 1.—The iodine was titrated with an approximately 0.1 *N* sodium thiosulfate solution. The hydrogen iodide was determined in the same solution by titration with 0.3 *N* sodium hydroxide. Both titrations can be done in the same solution since the titration of iodine by sodium thiosulfate[8] does not affect the hydrogen-ion concentration. All titrations were done with a weight buret.

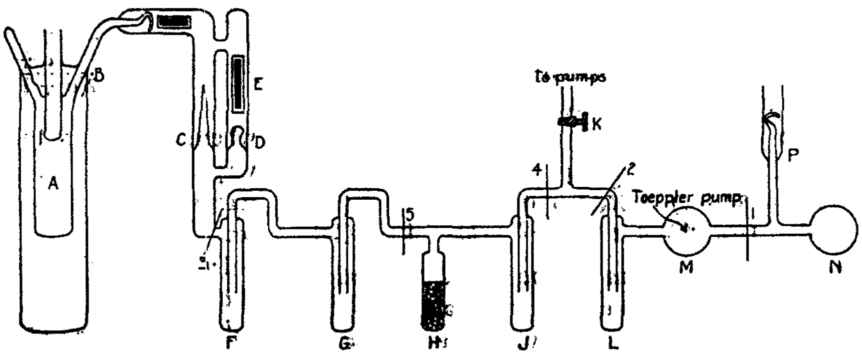

Fig. 3.

The 0.1 *N* sodium thiosulfate solution was standardized against pure iodine.[7] The starch indicator was made up fresh every day from a sample of finely ground potato starch; 0.25 g. of starch was added to 25 cc. of water at 75°. This was agitated until solution was complete and rapidly cooled to room temperature. The sodium hydroxide solution was standardized against potassium acid phthalate. The blank was 0.3 cc. of 0.015 *N* hydrogen iodide. Both the sodium hydroxide and the sodium thiosulfate solutions were restandardized the day before they were used. The analysis of known solutions showed that in mixtures of iodine and hydrogen chloride the iodine could be determined with a precision of 3 parts in 10,000 and the H^+ to within 10 parts in 10,000.

Method 2.—The free iodine was titrated with approximately 0.1 *N* sodium thiosulfate. Two grams of potassium iodide was added and after fifteen minutes the liberated iodine was titrated.[8] It is clear that the sodium thiosulfate does not have to be standardized since ζ is given by

$$\zeta = \frac{\text{Weight of } Na_2S_2O_3 \text{ solution used to titrate free iodine}}{\text{Weight of } Na_2S_2O_3 \text{ solution used in both titrations}}$$

The analysis of known solutions of iodine and hydrochloric acid by this method showed the ratio $2(I_2)/(2(I_2) + (HCl))$ could be determined with a precision of 8 parts in 10,000.

In all determinations of iodine, the end-point was overrun and the solution back titrated with 0.005 *N* iodine solution. The blank correction was 1–2 drops of 0.005 *N* iodine. The best end-points, as Washburn[9] pointed out, were pink.

Theoretical Calculation of ζ.—The theoretical investigation[1] gives the relationship between the fraction of hydrogen iodide decomposed at equilibrium, the concentration of deuterium iodide in the original hydrogen iodide, the concentration of deuterium iodide in the hydrogen iodide remaining at equilibrium, and the concentration of deuterium in the hydrogen produced by the decomposition of the hydrogen iodide. We may experimentally determine any pair of these quantities and compare the relationship between them with that theoretically predicted.

At equilibrium there are four equilibria involved

$$\overset{a}{H_2} + \overset{d}{I_2} \longrightarrow \overset{g}{2HI} \qquad (3)$$

$$\overset{c}{D_2} + \overset{d}{I_2} \longrightarrow \overset{h}{2DI} \qquad (4)$$

$$\overset{b}{HD} + \overset{d}{I_2} \longrightarrow \overset{g}{HI} + \overset{h}{DI} \qquad (5)$$

$$\overset{a}{H_2} + \overset{c}{D_2} \longrightarrow \overset{b}{2HD} \qquad (6)$$

The concentration in moles of the various molecular species at equilibrium will be denoted by the letters immediately above them. Let K_1,

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(7) Treadwell and Hall, "Analytical Chemistry," Vol. II, p. 552, 6th ed.

(8) Kolthoff and Furman, "Volumetric Analysis," Vol. II, p. 389; I. M. Kolthoff, *Pharm. Weekbl.*, 57, 68 (1920).

(9) E. W. Washburn, THIS JOURNAL, 30, 31 (1908).

K_2, K_3 and K_4 be the respective equilibrium constants of (3), (4), (5) and (6). Only three of the four equilibria are independent since K_3 can be expressed in terms of K_1, K_2 and K_4

$$K_3 = K_1K_2/K_4$$

The values of K_1, K_2 and K_4 have been calculated previously by the authors, for several temperatures. If we experimentally determine ζ and the concentration of deuterium iodide in the original hydrogen iodide, we can set up six independent equations which will permit us to solve for the six unknowns, a, b, c, d, g, h. Let x, y and u be the number of atoms of H and D and I, respectively, in the system. From the conditions of our experiment, $x + y = u$. Then

$$g^2 - K_1ad = 0 \tag{7}$$
$$gh - K_3bd = 0 \tag{8}$$
$$b^2 - K_4ac = 0 \tag{9}$$
$$2a + b + g = x \tag{10}$$
$$2c + b + h = y \tag{11}$$
$$2d + g + h = u \tag{12}$$

where equations (1), (11) and (12) express the condition that the number of atoms of each kind is constant. Three unknowns can easily be eliminated by use of equations (10), (11) and (12) to give

$$g^2 - (K_1d/2)(x - g - b) = 0 \tag{13}$$
$$g(u - 2d - g) - K_3bd = 0 \tag{14}$$
$$b^2 - (K_4/4)(2d + g + y - b - u) = 0 \tag{15}$$

These three equations can be solved by straightforward methods since they contain but three unknowns, but only with very great difficulty. When two of the unknowns are eliminated, one gets an equation of such complexity that it is practically impossible to find the roots. The equations (13), (14) and (15) can be solved, however, to any degree of precision by Newton's method of approximations.[10] Whittaker and Robinson illustrate the method for two unknowns, but it may easily be extended to three.

The ratio of the equilibrium constants calculated are given in Table I.

TABLE I

T, °K.	0	298.1	400	575	700
K_1/K_2	0.0	1.164	1.212	1.234	1.222

Also, the values of the equilibrium constant K_4 were calculated to be

T, °K.	298.1	400	575	700
K_4	3.269	3.494	3.710	3.800

These values have been confirmed experimentally.[11] By interpolation and extrapolation we have found that the values K_1/K_2 and K_4 for the temperatures which we used are for 398°, 1.225 and 3.781 and for 468°, 1.215 and 3.823, respectively.

From these equilibrium constants, it is possible to calculate the fraction of the hydrogen iodide decomposed as a function of the isotopic composition and temperature.

If we determine ζ and the concentration of deuterium in the hydrogen produced in the reaction, we may set up a set of analogous equations which will give us ζ in terms of the atomic concentration of H and D in the hydrogen instead of being given in terms of x, y and u as in the previous case.

The equations are

$$g^2 - K_1ad = 0 \tag{16}$$
$$gh - K_3bd = 0 \tag{17}$$
$$b^2 - K_4ac = 0 \tag{18}$$
$$a + b + c - d = 0 \tag{19}$$
$$\frac{2a + b}{2(a + b + c)} = \alpha \tag{20}$$
$$\frac{2c + b}{2(a + b + c)} = \beta \tag{21}$$

where α and β are the atomic fraction of H and D, respectively, in the hydrogen. These equations may be solved in the same manner as the previous set.

In practice the uncertainty of $\Delta\zeta$ calcd. due to the method was reduced to less than 0.00004 by a sufficient number of approximations.

The concentration of deuterium in Experiments 2 and 4 was determined by Dr. Walker Bleakney on his mass spectrograph.[12] The concentration of deuterium in Expt. 5 was determined by burning 400 cc. of the hydrogen iodide used in the run and determining the concentration of deuterium in the water by the interferometric method of Crist, Murphy and Urey.[13] The interferometer was calibrated with samples of water whose isotopic composition was determined by measuring the density and assuming that the density of deuterium oxide is that given by H. S. Taylor and P. W. Selwood.[14]

A summary of the results of our experiments is given in Table II.

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[10] Whittaker and Robinson, "The Calculus of Observation," p. 90. 2d ed.

[11] D. Rittenberg, W. Bleakney and H. C. Urey, *J. Chem. Phys.*, 2, 48 (1934).

[12] W. Bleakney, *Phys. Rev.*, [2] 41, 32 (1932).

[13] R. H. Crist, G. M. Murphy and H. C. Urey, *J. Chem. Phys.*, 2, 112 (1934).

[14] H. S. Taylor and P. W. Selwood, THIS JOURNAL, 56, 998 (1934).

TABLE II

The results of our experiments are given in this table. $\Delta\zeta$ is defined as the change in ζ caused by the presence of deuterium. The last column gives the time necessary for the HI to come within one part in 2000 of equilibrium calculated from M. Bodenstein's data. The values for experiment 5 differ slightly from those previously reported[2] because of a more exact calibration of the interferometer readings used in the analysis for deuterium.

Expt.	T, °C.	Concn. D	ζ Expt.	ζ Calcd.	$\Delta\zeta$ Expt.	$\Delta\zeta$ Calcd.	Time of run	Time for HI to come to equilibrium
1	398	0.0%	0.20719[a]	....	....	....	70 hours	26 hours
2	398	14.3[d]	.20838	0.20894	0.00119	0.00175	144	36
3	468	0.0	.22724[b]	....	....	....	30	0.9
4	468	41.7[d]	.23287	.23326	.00563	.00602	14[e]	0.8
5	468	75.5[c]	.23877	.23904	.01153	.01222	41	0.9

[a] Bodenstein's value for ζ at this temperature is 0.20703. [b] Bodenstein's value for ζ at this temperature is 0.22772. [c] Concentration of deuterium in the hydrogen iodide. [d] Concentration of deuterium in the hydrogen produced by the decomposition. [e] The reaction vessel was kept at 500° for two hours at the beginning of the run.

Precision of Results.—We estimate that the errors in the temperature at which the equilibria were measured to be 1° for the lower temperature and 3° for the higher. No attempt was made to determine the temperature more precisely since the rate of change of $\Delta\zeta$ with temperature is small. For run 5, $d(\Delta\zeta)/dT = 0.000017$. We estimate the accuracy of ζ to be 0.00050 for runs 1 and 2 and to be 0.00040 for the remainder. Our experimental results agree with the calculated ones to this precision. It is to be noted that all our experimental results are lower than the calculated ones. Our results do not have a sufficient precision to warrant any conclusion in regard to the reality of this deviation between experiment and theory. If, however, instead of using our formula (II), we had used formula (I) for the energy states of HD and D_2[(1)] it would lower our calculated values of ζ by about 0.00050 for the 75.5% sample, by 0.00030 for the 41.7% sample and by 0.00007 for the 14.3% sample. This would bring our experimental values into slightly better agreement with the calculated ones.

Summary

The percentage of thermal dissociation of mixtures of protium and deuterium iodide has been determined at 398 and 468°, and compared with the theoretical predictions. They are found to be in agreement within the limits of experimental error. A determination of the equilibrium constant for the protium iodide decomposition at these two temperatures agreed within our limits of experimental error with the values given by Bodenstein.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Hydrolysis of Ferric Ion. The Standard Potential of the Ferric–Ferrous Electrode at 25°. The Equilibrium $Fe^{+++} + Cl^- = FeCl^{++}$

BY WILLIAM C. BRAY AND ALLEN V. HERSHEY

Dilute aqueous solutions of ferric salts are known to contain considerable amounts of colloidal ferric hydroxide and hydrogen ion, but the possibility of isolating the first step in the hydrolysis

$$Fe^{+++} + H_2O = FeOH^{++} + H^+ \qquad (1)$$

has received little attention. Thus, although in 1907 Bjerrum,[1] from a study of the conductivity of 0.025 to 0.0003 molal ferric chloride solutions, calculated the equilibrium constant of this reaction to be $K_1 = 25 \times 10^{-4}$ at 25°, chemists seem to prefer the theory that $FeOH^{++}$ is unstable with respect to ferric ion and the colloid. In other words, it is usually assumed that equilibrium lies far to the right in the reactions

$$2FeOH^{++} = Fe^{+++} + Fe(OH)_2^+, \text{ and} \qquad (1b)$$

$$FeOH^{++} + Fe(OH)_2^+ = Fe^{+++} + Fe(OH)_3 \text{ (colloidal)} \qquad (1c)$$

Our approach to this problem is based upon the following ideas. When the hydrolysis of a ferric salt is gradually decreased by the addition of acid, the quantities of colloid and $Fe(OH)_2^+$ must decrease more rapidly than that of $FeOH^{++}$;

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(1) Bjerrum, *Z. physik. Chem.*, **59**, 350 (1907).