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The Hydrogen Isotope of Atomic Weight Two

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I. HISTORICAL INTRODUCTION

IN 1927, Aston,[1] using his mass-spectrograph, determined the atomic weight of hydrogen and obtained a value in close agreement with the chemical value previously obtained by others.* This result was believed to prove that hydrogen had no isotopes. The question was reopened, however, by the discovery of the oxygen isotopes by Giauque and Johnston,[4] for this showed that the apparent agreement between the mass-spectrographic and the chemical atomic weights was in fact a disagreement since Aston used $O^{16} = 16.0000$ as a standard while the chemical standard is the natural mixture of O^{16}, O^{17} and O^{18} taken as mass 16.0000. The determinations of the relative abundance of the oxygen isotopes by Mecke and Childs[5] made possible an estimate of the relative abundance of hydrogen isotopes of masses 1 and 2 by Birge and Menzel.[6] They estimated the abundance of the hydrogen isotopes of mass 2 (deuterium) as 1 : 4500 of the more abundant isotope. Recently more precise determinations of the relative abundance of the oxygen isotopes have been made by various observers[7] which require that the predicted abundance be 1 : 3700.

The discovery of the oxygen isotopes by molecular spectrum methods stimulated searches for other rare isotopes of the lighter elements. In the years following, C^{13}, N^{15} and Be^8(?)[8] were discovered. The addition of these to the known isotopes gave a completed appearance

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* The subject is critically reviewed by Moles[2] and Birge.[3]

to the proton-electron plot of known atomic nuclei in the region below sulfur and the regularities suggested the possible existence of H^2, H^3 and He^5.[9] Such empirical regularities, without adequate theoretical background, cannot be regarded as more than a suggestion of the possible existence of unknown nuclear species and, of course, cannot indicate the abundance to be expected.

An isotope as rare as one part in 4500 of the more abundant isotope had not been detected at the time of Birge and Menzel's work and some method of concentrating the isotope and more sensitive methods of detection were required. Urey, Brickwedde and Murphy[10] applied the theory of Debye to the calculation of the relative vapor pressures of H_2, HD and HT* in the solid state and found that very appreciable differences were to be expected and that fractional distillation of liquid hydrogen near its triple point should be an effective method for the concentration of any heavier isotopes. Since, by use of Bohr's theory, positions of the lines of the atomic spectra of deuterium and tritium could be calculated with considerable accuracy and since the lines in the atomic spectra are very intense, photographing lines in the atomic spectra was recognized as a sensitive and unambiguous method of detecting an isotope of hydrogen. The atomic spectra of ordinary tank hydrogen and the residue from the evaporation of 4000 cc of liquid hydrogen were therefore photographed. In both cases the presence of deuterium was detected; the spectral lines, however, were much more intense for the hydrogen enriched by distillation. The isotope of mass three was not found in either sample.

The discovery of deuterium was confirmed by Bleakney[11] by a mass-spectrographic examination of ordinary commercial electrolytic hydrogen and also of the enriched samples of Urey, Brickwedde and Murphy. He estimated the abundance of deuterium in ordinary electrolytic hydrogen as one part in 30,000 (preliminary, see Section II) and in the enriched sample as one part in 1050. Kallmann and Lasareff[12] in a similar study, likewise detected its existence in samples enriched by fractionation of liquid hydrogen. The existence of deuterium was also confirmed by Hardy, Barker and Dennison[13] in an investigation of the infrared spectra of HCl and DCl. Further, Rank,[14] by use of a high dispersion prism spectrograph, was enabled to photograph the $D\gamma$ line without the presence of "ghosts." The concentration of hydrogen by fractional distillation was confirmed by Kallmann and Lasareff, by Meissner and Steiner[15] and also by Keesom, van Dijk and Haantjes,[16] the latter authors securing a much greater increased concentration by using a distilling column.

As early as 1911 Sir J. J. Thomson[17] observed particles of molecular weight three in his apparatus for the detection of isotopes. These molecules were of two varieties, one transient and probably H_3^+ and the other permanent and probably $(HD)^+$. In recent experiments[18] he has been able to increase the intensity of the mass 3 parabola and he expresses the view that his earlier work actually detected the HD molecule. In 1919 Harkins[19] suggested the possible existence of deuterium because of regularities in atomic nuclei, though as yet there has appeared no very great evidence that the deuteron as such is a constituent of nuclei. Grubb[20] has suggested that an active form of hydrogen previously assumed to be H_3 is really H_2D, though conclusive proof of this view is lacking. In 1919 Stern and Volmer[21] attempted the concentration of a heavier isotope of hydrogen using a diffusion method with steam as a carrying gas. Their results were negative, due probably to the use of electrolytic hydrogen gas of low deuterium content obtained from a cell containing natural water or perhaps due to an exchange reaction between the hydrogen gas and the steam used in their experiments.

The great advances which have been made in the study of deuterium are due largely to the discovery by Washburn, during the spring of 1932, of the electrolytic method of separating hydrogen and deuterium. Washburn and Urey[22] reported that electrolytic cells used in the industry for the production of hydrogen and oxygen contained markedly increased concentrations of deuterium and that this method could be used for the preparation of pure

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* In this review, the symbols H, D and T and the names hydrogen, deuterium and tritium, will be used for H^1, H^2 and H^3, respectively.

deuterium oxide. Lewis and Macdonald[23] first used this method for the preparation of pure deuterium oxide and their demonstration of the comparative ease with which the process could be carried out has led many others to concentrate deuterium oxide in relatively large quantities.

The atomic weight of deuterium was determined by Bainbridge.[24] The value obtained is 2.01363 ± 0.00008, referred to O^{16} as 16.0000. Referred to the chemical standard, this becomes 2.01309. The atomic weight of hydrogen is 1.007775 and 1.007504, in terms of the physical and chemical scales. The abundance ratio, as given by Bleakney and Gould[25] from their most recent determinations, is 1 : 5000. This gives 1.00770 for the mean atomic weight of the natural element in terms of the chemical standard. The atomic weight of tritium has been found to be 3.0151 from the conservation of energy and mass in transmutation reactions producing it.[39] In this review we shall adopt these values of the constants.

That marked differences in the chemical properties of hydrogen and deuterium should exist was first demonstrated by the use of well established methods by Urey and Rittenberg,[26] who calculated the equilibrium constants of exchange reactions, by the differences in the vapor pressures and melting points of water by Washburn[27] and by the separation of hydrogen and deuterium by Washburn and Urey.[22] That kinetic phenomena involving the two isotopes should differ quite decidedly was first suggested on the basis of the "tunnel effect" by Cremer and Polanyi[28] and on the basis of zero point energy differences by these authors and Eyring,[29] independently.

Marked biological effects of deuterium oxide were first reported by Lewis[30] and by Taylor[31] and their co-workers. The first studies on the effects of deuterium oxide on cancer (negative in all cases) were made by Woglom and Weber[32] and by Suguira and Chesley.[33] The use of deuterium oxide as a physiological indicator was first introduced by von Hevesy and Hofer,[34] who studied the exchange of water of fish with their surroundings. This use of deuterium may prove to be one of the most important in the whole field of science. The biological effects, however, will not be discussed in this paper since they may more suitably be treated by biologists familiar with the general field of biochemistry.

Lewis, Lawrence and Livingston[35] found that deuterons are several times as effective as protons in the disintegration of lithium. Their work was immediately followed by that of Rutherford and his co-workers[36] and later by Crane, Lauritsen and Soltan[37] and by Tuve and his colleagues.[38] More recently, Oliphant, Harteck and Rutherford[39] and Harnwell, Smyth, Van Voorhis and Kuper[40] have produced a hydrogen atom of mass 3 by bombardment of deuterium with high speed deuterons and its existence in ordinary hydrogen has been proved by Tuve, Hafstad and Dahl[41] and Lozier, Smith and Bleakney.[42] The use of deuterium in disintegration experiments represents one of its most important applications. However, so many of the important points are related to observations with protons, neutrons and alpha-particles that they could not suitably be included in this review.

II. METHODS OF DETECTION AND ANALYSIS AND THE ABUNDANCE OF DEUTERIUM

1. Analytical methods

The examination of the spectrum of atomic hydrogen is the most definite method for detecting the isotopes of hydrogen. The displacements of the Balmer lines of deuterium from those of hydrogen have been calculated and are in good agreement with the experimentally observed value,[10] as may be seen by referring to Table XIV, Section VII. As a quantitative method of isotopic analysis, however, the use of the atomic spectrum involves all the usual difficulties and errors in determining relative intensities of light, and, in addition, great difficulty is had in avoiding partial reversal of the lines of the more abundant isotope when it constitutes an overwhelmingly large part of the sample, as is the case in ordinary hydrogen.[43] By comparison of the intensity of the deuterium lines and ghosts of the Columbia grating relative abundances of deuterium were estimated to better than a factor 2 when approximately the same conditions were maintained in the discharge tube during successive runs.[*] Relative intensities can be estimated more precisely than this, but difficulties with the "clean up" of deuterium as well as the existence of other more quantitative methods of analysis make this one unworthy of further refinement.

Any of the various "mass spectrographic" methods for the detection of isotopes such as those devised by Thomson,[44] Dempster,[45] Aston[46] and Bainbridge[47] might be used for the estimation of the relative abundances of isotopes.[48] However, only the method of Bleakney[49] has been used for a really quantitative estimate of deuterium. In the case of this latter apparatus, a long ionization source is secured by bombarding gas at low pressures (about 10^{-5} mm of mercury) with an electron beam which is prevented from diverging by the use of a magnetic field parallel to it. The ions formed are drawn from the region of ionization by an electric field, are collimated by a long slit system, and are analyzed by acceleration in an electric field with subsequent bending of the sheet of ions in a magnetic field. The charges on the ions are collected on a long electrode. The ratio of charge to mass of the ions striking the electrode is determined from the strengths of the magnetic field and the accelerating electric field. High resolution and intensities are secured in this way.

In a mixture of hydrogen and deuterium, ions of masses 1 to 6 are secured. Their concentrations depend on the first and second powers of the pressure in the apparatus, as given in Table I. The concentrations of the H^+, H_2^+ and H_3^+ ions have been shown experimentally to depend on the powers of the pressure as given in the table and the first and second power terms are interpreted as indicating the production of ions by primary and secondary processes, respectively.[50] It is to be expected that the probabilities of primary ionization are the same for atoms or molecules containing either hydrogen or deuterium or both of them, and all experimental evidence points to the validity of this assumption. That the probabilities of secondary processes involving deuterium are the same as those involving hydrogen can hardly be expected, since the velocities of chemical reactions involving the one or the other isotope are markedly different in most cases.

TABLE I. *Possible ions resulting from a mixture of two hydrogen isotopes in which H is much more abundant than D.*

	Ion	*m/e*	$f(p)$	Intensity
1	H^+	1	$a_1p+b_1p^2$	weak
2	H_2^+	2	a_2p	very strong
3	D^+	2	$a_3p+b_3p^2$	very weak
4	H_3^+	3	b_4p^2	weak
5	HD^+	3	a_5p	weak
6	D_2^+	4	a_6p	v. v. weak
7	H_2D^+	4	b_5p^2	v. v. weak
8	HD_2^+	5	b_6p^2	v. v. weak
9	D_3^+	6	b_7p^2	v. v. weak

The method of analysis consists in determining the intensities of the ions as a function of the pressure with subsequent analytical or graphical solution of the curves for the first and second power terms and comparison of the constants so secured with those determined for natural hydrogen-deuterium mixtures or other mixtures of known composition. Fig. 1 shows curves secured by Bleakney. In this case the intensity of H_2^+ ions is used as a measure of the pressure. This figure gives the confirming evidence for the existence of deuterium in Urey, Brickwedde and Murphy's "Sample III" of the residue from the reduction by evaporation of 4000 cc of hydrogen to about 1 cc. The more detailed analysis of Curve I showed the presence

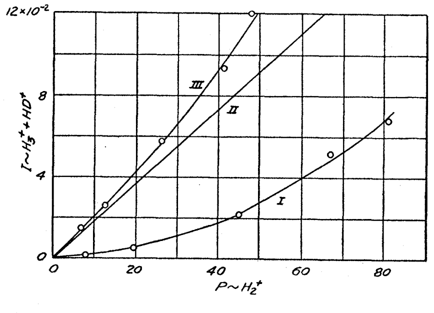

FIG. 1. Total number of ions $H_3^+ + HD^+$ of mass 3 as a function of the number H_2^+ of mass 2. Curve I, ordinary commercial electrolytic hydrogen. Curve III, Brickwedde's concentrated sample. Curve II, difference.

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[*] One of us (H. C. U.) reported to Dr. E. W. Washburn that the concentration of deuterium in the electrolyte of a commercial cell was somewhat less than that in the samples prepared by Brickwedde by distillation of liquid hydrogen and that the concentration was about one part in 2000, while the subsequent density determination showed that the concentration was one part in 1400.

of deuterium in the sample of hydrogen used to the extent of one part in 30,000±20 percent.

The mass-spectrographic method of analysis has proved particularly useful in determining the relative abundances of H_2, HD and D_2 molecules in gas samples.[51]

Farkas and Farkas[52] have used the differences in thermal conductivities of H_2, HD and D_2 to analyze for the ratio of hydrogen to deuterium in a gas. The method has the particular advantage that it requires but small quantities of gas (about 0.002 cc at N. T. P.) and yet should have a precision of somewhat better than one percent of deuterium. At pressures so low that the mean free path is much greater than the diameter of the wire, the heat lost from a hot wire at temperature T to a cooled surface at temperature T_0 is given by the relation

$$E \propto \left[N_{11}\frac{1}{\sqrt{M_{11}}}\int_{T_0}^{T} C_{11}dT + N_{12}\frac{1}{\sqrt{M_{12}}}\int_{T_0}^{T} C_{12}dT + N_{22}\frac{1}{\sqrt{M_{22}}}\int_{T_0}^{T} C_{22}dT \right] P, \quad (1)$$

where N_{11}, N_{12} and N_{22} are the mole fractions, C_{11}, C_{12} and C_{22} the heat capacities, M_{11}, M_{12} and M_{22} the masses of H_2, HD and D_2, respectively, and P is the total pressure. Differences that might exist in the accommodation coefficients of the surface of the wire for the three molecules would require the integrals to be multiplied by additional factors that cannot at present be estimated. The integrals, which we shall refer to as $F_{11}(T)$, $F_{12}(T)$ and $F_{22}(T)$, can be evaluated analytically or graphically, as has been done by these authors, but the use of Johnston's and Long's tables[104] after adding the translational energies is now most convenient.

In carrying through an analysis, a pressure of approximately 0.04 mm of hydrogen gas ($N_{12} = N_{22} = 0$) is first introduced into the apparatus that consists of a glass tube, cooled in liquid air (at T_0), in which is stretched a platinum wire 5 cm long and 0.01 mm in diameter. The mean free path is, therefore, about 200 times the diameter of the wire. A current, i_1, is passed through the wire bringing it to a temperature, T_1, which is determined from the resistance of the wire. The energy lost from the wire is equal to the energy supplied, namely, $R_1 i_1^2$, or assuming that the resistance R varies linearly with the temperature, $rT_1 i_1^2$. An increased current, i_2, is then passed through the wire and the new temperature, T_2, is measured. The hydrogen gas is replaced by a hydrogen-deuterium mixture which may be either a mixture of H_2 and D_2 ($N_{12} = 0$) or a mixture of H_2, HD and D_2, though an arbitrary mixture of the three molecules cannot be analyzed by this method alone, as will be shown later. The pressure is so adjusted that, when a current i_1 is flowing in the wire, the temperature of the wire is again T_1. Then

$$\left[\frac{1}{\sqrt{M_{11}}} N_{11}F_{11}(T_1) + \frac{1}{\sqrt{M_{12}}} N_{12}F_{12}(T_1) + \frac{1}{\sqrt{M_{22}}} N_{22}F_{22}(T_1) \right] \bigg/ \frac{1}{\sqrt{M_{11}}} F_{11}(T_1) = \frac{P_{11}}{P}. \quad (2)$$

A current i_2 is now passed through the wire which comes to a temperature higher than T_2, say T_3. Then

$$\frac{rT_2 i_2^2}{rT_3 i_2^2} = \frac{T_2}{T_3} = \frac{1}{\sqrt{M_{11}}} P_{11}F_{11}(T_2) \bigg/ P\left[\frac{1}{\sqrt{M_{11}}} N_{11}F_{11}(T_3) + \frac{1}{\sqrt{M_{12}}} N_{12}F_{12}(T_3) + \frac{1}{\sqrt{M_{22}}} N_{22}F_{22}(T_3) \right]. \quad (3)$$

The elimination of P_{11}/P between these equations gives one equation for the three unknowns N_{11}, N_{12} and N_{22}. In addition, we have the relation,

$$N_{11} + N_{12} + N_{22} = 1.$$

The three quantities, N_{11}, N_{12} and N_{22} cannot be determined without knowledge of some further relation between these quantities, such as the ratio $(2N_{11} + N_{12})/(2N_{22} + N_{12})$ from an analysis of the gas using another method, or, in the case of an equilibrium mixture of the gases H_2, HD and D_2, the equilibrium constant for the reaction between these molecules. In practice the instrument is calibrated against mixtures of H_2

and D_2 of known composition and against known equilibrium mixtures of H_2, HD and D_2.*

The density of water containing deuterium referred to that of natural water has been widely used to determine its isotopic composition. For this purpose the usual methods of precise density determinations by use of pycnometers serve very well. With sufficiently large samples, a precision of one part per million in density or one part per hundred thousand in deuterium content could be attained over the entire range of concentration if the density of pure D_2O were known with sufficient precision. The correction for deviations from a linear relationship between the mole fraction and density that must be made are small, as has been shown by Lewis and Luten.[53] Their results, corrected to density 25°C/25°C equal to 1.1079 give the following formula for the relation between density and mole fraction of deuterium in water:

$$d(25°\text{C}) = 0.99701 + 0.1087N_2 + 0.0012N_2^2 \quad (4)$$

which, however, is not as precise as the possible measurements of the density of water. Though the pycnometer method is capable of great precision, it has the disadvantage that more than a day may be required for a determination.

Small differences in the densities of two samples of water can be determined by means of the buoyancy balance devised by Dufour[54] and improved by Richards and his co-workers[55] and first used for the determination of deuterium in water by Lewis and Macdonald.[56] It consists of a glass float which will just remain suspended in the reference sample at a convenient temperature. The float, when placed in the unknown sample, will remain suspended at some other temperature. From the differences in the coefficient of expansion of glass and water and a determination of the difference in the temperatures at which the float remains suspended in the two samples of water, the density of the unknown can be determined. A change of 0.006° in the temperature at 16°C corresponds to a difference in density of one part per million in the case of the apparatus used by Lewis and Macdonald. The water must be carefully distilled and freed from dissolved air. The method is particularly useful for the investigation of water containing a concentration of deuterium only slightly greater than that of natural water.

A float method for the determination of density of water has been devised by Gilfillan and Polanyi[57] using the principle of the Cartesian diver, the density being determined from the pressure under which the diver just sinks. Another method used by Gilfillan[58] and by Green and Voskuyl[59] makes use of the different compressibilities of a closed glass float and of water. The floats may be made more compressible than water by making them flat and of thin glass, or less compressible than water by making them of thick glass. The former are suitable for determining wide ranges of densities, while the latter are suitable for the measurement of small differences in the densities of the reference liquid, which is natural water, and the water of unknown composition. The floats of low compressibility can be used to detect differences in density of a few parts in ten million. The apparatus may be calibrated empirically by noting the pressures under which the floats remain suspended in natural water and in water of known density.

Analyses of water can be made easily and rapidly by use of the differences in refractive index of water and water containing increased concentrations of deuterium. This method has been investigated by Lewis and Luten[53] and by Crist, Murphy and Urey.[60] Analyses with the Zeiss interferometer can be made within about ten minutes, to a precision of about 0.02 percent of deuterium in the range of 0 to 20 percent, 0.05 percent of deuterium from 20 to 80 percent and 0.5 percent deuterium from 80 to 100 percent. The water must be carefully purified just as in all other methods of analysis of water for deuterium content. The calibration of the instrument is a rather tedious task but, once done, the method is very satisfactory.

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* Farkas and Farkas neglected the mass factors giving the relative number of collisions of these molecules; their equation may, therefore, be secured by deletion of the mass factors from the above relations. Though it is impossible to decide between the two developments of the theory on the basis of the published data, it is evident that these factors greatly alter the calculations. The error here implied does not, however, apply to these authors' use of the thermal conductivity method in the analysis of ortho-para hydrogen or deuterium and, moreover, does not invalidate their work on the analysis of hydrogen-deuterium mixtures since they used an empirically determined calibration curve.

The gas balance used by Aston[46] to follow the partial separation of neon by diffusion has not been used for the analysis of the hydrogen isotopes. Aston determined the density of small samples of gas to about 0.1 percent and it appears possible that the sensitivity could be increased by using higher pressures of gas and hence larger samples, and by carefully thermostatting the instrument. This apparatus should be particularly useful in the range of low concentrations and small samples as are likely to be encountered in biological work. The method is described by Aston and need not be presented here.

The concentration of deuterium in hydrogen-deuterium mixtures has been determined by Rutherford and his co-workers[61] by determining the number of 13 cm range alpha-particles resulting from the high voltage bombardment of lithium with ions of the mixture. These alpha-particles result only from nuclear collisions involving the deuteron. The method is rapid, but can hardly be used by most research workers.

2. The abundance of deuterium

The original estimate, by Birge and Menzel,[6] of one part of deuterium in 4500 of hydrogen was first confirmed by Urey, Brickwedde and Murphy[10] (1 : 4000). Then Bleakney[11] reported 1 : 30,000 using his mass-spectrographic method, and this was confirmed by Tate and Smith.[62] Urey, Brickwedde and Murphy[40] showed that their spectroscopic estimate was probably too high because of partial reversal of the hydrogen lines. From the concentration that occurred in an electrolytic cell, Lewis and Macdonald[56] concluded that the ratio is 1 : 6500. Finally, Bleakney and Gould[63] determined the relative abundance in a sample of hydrogen prepared from water by its complete reduction with metallic iron as 1 : 5000 and this value is generally accepted today.* The value deduced by the method of Birge and Menzel, using the most recent value for the ratio of the oxygen isotopes, namely, $O^{16} : O^{18} = 514 : 1$ is about 1 : 3700, and thus the two values are in approximate agreement. The discrepancy is due most likely to errors in the chemical atomic weight of natural hydrogen-deuterium because of the fractionation of the isotopes of hydrogen in electrolysis, distillation of water and chemical reactions generally. Menzel[64] has found that the cosmic abundance of deuterium must be much less than that on earth and probably $<1 : 600{,}000$, and Unsold[64] finds that it is less than about 1 : 100,000. This is very likely due to a loss of large amounts of hydrogen from the earth with most of the deuterium remaining because of its slower rate of escape as compared to the light isotope. Menzel's estimate of the maximum abundance in the sun, nebulae and stars indicates that the earth originally had at the beginning at least 150 times as much hydrogen as it has at present.

The variations in the relative abundance of deuterium and hydrogen in natural sources, animal, plant and inorganic, have been investigated by a number of workers. It was early shown that no great differences in relative abundance existed between meteoric water and fossil waters by Urey and Bradley.[65] Washburn and his co-workers[66] reported the first appreciable variations in relative abundances in waters from plants and mineral sources. Dole,[67] Snow and Johnston,[68] Gilfillan,[58] Greene and Voskuyl,[50] Stewart and Holcomb[74] and Ball[69] investigated samples of water from a number of sources, and recently Emeléus[70] and his co-workers have given a very comprehensive survey on the densities of water from animal, plant, mineral and industrial sources, which, because of the high precision and extensive character of the work, eclipses all previous work. Variations in density of one part per million or more are very common and one wonders how it could happen that this variation in density was not observed many years ago.[71] The observations are too detailed to reproduce here and it is difficult to see much regularity in the results.

Rasorite from California contains water of the highest density of any from mineral sources, though other salt deposits contain water of higher density than rain water. These increased densities must be due to the evaporation of salt

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* Ingold, Ingold, Whitaker and Whytlaw-Gray (Nature **134**, 661 (1934)) report an attempt to prepare pure hydrogen oxide. They succeeded in getting water whose density was 12 parts per million less than that of ordinary water and hence believe that deuterium is present in natural water to the extent of one part in 9000. In this laboratory we have prepared water having a density 21 parts per million less than that of natural water. This corresponds to approximately one part in 5000 of deuterium, and we believe that the estimate of these authors is too low.

lakes, with a resulting increased concentration of deuterium in the residual water.

A maximum increased density of 4.41 parts per million in waters from vegetable origins was observed except that sucrose, a relatively pure chemical, gave water 8.6 parts per million greater than London water. These variations may be due to the different vapor pressures of the waters influencing the evaporation rates from the leaves, the different rates of diffusion through the stomata of the leaves, or, most likely, to equilibrium constants for exchange reactions between water and the organic substances of the plants, which favor increased concentrations in these organic substances. Appreciable variations in the densities of water from different animal origins also occur.

The variations in densities of waters from commercial sources can be explained as due to known fractionation processes, distillation, electrolysis, adsorption or chemical fractionations of the types discussed in the following sections. The water of crystallization of alum contains more deuterium that the mother liquor. Slight fractionation occurs in adsorption on silica gel and charcoal (as also observed by Washburn), and by freezing water, the first ice containing an increased concentration of deuterium.*

Washburn and Smith[58] find that Atlantic Ocean water has a higher density than rain water by ~2 parts per million.[66, 50] Such a difference is to be expected because of the different vapor pressures of water and water-*d*. Wahl and Urey[72] find that the vapor pressures have the ratio 1.085 at 11°C.

A. Farkas and L. Farkas[73] have shown that hydrogen in equilibrium with water should contain about $\frac{1}{3}$ to $\frac{1}{4}$ as much deuterium as the water. However, no extensive deposits of free hydrogen gas are known.

III. Methods of Separating Hydrogen and Deuterium

1. The electrolytic method

a. Experimental observations. The electrolytic separation[22] of hydrogen and deuterium is the most convenient and rapid method so far devised for securing deuterium in large quantities. The great importance of deuterium in many fields of science is due largely to the success of this method. The fractionation factor, defined as the ratio of hydrogen to deuterium in the gas divided by the same ratio in the water from which it is electrolyzed, first appeared to be very large, since the natural abundance of deuterium was thought to be small, about 1 : 30,000. Since the water in industrial electrolytic cells differs in density from natural water by as much as 70 parts per million, it must contain about 0.06 percent more deuterium than natural water. Thus the effective fractionation factor should have been at least 19, so large, in fact, that the evaporation of the water from the cells would account for the entire loss of deuterium.[75] Since the abundance is now known to be 0.02 percent, the effective fractionation factor in commercial cells is about 4, with many cells operating with considerably smaller fractionation factors, the lowest observed by us being approximately 2. The fractionation factor of laboratory cells may be much greater than this; the highest average effective fractionation factor we have observed is 8.5, which is greater than any reported in the literature. This is obtained with a bank of thirty laboratory cells which have steel cathodes and nickel anodes, and which are now operating in our laboratories. The escaping gases in this plant are not dried. Almost a continuous series of values between the limits 2 and 8 have been reported.[83, 84, 85] Since within the rather rough limits of experimental error, the fractionation factor is independent of the concentration of deuterium in the water, the differential equation for the fractionation may be written[23]

$$dN_1/dN_2 = \alpha N_1/N_2 \quad \text{or} \quad d \ln N_1 = \alpha d \ln N_2, \qquad (5)$$

where N_1 and N_2 are the number of moles of hydrogen and deuterium, respectively, in the water and α is a constant.

Because of the evaporation of water, the effective fractionation factor, α', secured when the gases are not dried, differs from the true fractionation factor, α, of the electrolytic process.

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* Emeleus' explanation of the difference in density of natural and artificial ice as due to a difference in deuterium content cannot be accepted. In order to account for a difference in density of one part in 900, it would be necessary to assume that the natural ice contained 1 percent of deuterium.

Neglecting the difference in the vapor pressures of the waters, Rank[75] shows that α' equals $(n_1+\epsilon N_1)N_2/(n_2+\epsilon N_2)N_1$ while α equals n_1N_2/n_2N_1, where n_1 and n_2 are the mole fractions of H and D in the gases evolved, N_1 and N_2 these fractions in the water, and ϵ is the moles of the water evaporated per mole of water electrolyzed. α is the constant of theoretical interest, while α' is the one of importance in practical separation methods.

Nearly any fractionation process can be used in a variety of ways to secure increased concentration of the pure substances. In commercial cells, water is added from time to time in amounts that are small compared to the volumes of the cells. The gas escaping from new cells contains less deuterium than natural water, but after a sufficiently long time, the concentration of deuterium increases until the ratio of concentrations in the gas to this ratio in the electrolyte equals the fractionation factor. No concentration beyond this point can be expected.

In what we shall call the "batch method," a volume of a dilute electrolytic solution, usually of KOH or NaOH, is electrolyzed down until the electrolyte becomes too concentrated for satisfactory operation of the cell. Part of the concentrated solution is then removed from the cell, the alkali is neutralized with carbon dioxide gas, and the separation of the solvent and the alkali metal carbonate is accomplished by distillation. The distillate is added to the concentrated solution remaining in the cell in order to dilute it, and the electrolytic concentration process is then repeated. The Rayleigh distillation formula integrated for a constant fractionation factor, α', gives the relation between initial and final mole fractions of deuterium in the water, N_0 and N, respectively, and the initial and final volumes, W_0 and W. The relation is

$$\left(\frac{1-N}{1-N_0}\right)^{1/(\alpha'-1)}\left(\frac{N}{N_0}\right)^{\alpha'/(\alpha'-1)}=\frac{W_0}{W}. \qquad (6)$$

If α' equals 6 and 0.07 percent water is used as the starting material, approximately 25 liters must be electrolyzed to a residue of 1 cc in order that this residue shall be 99.9 percent D_2O. This initial water contains 17.5 cc of deuterium oxide. It is obvious that the gases from the electrolysis of the more concentrated water must be burned and reworked in order to avoid the loss of large amounts of deuterium. This method was first used by Washburn[76] to secure water containing a few percent of deuterium and by Lewis and Macdonald[23] to produce first the nearly pure deuterium oxide.

Continuous flow methods have been used by Anderson, Halford and Bates[77] with but slight loss in efficiency in the region of low concentrations. In this process, a dilute alkaline solution flows successively through a series of cells, becoming slightly more concentrated on passing from one cell to the next. The portion withdrawn from the last cell is a highly concentrated solution of alkali containing an increased concentration of deuterium over that of the initial water only slightly less than that calculated from Eq. (6). The gases cannot be conveniently burned when this process is used, and hence it is not suitable for the more highly concentrated waters.

A cascade process has been reported by Urey and Wahl.[78] In this, water is distilled from one cell of a series to the next at the same rate as the burned gases obtained by electrolysis in the latter are condensed into the former. The fractionation secured follows the same laws that apply to a plate type of fractionation column. The fractionation secured and the speed of the process was approximately that expected from theory, but the difficulty of operation, at least on a laboratory plant scale, is very great. The "batch method" is preferable for small scale operation.

In order to secure low resistance in a cell and hence large currents with low heat production, most workers place the electrodes close to each other and allow the hydrogen and oxygen to escape together without separation. The problem of burning these gases has been overcome by Taylor and his co-workers[79] by passing the gases through a short sand trap (60 mesh sand) and then through nozzles so small that the flame does not strike back. The gas velocity in the nozzle should be approximately 35 meters per second. When the plant is shut down the sand trap stops the explosion wave, thus preventing an explosion of the gas in the cells. Rank resorted to the simple expedient of using iron cells of sufficient strength to withstand the explosion pressure. Spray condensing in the tip sometimes extinguishes the flame which must be immediately relighted if deuterium is not to be lost. Heated filaments have been used for this purpose. In our laboratories two or more intersecting jets fed by different banks of cells are mounted in the same burning chamber, so that an extinguished jet is lighted by the other jet or jets. One jet can be made to burn the hydrogen produced by 1000 amperes and probably larger ones can be used. Details of several laboratory plants have been described[80] in the literature.

Studies of the efficiency of the electrolytic process have given some pertinent facts, although the data are often contradictory and lacking in precision. The concentration of deuterium in the alkaline electrolytic solutions which have been used for long periods of time varies considerably. In some cases[81] increased concentrations have been observed in old storage batteries and not in other cases.[82] Published fractionation factors often differ markedly and, as pointed out above, we have observed fractionation factors higher than any reported in the literature. The fractionation factor varies during the course of the electrolysis and from run to run. It is probably to be expected that great care must be taken in order to construct electrodes which are reproducible with respect to the fractionation factor.

Topley and Eyring,[83] Bell and Wolfenden[84] and others [85] have investigated the fractionation factor as it depends on the electrode, the electrolyte and the current density. The current density apparently influences the fractionation slightly, higher densities favoring increased fractionation factors. The concentration of the electrolyte has little effect. Alkaline solutions give better separation than acid solutions. The order of efficiency of combinations of metallic electrodes and solutions, according to Topley and Eyring, is as follows: Pt, KOH; Fe, KOH; Pb, KOH; Cu, KOH; Pb, H_2SO_4; Pt, H_2SO_4; Cu, H_2SO_4; Ag, KOH and H_2SO_4; Ni, KOH; Pt black, H_2SO_4; Hg, H_2SO_4. Bell found the order; Ni, Pt and Cu with NaOH about equally effective; Pb, H_2SO_4; Pt black, H_2SO_4. The reported fractionation factors run from 3.4 to 7.6, though 5 or 6 is the most common value. The lower efficiency of commercial cells may be due to their high temperature of operation (50°–60°C) and some carry-over of water as spray or vapor.[75]

The temperature coefficient of the fractionation factor has been investigated by Bell and Wolfenden[84] and by Urey[80] though the determination is not precise in either case. α is the ratio of two velocity constants, and thus we may assume that

$$d \ln \alpha/dT = -Q/RT^2, \quad \ln \alpha = Q/RT + C, \qquad (7)$$

where Q is the difference in activation energies for discharge of H^+ and D^+. If C is zero so that the entire separation is due to a difference in activation energy, Q can be calculated from the value of α or from its temperature coefficient. Bell's values give 1160 and 1220 calories per mole, while Urey's corresponding values are 1050 to 1500 calories per mole. These values are for nickel electrodes. These results indicate that the entire fractionation is due to the exponential term and not to a constant C.

Since at ordinary temperatures the equilibrium

$$H_2 + HDO = HD + H_2O$$

favors a ratio of hydrogen to deuterium atoms in the gas three times as great as this ratio in the water, the fractionation factor should be 3 if equilibrium conditions were maintained. If hydrogen gas containing more hydrogen than corresponds to this ratio is produced by an electrolytic cell, catalytic exchange between the hydrogen and water tends to decrease the fractionation factor, and, in fact, requires that it should approach the value 3 as a limit. This effect may account for the erratic variations in observed fractionation factors. Washburn, Smith and Frandsen[86] carried out a fractionation using a platinized electrode with rather low current densities so that equilibrium conditions should have been approached. The results of the electrolysis were as follows:*

Density	Volume	α	Density	Volume	α
1.000056	15000		1.000355	1000	3.14
1.000072	7000	1.49	1.000696	300	2.81
1.000129	4000	2.71	1.001398	100	2.79

The fractionation factor calculated from the first two sets of data appears to be very low but

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* We are indebted to Dr. E. R. Smith for the detailed data used to calculate these values.

the remaining values are fairly constant, giving a fractionation factor slightly less than 3.

Recent experiments by Farkas and Farkas[87] in which nickel electrodes were used confirm these results of Washburn and also show that the hydrogen-deuterium mixture produced was indeed an equilibrium one. They secure 3.16 as the enrichment factor when 26.2 percent heavy water is used. Calculations of the equilibrium constants for all the reactions between H_2, HD, D_2, H_2O, HDO and D_2O made by several authors* show that the fractionation factor should increase with increasing deuterium concentration and thus these results agree substantially with those of Washburn. Fractionation factors greater than 3 must be due to the velocity of the discharge process.

b. Theory of the electrolytic separation. Several kinetic processes in electrolysis must be considered as possible sources of the difference in rate of discharge of the two substances. Obviously, processes at the anode need not be considered. At the cathode, an electron is transferred from the metal to the solution with the simultaneous attachment of an atom of hydrogen or deuterium to the electrode. The hydrogen is generally believed to be adsorbed on the electrode in the atomic form and this then combines to form molecular hydrogen. The discharge of the ion by an electron and the adsorption of the atom to the metal surface must be regarded as one process, for the production of atoms of hydrogen in the solution and free from the electrode would require a very much larger normal potential than the formation of hydrogen atoms on the surface in equilibrium with molecular hydrogen. Either or both of these two processes may be slow and the slow process must be responsible for the separation since any fast reaction would soon establish equilibrium conditions and make the separation depend only on the normal electrode potential difference which, as has been indicated, must be too small to account for the observations. Other processes such as the rate of diffusion of atoms or ions to the surface and differences in the mobility of the ions might be considered important at first sight. Fowler[88] shows that these factors are not important.

Older studies on the overvoltage of hydrogen give very interesting information in regard to the processes taking place. The relation between current and overvoltage has been shown, particularly by Bowden,[89] to be independent of the hydrogen ion activity though, of course, the equilibrium electrode potential depends on the activity of the hydrogen ion. Though the discharge, according to the equation

$$M^- + H_2O \rightarrow OH^- + MH,$$

where M^- represents an electron in the metal and MH a hydrogen atom adsorbed on the metal, may not be a unique solution, it appears from this independence of the hydrogen ion activity to be a likely mechanism and one that may be treated simply. This mechanism would mean that the ease with which the electron enters the solution would not greatly depend on the concentration and the particular kind of positive ions in the solution, which is in accord with observation. This reaction is then followed by

$$2MH \rightarrow H_2 + 2M.$$

At low current densities the relation between current and overvoltage can be explained on the assumption that the slow reaction is the rate of recombination of atoms on the surface of the electrode, while at higher currents and overvoltages the relation can be explained as due to the slowness of the rate of discharge of water molecules. Thus Hammett[90] gives the following equation for low hydrogen overvoltages on platinum:

$$I = k_2(1 - \exp(-2F\Delta E/RT)), \qquad -0.01 < \Delta E < +0.01, \quad (8)$$

where ΔE is the overvoltage, F the Faraday, I the current and k_2, a constant. The equation for high overvoltages, as given by Bowden[89] is

$$I = -k'(\exp(-0.5F\Delta E/RT)), \quad (9)$$

where k' is a constant. No exact explanation of the factor 0.5 has been given except that a quantity γ occurs in Gurney's theory, which can be assigned the value 0.5. The theory, moreover, does not show why it is so exactly this value for a wide variety of electrodes. These equations can be combined, as has been done

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* See Section IV.

by Hammett, so as to reduce to one or the other equation, depending on whether the current is low or high. The change in the character of the equation is due to a change in the order of the two reactions involved. The fractionation of hydrogen and deuterium obtained in general practice occurs in the high overvoltage region, so that the separation on the basis of this reasoning is associated with the discharge reaction rather than the reaction of adsorbed atoms to molecular hydrogen and deuterium.

Fowler[88] has stated the problem very generally and has considered the possibilities of the slow process being the discharge of ions at the electrode and of its being the recombination of the hydrogen atoms on the electrodes to gaseous molecules. In the first case he assumes that the probabilities of deposition of hydrogen and deuterium atoms on the electrode are proportional to the mole fractions of hydrogen and deuterium in the solution regardless of whether they are constituents of one or another variety of water molecule. We shall modify Fowler's argument to include the possibility that the rate of deposition of hydrogen and deuterium atoms depends on the molecular species in the solution.

We assume that the processes of discharge are:

$$\begin{aligned} H_2O+M^- &= OH^- + MH,\\ D_2O+M^- &= OD^- + MD,\\ HDO+M^- &= OD^- + MH,\\ HDO+M^- &= OH^- + MD, \end{aligned} \tag{10}$$

and that the atoms on the metal surface form molecules according to the equations:

$$\begin{aligned} 2MH &= 2M+H_2,\\ 2MD &= 2M+D_2,\\ MH+MD &= 2M+HD. \end{aligned} \tag{11}$$

In these equations *MH* and *MD* are used to refer to hydrogen and deuterium atoms adsorbed on the metal. Any of these reactions may be reversible, and, indeed, they must be for the conditions obtaining in the reversible electrode. We shall use the following symbols:

I_1, I_2 = the current carried by the discharge of H and D atoms, respectively, measured in Faradays per unit time;

N_{11}, N_{12}, N_{22} = the mole fractions of H_2O, HDO and D_2O in the solution;

n_1, n_2 = the concentrations of adsorbed H and D atoms per unit area of the electrodes;

x_1, x_2 = the concentrations of OH^- and OD^- in the solutions,

n_{11}, n_{12}, n_{22} = the mole fractions of H_2, HD and D_2 in the gas.

The relative mole fractions of H_2O, HDO and D_2O molecules and of H_2, HD and D_2 molecules, when equilibrium conditions obtain, are determined by the following equilibria:

$$H_2O+D_2O=2HDO, \quad \text{where} \quad N_{12}^2/N_{11}N_{22}=K_w,$$

$$H_2+D_2=2HD, \quad \text{where} \quad n_{12}^2/n_{11}n_{22}=K_g,$$

and by the conditions,

$$N_{12}+N_{11}+N_{22}=1 \text{ and } n_{12}+n_{11}+n_{22}=1.$$

The equilibrium constants K_w and K_g have been calculated to be 3.28 and 3.27,[26, 83] respectively.

The rates of reactions (10) may be assumed to follow simple mass action laws, so that

$$\begin{aligned} I_1 &= (2\kappa_{11}N_{11}+\kappa_{12}N_{12})-(\mu_{11}n_1x_1+\mu_{12}n_1x_2),\\ I_2 &= (2\kappa_{22}N_{22}+\kappa_{21}N_{12})-(\mu_{22}n_2x_2+\mu_{21}n_2x_1). \end{aligned} \tag{12}$$

The factors, 2, are introduced since the probability of a hydrogen atom being discharged from water is twice the probability that it will be discharged from water-*d*, other factors being the same, and since a similar argument holds for deuterium atoms from water-d_2 and water-*d*. Also for reactions (11),

$$\begin{aligned} &I_1=(2\nu_{11}n_1^2+\nu_{12}n_1n_2)-(2\lambda_{11}n_{11}+\lambda_{12}n_{12})\\ &\text{and}\\ &I_2=(2\nu_{22}n_2^2+\nu_{12}n_1n_2)-(2\lambda_{22}n_{22}+\lambda_{12}n_{12}). \end{aligned} \tag{13}$$

The κ's, μ's, ν's and λ's are velocity constants which may be expected to be functions of the temperature. The κ's and μ's should depend on the overvoltage, but the other constants may reasonably be expected to be independent of this. κ_{12} and κ_{21} may be different. Eqs. (12) refer to the discharge process and Eqs. (13) to the recombination of hydrogen and deuterium atoms. The terms in the first and second parentheses of (12) and (13) refer in turn to the forward and reverse reactions of Eqs. (10) and (11) respectively.

If the terms on the right of these equations are all large as compared to I_1 and I_2, essentially equilibrium conditions would obtain and the separation factor would be approximately 3 as shown by Farkas and Farkas. In order to account for the separation observed, it is necessary that some reaction must be slow so that the separation depends on the velocity of a reaction instead of on the equilibrium conditions. We may consider two special cases in which it is assumed (I) that the velocity with which adsorbed atoms pass into the solution is negligibly small as compared with the velocity of formation of adsorbed atoms from the water molecules, and that the velocity of formation of molecules from adsorbed atoms is large, and (II) that the velocity of adsorption of molecules is negligible as compared to the velocity of formation of molecules from adsorbed atoms and that the velocity of formation of adsorbed atoms from water molecules is large. A third possibility may also be considered, namely, that none of the velocities forward or backward can be neglected.

The usual interpretation of overvoltage discussed above and other considerations such as the high catalytic effect of metals on the recombination of atomic hydrogen favor case (I). This conclusion is supported by the work of Horiuti and Polanyi[91] on the rate of ionization of hydrogen, since they find that the rate is proportional to the square root of the hydrogen pressure, which shows that the slow reaction involves atomic hydrogen and thus that the slow reaction is the passage of adsorbed atoms into the solution. On the other hand, it is a striking fact that marked overvoltages are observed in general only when a gas or complex ion is involved in the electrolytic process and hence the hypothesis that the slow process is the recombination process cannot be entirely excluded. We shall present both cases briefly.

Case (*I*). In this case $\mu_{11}n_1x_1$, $\mu_{22}n_2x_2$, $\mu_{12}n_1x_2$, and $\mu_{21}n_2x_1$ may be set equal to zero; then from (12)

$$\frac{I_1}{I_2}=\frac{2\kappa_{11}N_{11}+\kappa_{12}N_{12}}{2\kappa_{22}N_{22}+\kappa_{21}N_{12}}. \tag{14}$$

This reduces to the observed fractionation formula, namely,

$$\frac{I_1}{I_2}=\frac{\kappa_{11}{}^{1/2}}{\kappa_{22}{}^{1/2}}\frac{2N_{11}+N_{12}}{2N_{22}+N_{12}}, \tag{15}$$

if the equilibrium constant $K_w=4$, $\kappa_{12}=\kappa_{21}$ and $\kappa_{12}{}^2=\kappa_{11}\kappa_{22}$. That the relation $\kappa_{12}{}^2=\kappa_{11}\kappa_{22}$ should hold means that each of these constants is of the form $ce^{-E/kT}$ where c is the same constant for κ_{11}, κ_{12} and κ_{22} and the E for the κ_{12} is the mean of the other energies. This condition on the energies is reasonable since the difference in activation energies lies in the zero point energy differences and the zero point energy of a mixed molecule such as HDO is nearly the mean of the two values of the homogeneous molecules. The assumption that $\kappa_{12}=\kappa_{21}$ is equivalent to assuming that the H and D atoms of HDO pass equally easily over a potential hill if the same energy is supplied. Since K_w is 3.28 instead of 4, Eq. (15) is approximate in any case. However, this statement of the problem indicates that the observed fractionation formula may be consistent with the assumptions of Case (I).

The assumptions which are made so far apply only to the contribution of the zero point energies of H_2O, HDO and D_2O to the activation energies and do not take into account other differences in the normal states of the molecules. They also ignore all possible differences in the behavior of the excited states. The assumption that the probabilities of H and D atoms passing over the barrier at the same rate may be questioned but if this assumption is in error by the same factor for both κ_{22} and κ_{21}, the right-hand side of (14) must be multiplied by this constant factor, with no other change being necessary.

Case (*II*). Here we assume that the terms of Eq. (13) proportional to the λ's may be neglected and that n_1 and n_2 are functions of the mole fractions of hydrogen and deuterium in the water, and may be expected to be approximately proportional to $(2N_{11}+N_{12})/2$ and to $(2N_{22}+N_{12})/2$, respectively. Then, letting $(2N_{11}+N_{12})/2$ equal β, Eqs. (13) become

$$I_1=2\nu_{11}\beta^2k_1{}^2+\nu_{12}\beta(1-\beta)k_1k_2,$$

$$I_2=2\nu_{22}(1-\beta)^2k_2{}^2+\nu_{12}\beta(1-\beta)k_1k_2,$$

where k_1 and k_2 are proportionality constants, and thus,

$$\frac{I_1}{I_2}=\frac{2\nu_{11}\beta^2+\nu_{12}\beta(1-\beta)k_2/k_1}{2\nu_{22}(1-\beta)^2(k_2/k_1)^2+\nu_{12}\beta(1-\beta)k_2/k_1}. \tag{16}$$

If $\nu_{12}^2=4\nu_{11}\nu_{22}$, this reduces to

$$\frac{I_1}{I_2}=\frac{k_1}{k_2}\cdot\frac{(\nu_{11})^{1/2}}{(\nu_{22})^{1/2}}\cdot\frac{\beta}{(1-\beta)}=\frac{k_1}{k_2}\cdot\frac{(\nu_{11})^{1/2}}{(\nu_{22})^{1/2}}\cdot\frac{2N_{11}+N_{12}}{2N_{22}+N_{12}},\tag{17}$$

which again is in agreement with experiment and $(k_1/k_2)(\nu_{11})^{\frac{1}{2}}/(\nu_{22})^{\frac{1}{2}}$ equals the enrichment factor. ν_{12}^2 should be approximately equal to $4\nu_{11}\nu_{22}$, since the number of collisions of H atoms with H atoms, of H atoms with D atoms and of D atoms with D atoms, all on the metal surface, should be in the ratio

$$\frac{1}{2}\left(\frac{2}{m_1}\right)^{1/2}:\left(\frac{m_1+m_2}{m_1m_2}\right)^{1/2}:\frac{1}{2}\left(\frac{2}{m_2}\right)^{1/2}$$

and if the activation energy necessary for an effective collision between an H and a D atom is the mean of the activation energies for effective collisions between two H atoms and between two D atoms, it follows that

$$\nu_{12}^2/\nu_{11}\nu_{22}=12/2\sqrt{2}=4.26.$$

Thus on reasonable assumptions it is possible that placing the slow process at the formation of molecules from the adsorbed atoms would give a fractionation of the kind observed.*

Two theories in regard to the potential barrier for electrolytic discharge have been proposed. Erdy-Gruz and Volmer[92] postulate a barrier to the passage of protons from the solution to the electrode, while Gurney[93] postulates a barrier to the passage of electrons into the solution. Either of these could be used to account for a fractionation of hydrogen and deuterium. Bell[94] has discussed the application of the Gurney theory to this problem using the discharge of two water molecules differing in zero point energy and has found that the fractionation is of the order of magnitude to be expected. In this case, it is only necessary to calculate κ_{11}, κ_{22} and $\kappa_{12}(=\kappa_{21})$ and introduce the values into the formula (14) together with the relations $N_{11}+N_{22}+N_{12}=1$ and $K_w=3.28$ in order to obtain the fractionation to be expected. The κ's, according to Gurney, are proportional to

$$\frac{T}{1-\gamma}\exp\frac{E-E_M+eV}{\gamma kT}+\Phi,$$

where γ is a constant greater than 1, Φ is a function of V and T which does not vary rapidly with mass, E is the energy of neutralization of an ion (water, according to the picture presented here) in its lowest energy state, E_M the work function of the metal and V the applied potential. Introducing this expression into (14) with appropriate values of E for the three molecules, we get, if the possible variations in the γ's are ignored,

$$\frac{I_1}{I_2}=\frac{2N_{11}e^{E_{11}/\gamma kT}+N_{12}e^{E_{12}/\gamma kT}}{2N_{22}e^{E_{22}/\gamma kT}+N_{12}e^{E_{12}/\gamma kT}}.$$

It is evident that the E's can be set equal to a constant which is the same for all the molecules plus the zero point energy of each molecule. Then

$$\frac{I_1}{I_2}=\frac{2N_{11}e^{E_{11}{}^0/\gamma kT}+N_{12}e^{E_{12}{}^0/\gamma kT}}{2N_{22}e^{E_{22}{}^0/\gamma kT}+N_{12}e^{E_{12}{}^0/\gamma kT}},\tag{18}$$

where the E^0's are now the zero point energies. Taking $K_w=4$ and $E_{12}{}^0=(E_{11}{}^0+E_{22}{}^0)/2$, this reduces to

$$\frac{I_1}{I_2}=\left(\frac{N_{11}}{N_{22}}\right)^{1/2}\exp\frac{E_{11}{}^0-E_{22}{}^0}{2\gamma kT}.\tag{19}$$

Since $(N_{11}/N_{22})^{\frac{1}{2}}$ is the ratio of hydrogen to deuterium atoms in the water when $K_w=4$, the exponential factor equals α and

$$\ln\alpha=+(E_{11}{}^0-E_{22}{}^0)/2\gamma kT.\tag{20}$$

This formula is of the form required by the experiments on the temperature coefficient of the fractionation factor and on the fractionation factor itself.

Using the frequencies for H_2O and D_2O given by Topley and Eyring[83] and γ equal to 2, as expected from the observed overvoltage Eq. (9), we get 4.3 for the fractionation factor. Taking

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* We have had the pleasure of discussing these problems with Professor O. Halpern, who has given arguments in favor of this view of the separation. These will be published shortly elsewhere.

K_w equal to 3.26 at 298.1°K and using Eq. (18), we find that α equals 4.0, 4.3 and 4.55 at 0, 50 and 100 mole percent of deuterium, respectively, while the highest value for α observed in this laboratory is approximately 12.

There are several possible considerations which might increase these factors and thus bring them more nearly in accord with experimental values. In the first place, since Gurney's theory does not account for the exact value of γ, and its constancy for different electrodes, it may be that the theory is incomplete and that γ should not be included. The theory would then place the difference in the rate of discharge as due to the differences in zero point energies of the waters and the fractionation factors would be the square of those recorded. The lower values that are observed would then be expected if the second terms of Eq. (12) cannot be entirely neglected. A second possibility is that the probabilities of hydrogen and deuterium atoms passing to the electrode from H_2O, HDO and D_2O molecules of equal energy is not the same. In this case the fractionation factors should be increased by perhaps more than the ratio of the square roots of the masses of hydrogen and deuterium because of possible penetration through a barrier (see Section V). Either of these possibilities would mean that the fractionation factor should depend to some extent on the electrodes, as is observed, while the simple theory given above does not include any such dependence.

Topley and Eyring[83] have suggested that the activated state for the discharge process consists of quasi free atoms or ions and that an approximately equilibrium concentration of these is maintained with the velocity of the reaction proportional to this concentration. However, as the authors have pointed out, the activated state cannot be really free atoms for the number of such atoms in equilibrium with water molecules would be far too small to account for the velocity of the discharge at the overvoltages observed. It is doubtful if the description of the activated state as quasi free atoms has any meaning, for if the atoms are attached to molecules, the group would be a molecule and the additional atoms would not behave as free atoms. They obtain 17.68, 19.46 and 21.42 for the fractionation factor at 298.1°K and for 0, 50 and 100 mole percent of deuterium, respectively. These factors depend largely on the differences in zero point energies of the molecules H_2O, HDO and D_2O and differ from those calculated above mainly through the omission of the factor γ by Topley and Eyring. The disagreement with experiment may be explained, as mentioned above, by a partial establishment of the equilibrium conditions.

2. Other separation methods

a. Distillation of liquid hydrogen and of water. The first method used for concentrating deuterium, namely, the fractional distillation of liquid hydrogen, cannot be used for the production of large quantities of deuterium though increased concentrations have been produced by this method by a number of workers.[10, 12, 15] Keesom, van Dijk and Haantjes[16] have used a fractionation column of the type previously used for the partial separation of the neon isotopes and in this way have increased the concentration of deuterium to approximately 1 part in sixty.

Since there is a difference in vapor pressures of H_2O, HDO and D_2O, a separation of the isotopes can be effected by distillation, as was shown by Washburn and Smith[95] and by Lewis and Cornish.*[96] Hall and Jones[97] secured partial separations in laboratory fractionation columns. The ratio of hydrogen atoms to deuterium atoms in the gas divided by this ratio in the liquid is

$$\frac{2AB+(ABkK)^{1/2}}{2+(ABkK)^{1/2}}\cdot\frac{2+(BK)^{1/2}}{2B+(BK)^{1/2}}, \qquad (21)$$

where A is the ratio of the vapor pressures of pure H_2O and D_2O and B is the ratio of their mole fractions in the liquid, $k=p_{12}^2/p_{11}p_{22}$ where p_{12}, p_{11} and p_{22} are the vapor pressures of the pure liquids HDO, H_2O and D_2O, respectively. This reduces to $\sqrt{A}$, if $K=4$ and $k=1$, which is the relation given by Lewis and Cornish. With $k=1$, the fractionation factor equals $(4A/K)^{\frac{1}{2}}$ when B is large and $(KA/4)^{\frac{1}{2}}$ when B is zero. At the boiling point $A=1.05$ and hence the fractionation factor is approximately 1.025. With a fractionation column having 100 theoretical plates, this

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* Lewis and Cornish showed that an appreciable separation of the oxygen isotopes could be effected by this method.

would give a fractionation factor of about 10 for the column as a unit. Columns with this number of plates have been constructed and it does not seem improbable that similar ones may be employed with sufficient efficiency to make fractional distillation an important competitor of the electrolytic method.

b. Diffusion methods. The diffusion of hydrogen and deuterium through palladium has been investigated by a number of workers.[98] Under ordinary conditions, it is found that hydrogen passes more rapidly through the metal; at higher temperatures, however, the ratio of the velocities of diffusion approaches one.

Gas diffusion methods have been used by MacGillavry[99] and by Hertz.[100] Though Hertz has succeeded brilliantly in producing spectroscopically pure deuterium, the usefulness of the method as applied to the hydrogen isotopes and their compounds suffers because of its inability to handle large quantities.

c. Chemical methods. Adsorption phenomena might be used to effect a separation of the hydrogen isotopes, for it has been shown by Washburn and Smith[101] and by Gould, Bleakney and Taylor,[102] respectively, that charcoal, in the presence of hydrogen-deuterium mixtures or of water containing deuterium, preferentially adsorbs the molecules containing deuterium or desorbs them less readily than those containing hydrogen.

If the velocities of reaction of hydrogen and deuterium or of their respective compounds with other compounds differ markedly, the reactions may be used to separate hydrogen and deuterium. Also, any exchange reactions whose equilibrium constants differ from the values calculated by simple statistical distribution of hydrogen and deuterium among the molecules involved in the equilibrium might be used. Farkas and Farkas[73] have pointed out that the reaction, $H_2O + DH = HDO + H_2$, is particularly favorable for the separation. It might easily be adapted to a countercurrent process by use of apparatus similar to fractionation columns. Even without the electrolytic method of separation, pure deuterium could be prepared at the present time without prohibitive effort. The electrolytic method, however, is so simple that as yet no chemical method gives great promise of displacing it.

IV. The Physical Properties of Hydrogen and Deuterium and Their Compounds

1. Properties of gases

a. General equations for thermodynamic properties. The thermodynamic properties of gases can be described in many respects by the aid of statistical mechanics and the data secured from molecular spectra. It is necessary to know the energy levels of the molecules and their statistical weights. The free energy, entropy, heat capacity, energy and heat content can then be calculated from the following equations if the summation of state, $Q = \sum p_J e^{-E/kT}$, is known:

$$F = -RT \ln \frac{(2\pi k)^{3/2}k}{h^3 N^{3/2} A} - RT \ln \frac{T^{5/2} M^{3/2} Q}{P} + C, \tag{22a}$$

$$S = R \ln \frac{(2\pi k)^{3/2}}{h^3 N^{3/2} A} + R \ln \frac{T^{5/2} M^{3/2}}{P} + \frac{5}{2}R + R\left[\ln Q + T\frac{d \ln Q}{dT}\right], \tag{22b}$$

$$C_p = \frac{5}{2}R + \frac{R}{k^2 T^2}\left\{\frac{\sum E^2 p_J e^{-E/kT}}{Q} - \left[\frac{\sum E p_J e^{-E/kT}}{Q}\right]^2\right\} = C_v + R, \tag{22c}$$

$$H = \frac{5}{2}R + RT^2 \frac{d \ln Q}{dT} + C = E + R. \tag{22d}$$

In these equations R, k, h, N and T have their usual meanings, M is the gram molecular weight, P is pressure in atomospheres, A is the normal atmosphere in dynes, p_J is the statistical weight of the Jth rotational state and C is an energy constant and, if the solid at absolute zero of temperature is taken as having zero energy, is the heat of vaporization at absolute zero.

The validity of these equations has been beautifully confirmed, particularly during the past decade, and they can be used with confidence.[103]

b. Properties of hydrogen and deuterium in the gaseous state. The spectroscopic data and energy levels are discussed in Section VII and the numerical data are recorded there. In order to proceed with the thermodynamic calculations, it is necessary to specify the values of the statistical weights p_J. In the case of diatomic molecules in $^1\Sigma$ states we have the relation $p_J = g(2J+1)$, where g depends on the nuclear spin and statistics. Its values for hydrogen and deuterium are as follows:

$$\begin{array}{ll} \text{Para } H_2 \text{ (even states)} & g=1 \\ \text{Ortho } H_2 \text{ (odd states)} & =3 \\ \text{Ortho } D_2 \text{ (even states)} & =6 \\ \text{Para } D_2 \text{ (odd states)} & =3 \\ \text{HD (all states)} & =6 \end{array} \qquad (23)$$

These values follow from a spin of 1/2 and the Fermi-Dirac statistics for H^+ and a spin of 1 and the Bose-Einstein statistics for D^+. (See Section VII.) In the case of diatomic molecules composed of unlike nuclei the g factor is $(2i_1+1)(2i_2+1)$ where i_1 and i_2 are the spins of the two nuclei. However, the spins do not influence the values of equilibrium constants of chemical reactions except those involving H_2, HD and D_2 at low temperatures and hence the g factor can be ignored in most cases if a symmetry number is used and the g's for all molecules concerned in the reaction are ignored.

The heat capacities of the various modifications of hydrogen and deuterium have been calculated by a number of authors.[104] Experimentally, since the conversions of ortho and para forms of H_2 and D_2 is slow, it is possible to measure the heat capacities of gases of the following compositions: (1) a three to one mixture of ortho and para hydrogen; (2) a two to one mixture of para and ortho deuterium; (3) pure para hydrogen; and (4) pure ortho deuterium. The two mixtures are the equilibrium mixtures at ordinary temperatures. Since mixtures of these may be studied, the heat capacities of pure ortho hydrogen and pure para deuterium may be obtained by difference. And finally, the heat capacity of HD can be secured by difference from the heat capacity of a mixture of H_2, HD and D_2.

In the case of the pure ortho and para forms of hydrogen and deuterium and also of the pure HD molecule, the heat capacities may be readily calculated by use of Eq. (22*c*) and the following conditions:

$p-H_2$ and $o-D_2$, the summations are over the even states only;
$o-H_2$ and $p-D_2$, the summations are over the odd states only;
HD, the summations are over all rotational states.

Obviously, therefore, the heat capacities of any mixture of these five molecules in which their concentrations are specified may be calculated. If a catalyst is present, the equilibrium between the ortho and para forms may be established during the heat capacity measurement and such heat capacities can be calculated by using the formula and summing over all states using the statistical weights given above.

The heat content, energy, free energy and entropy may be secured in the same way, though it should be remembered that the g of $p_J = g(2J+1)$, which drops out of the expression for some of the heat capacity calculations, must be included. The values of the heat contents, energies and free energies obtained in this way include their entire dependence on the masses and spins of the nuclei except for the electronic isotope effects, which cannot be calculated and are not yet known from experiment. The difference in the electronic zero point energies of the H_2 and HD molecules is small according to Beutler and Mie.[221] In the case of the free atoms the electronic isotope effect is, of course, the difference of the Rydberg constants, namely,

$$R_D - R_H = 109{,}707.62 - 109{,}677.76 = 29.86 \text{ cm}^{-1}$$

In the following discussion of equilibrium constants the electronic isotope effect will be ignored since it is known only for the molecules H_2 and HD and for the free atoms H and D.

The calculations of Johnston and Long[104] on these thermodynamic properties are the most detailed and extensive that have been published. Tables of heat capacities, entropies, free energies, and energies are given. Fig. 2 shows the course of the heat capacity curves. It is interesting to note that the heat capacities of $o-H_2$ and $p-H_2$ at the absolute temperature T are the same as those of $p-D_2$ and $o-D_2$, respectively, at $T/2$. This follows from the circumstance that the

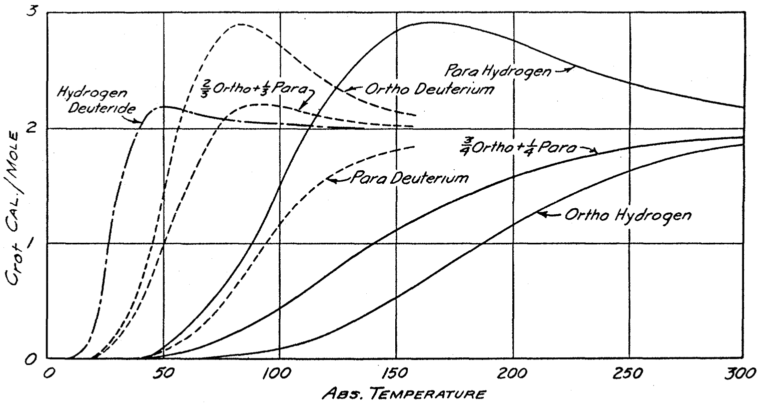

FIG. 2. The rotational heat capacity of ortho and para hydrogen and deuterium and of hydrogen deuteride.

ratio of the spacings of the rotational levels of the hydrogen and deuterium molecules are 2 : 1 and that the statistical weight factors, g, do not modify the heat capacity equation. The heat capacity curve for hydrogen deuteride is not related in a simple manner to any of the other curves since the value of g for all the levels of HD are equal, contrary to what is found for the other molecules.

The experimental heat capacities of hydrogen deuteride and deuterium determined by Patat and Hoch[104] and by Clusius and Bartholomé[104] agree well with the calculated values, though the latter authors have calculated the concentrations of H_2, HD and D_2 in their sample by using the value 4 for the equilibrium constant of the reaction $H_2+D_2=2HD$ instead of the well-established value 3.26. Use of this corrected value, however, does not change their observed results appreciably.

The ratios of the equilibrium concentrations of the ortho and para forms of hydrogen and of deuterium may be calculated by introduction of the theoretical values of the free energy into the equation

$$\Delta F^0 = -RT \ln K, \tag{24}$$

where ΔF^0 is the change in free energy of the gases all taken at $P=1$. One thus obtains the relation from (24) and (22a),

$$\frac{N_{(\text{even})}}{N_{(\text{odd})}} = \frac{\sum\limits_{J_{(\text{even})}} g_{\text{even}}(2J+1)e^{-E(J,\ v)/kT}}{\sum\limits_{J_{(\text{odd})}} g_{\text{odd}}\,(2J+1)e^{-E(J,\ v)/kT}}, \tag{25a}$$

which, at high temperatures, reduces to

$$N_{(\text{even})}/N_{(\text{odd})} = g_{(\text{even})}/g_{(\text{odd})}. \tag{25b}$$

The full expression leads to the values of the equilibrium percentages of para hydrogen in hydrogen and ortho deuterium in deuterium given, in Table II, for several temperatures.

TABLE II. *Equilibrium percentages of para hydrogen in hydrogen and ortho deuterium in deuterium.*

T°K	% $p-H_2$	% $o-D_2$	T°K	% $p-H_2$	% $o-D_2$
0	100.00	100.00	200	25.96	66.67
20	99.82	97.97	250	25.24	66.67
50	76.89	79.19	273	25.13	66.67
100	38.51	67.82	300	25.07	66.67
150	28.54	66.75			

The calculated concentrations of ortho and para hydrogen have been confirmed in detail by many workers,[105] and Farkas, Farkas and Harteck[106] have found that the concentrations of the ortho and para deuterium agree with these values. The method of analysis depended on the difference in thermal conductivity of ortho and para deuterium due to the difference in heat capacities as discussed in Section II. They were able to conclude that the deuteron has a spin of 1 and that it follows the Bose-Einstein statistics as assumed for the calculations given above.

c. Equilibrium constants of exchange reactions. The equilibrium constants of chemical reactions can be calculated from Eq. (24) using the formula (22a) for the free energy under standard conditions ($P=1$). In calculating these constants at ordinary temperatures and above, the value of Q can be secured more conveniently by a series due to Mulholland[107] and to Giauque and Overstreet.[108] This series is

$$Q=e^{-E_0/kT}\frac{1}{\sigma}\sum_v\left[\frac{kT}{B_vhc}+\frac{1}{12}+\frac{7}{480}\frac{B_vhc}{kT}-\frac{2D_v}{B_v}\left(\frac{kT}{B_vhc}\right)^2\right]\exp\frac{hc}{kT}\left[\frac{B_v}{4}+\frac{D_v}{16}-\tilde{\omega}_ev+x\tilde{\omega}_ev(v+1)\right]. \qquad (26)$$

In all cases except for H_2, HD and D_2, this can be replaced by

$$Q=\frac{8\pi^2kTI}{\sigma h^2}\frac{\exp\left[-h\tilde{\omega}_ec/2kT\right]}{1-\exp\left[-h\tilde{\omega}_ec/kT\right]} \qquad (27)$$

at ordinary temperatures and somewhat above without appreciable error. In the case of polyatomic molecules, we have the relation

$$Q=\frac{8\pi^2(8\pi^3ABC)^{1/2}}{\sigma h^3}\cdot\Pi_i\frac{\exp\left[-h\tilde{\omega}_ic/2kT\right]}{1-\exp\left[-h\tilde{\omega}_ic/kT\right]}. \qquad (28)$$

The product should be extended over all vibration frequencies and if any frequency is degenerate, its factor should be raised to a power equal to the multiplicity of the frequency. This equation for Q can be expected to give approximate results only, for it neglects higher order and cross product terms in the rotational and vibrational quantum numbers.

The approximate values for the Q's obtained by the above equations are corrected for alternation in *a priori* probabilities of molecules having like nuclei through the symmetry number σ but do not include the statistical weight factor for the nuclei. In calculating exchange equilibria at ordinary temperatures, the nuclear spins can be ignored, providing this is done for all molecules in the reaction.

Urey and Rittenberg[26] have calculated the constants of the following equilibria:

$H_2+D_2=2HD$, K_1,
$H_2+2DI=2HI+D_2$, K_2,
$H_2+2DCl=2HCl+D_2$, K_3.

For the first two equilibria one secures the equations:

$$K_1=\left[\frac{M_{HD}^2}{M_{HH}M_{DD}}\right]^{3/2}\frac{Q_{HD}^2}{Q_{HH}Q_{DD}}\exp-\left[\frac{\Delta E_0}{RT}\right] \qquad (29)$$

and

$$K_2=\left[\frac{M_{HI}^2M_{DD}}{M_{DI}^2M_{HH}}\right]^{3/2}\frac{Q_{HI}^2Q_{DD}}{Q_{DI}^2Q_{HH}}\exp-\left[\frac{\Delta E_0}{RT}\right], \qquad (30)$$

and a similar equation may be obtained for K_3. The Q's are the summations of state over all levels, but the energy in these summations is referred to that of the lowest vibrational rotational level whose energy appears as the so-called zero point energy. ΔE_0 is the sum of the zero point energies for the reaction products minus those of the reactants. The calculated values for these equilibrium constants are given in Table III. If spins other than 1 and the Fermi-Dirac instead of the Bose-Einstein statistics are assumed for the nucleus of deuterium, large differences occur in the values of K_1 at low

TABLE III. *Equilibrium constants calculated from Eq. (29).*

T°A	K_1	K_2	K_3
0.0	0	0.0	0.0
20.4	0.1515	—	—
50	1.345	—	—
100	2.265	—	—
200	2.903	—	0.309
298.1	3.269	1.164	0.502
400	3.494	1.212	0.647
575	3.710	1.234	0.807
700	3.800	1.222	0.874

temperatures, and these differences may be used to determine the spin and statistics of the deuteron, assuming those of the proton to be known. The values of K_2 were confirmed experimentally by Rittenberg and Urey[109] by comparing the percent dissociation of mixtures of HI and DI found experimentally with the values expected from the calculated equilibrium constants. Their results are summarized in Table IV. The values secured for zero percent deuterium checked Bodenstein's[110] values very closely.

TABLE IV. *Calculated and observed dissociation of mixtures of HI and DI.*

T°C	% D	% Dissociation observed	% Dissociation calculated
398	0.0	20.72	—
398	14.3	20.84	20.89
468	0.0	22.72	—
468	41.7	23.29	23.33
468	75.5	23.88	23.90

The constant K_1 was determined experimentally by Rittenberg, Urey and Bleakney[111] and in great detail by Gould, Bleakney and Taylor.[51] These latter authors established the equilibrium on catalytic surfaces, approaching the equilibrium from both sides. The solid line of Fig. 3 represents the calculated values of K_1 and the circles their experimental data. The agreement is convincing evidence of the correctness of the theory.

Topley and Eyring[83] have calculated the equilibrium constant of the reaction $H_2O+D_2O=2HDO$ and find 3.26 at 25°C and 3.40 at 100°C for the gaseous reactions.* These will also be the equilibrium constants for liquid water, if the vapor pressure of water-d is the geometric mean of the vapor pressures of water and water-d_2, which is approximately the case.† Though the equilibrium between hydrogen and deuterium gas and the three waters depends on this constant, no direct experimental determination of the constant has been reported.

Bonhoeffer and Rummel,[112] and Farkas and Farkas[73] have calculated the equilibrium constant of the reaction $H_2+HDO=H_2O+HD$, at 20°C and find $K=3$.‡ Crist and Dalin[113] have calculated the constants for the complete equilibrium of hydrogen and deuterium with the three waters for all concentrations at 373° and 800°K and have confirmed these values for the higher temperature.

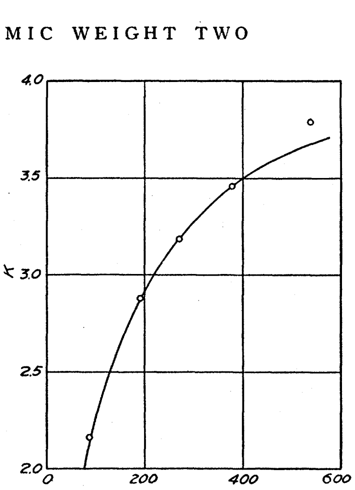

FIG. 3. The equilibrium constant of the reaction, $H_2+D_2=2HD$, as a function of temperature.

The complete equilibrium can be made to depend on three reactions:

$$\begin{array}{ll} H_2+D_2=2HD, & K_1 \text{ at } 800°K=3.83, \\ D_2O+H_2=H_2O+D_2, & K_2 \text{ at } 800°K=0.61, \\ H_2+HDO=HD+H_2O, & K_3 \text{ at } 800°K=0.79. \end{array}$$

The equilibrium constant of the third reaction can be checked directly by using low concentrations of deuterium, and this has been done at low temperatures by the first authors and at high temperatures by the latter authors. The equilibrium constant of the first reaction is known from the work mentioned above and the value of the

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* Crist and Dalin give 3.74 at 627°C.

† Urey and Wahl, research in progress.

‡ The calculated values of Bonhoeffer and Rummel and of Farkas and Farkas are not in agreement. In a recent paper, Förster (Zeits. f. physik. Chemie **B27**, 1 (1934)) has discussed this discrepancy and finds that it is due to the choice of frequencies for the HDO molecule. Using Bonner's theory for the HDO vibrational frequencies, Förster calculates the constant as 2.89 at 20°C, while using a valence force formula for the potential energy of such a molecule and calculating another set of frequencies for HDO he finds 3.77 for the constant of the gaseous reaction at 20°C and 4.04 for this constant if the water is in the liquid state. Also he finds that the experimental value for this constant is 3.8. The calculated values must be regarded as uncertain, but there seems to be no satisfactory explanation for the difference in the experimental values. It may be that the value 4 should be used for this constant instead of 3 as used throughout this review.

constant of the third reaction has been shown to be in agreement with the observed ratios of isotopes in the hydrogen-deuterium mixture and in the waters. By adding the first two equations and subtracting twice the third we secure

$$H_2O+D_2O=2HDO,\ K_w=\frac{K_1K_2}{K_3^2}=3.74.$$

K_w is calculated by the method and with the constants used by Topley and Eyring and hence the value of 3.26 for this constant at ordinary temperatures is supported by this work.

At low temperatures the equilibrium constant of the third reaction above favors the fractionation of the isotopes by a factor 3. This is larger than that observed by Washburn (see Section III).

2. The properties of liquids and solids

a. Hydrogen and deuterium. The vapor pressures of solid and liquid deuterium as functions of the temperature have been investigated by Scott, Brickwedde, Urey and Wahl[114] and by Lewis and Hanson.[115] The vapor pressures of deuterium given by the former authors are the lower and hence it seems probable that the latter used a less pure sample of deuterium. We shall report the lower results as the best available; it may even be necessary, however, to revise these downward later.

The vapor pressures at the triple points and boiling points of hydrogen are given in Table V. The empirical equations for the vapor pressures of solid and liquid deuterium in terms of the vapor pressure of hydrogen at the same temperature are:

$$\log_{10} P(D_2\text{ liquid}) = -1.363+1.310 \log P(H_2\text{ liquid}), \quad (31)$$

TABLE V. *Vapor pressure of H_2 and D_2 at triple points and boiling points.*

	Vapor pressure (mm Hg) H_2	D_2
23.5°K (boiling pt. of normal D_2)	1740	760
20.38 (boiling pt. of normal H_2)	760	257
18.58 (triple pt. of normal D_2)	429	121
13.92 (triple pt. of normal H_2)	54	5

and

$$\log_{10} P(D_2\text{ solid}) = -1.954+1.534 \log P(H_2\text{ solid}). \quad (32)$$

The latest measurements on the vapor pressure of hydrogen follow the equation,

$$\log_{10} P(\text{mm of Hg}) = 4.6633-44.7291/T+0.02023T. \quad (33)$$

Substituting this in Eqs. (31) and (32) we secure,

$$\log_{10} P(D_2\text{ liquid}) = 4.7459-58.5951/T+0.02650T, \quad (34)$$

$$\log_{10} P(D_2\text{ solid}) = 5.1995-68.6144/T+0.03103T. \quad (35)$$

The equation of state of deuterium may be assumed to be nearly the same as that of hydrogen. After considering all measurements of the virial coefficients of hydrogen, the following equation of state was selected for both hydrogen and deuterium:

$$PV=RT\left[1-\frac{0.0381}{V}\left(1+\frac{1150}{T^2}\right)\right], \quad (36)$$

where the volume is measured in liters. This equation agrees well with the latest Leiden investigations. The theoretical vapor pressure equation for solid hydrogen and deuterium then takes the form

$$\ln P=-\frac{\Delta H_0}{RT}+\frac{5}{2}\ln T+\frac{3}{2}\ln M+2.30259i+\frac{PV_s}{RT}+\frac{F_s}{RT}+\ln\left[1-\frac{0.0381}{B}\left(1+\frac{1150}{T^2}\right)\right]+\frac{2\times 0.0381}{V}\left(1+\frac{1150}{T^2}\right), \quad (37)$$

where ΔH_0 equals 182.9 and 276.0 for hydrogen and deuterium, respectively, and F_s is a Debye free energy function with Θ' equal to 91 for hydrogen and 100 for deuterium, Θ' being a Debye function for constant pressure. The constant $\Theta'=91$ for hydrogen was secured by Simon and Lange[116] from a study of the heat capacity of solid hydrogen. The constant 182.9 was derived from the vapor pressure equation using this value of Θ'. In the case of solid deuterium, a value of 100 for Θ' was found by trial such that the value of ΔH_0 calculated from the equation was constant, and Table VI shows the values of ΔH_0 calculated from the observed vapor pressures at four temperatures. The values so secured are strikingly constant though the temperature range is small. The values of ΔH_0 and Θ' for deuterium cannot be changed much by other equations of state for the gas and probably only by small amounts by a hydrogen impurity in the deuterium.

TABLE VI.

T	15.188	16.463	17.479	18.182
ΔH_0	276.11	275.97	276.09	276.08

Eq. (37) assumes that the free energy of the solid and, hence, the heat capacity at zero pressure follows the Debye formula. This is true of hydrogen as shown by the heat capacity data of Simon and Lange.[116] The use of the Θ''s is only an empirical way of describing the heat capacity at constant pressure (zero pressure as the authors have given the equation) since the Debye theory does not apply to the solid at constant pressure. In order to secure a true Debye Θ for a substance, one must know the heat capacity at constant volume, and this is unknown for both hydrogen and deuterium. However, the difference in the ΔH_0's, the heats of vaporization at absolute zero, must be due in part to the differences in zero point energies which, according to the theory, should be $9/8\ R\Theta$. Assuming that the Θ's are inversely proportional to the molecular weights, we have

$$\Theta_1/\Theta_2 = (4.0273/2.0156)^{1/2}, \qquad (38)$$

where Θ_1 and Θ_2 are the true Debye functions for hydrogen and deuterium, respectively. Then if the heat of vaporization from the hypothetical vibrationless solid, χ, is the same for both hydrogen and deuterium, we have

$$\chi = 182.9 + (9/8)R\Theta_1 = 276.0 + (9/8)R\Theta_2.$$

Θ_1 and Θ_2, and χ, can be secured from these equations. The authors secure 142.4 and 100.7 for Θ_1 and Θ_2, respectively, and 501.2 for χ. Since Θ_1 is greater than Θ_1', the heat capacity of hydrogen at constant pressure is greater than its heat capacity at constant volume; for deuterium, however, the two heat capacities are approximately equal. Since $C_P - C_V = \alpha^2 VT/\beta$, where α and β are the coefficients of thermal expansion and compressibility, respectively, it appears that the coefficient of expansion of deuterium is less than that of hydrogen. This may be expected because the zero point energy of hydrogen is 64 percent of χ while that of deuterium is 46 percent of this quantity, so that the oscillators of hydrogen are more anharmonic than those of deuterium, and thus the coefficient of expansion of deuterium should be larger than that of hydrogen. If the oscillators are anharmonic, Eq. (38) should not be exactly correct; thus the above calculation probably requires revision. A possible contribution of the rotational and internal vibrational degrees of freedom has been considered by the authors but such effects appear to be small.

Clusius and Bartholomé[117] have measured the heat capacity of solid deuterium, the heats of fusion of hydrogen and deuterium, and the gram molecular volumes. They report a vapor pressure of 128.3 mm of mercury at the triple point which they find to be 18.7°K. Further, the gram molecular volume of deuterium is about 11 percent less than that of hydrogen and this difference persists as the temperature approaches absolute zero. The smaller gram molecular volume is in accord with the conclusions of Scott, Brickwedde, Urey and Wahl. The difference in gram molecular volumes should be fairly large and should be present at absolute zero, because of the large differences in zero point energies. Clusius and Bartholomé find that Θ_2' equals 89, which is undoubtedly better than the value 100 secured from the vapor pressures though it does not differ greatly from 100.

The heats of transition and gram molecular volumes of hydrogen and deuterium as determined from the vapor pressure data and by direct measurement are given in Table VII. Some of the variations in the constants given are due to the different temperature scales used.

Table VII. *Heats of transition and gram molecular volumes of H_2 and D_2.* References to sources of data are given in parentheses.

	H_2	D_2
Gram molecular volume of solids	26.15 cc	23.17 cc (117)
ΔH of fusion	28.0 cal. (116, 117)	47.0 cal. (117)
		52.3 " (114)
		48.9 " (115)
ΔH of vaporization at triple points	217.7 cal. (116, 114)	303.1 " (114)
		308.3 " (117)
Triple point	13.92°K	18.58°K (114)
	13.98°K	18.7 " (117)
		18.66 " (115)

The large difference in the triple points of hydrogen and deuterium is well established and is of great interest. It appears also, from the vapor pressure equations, that the heat capacity of liquid deuterium is considerably less than that of hydrogen. A further study of the two liquids should make possible a better understanding of the liquid states and, therefore, also of the triple points.

Lewis and Hanson[115] find that there is little difference between the vapor pressure of a mixture of H_2 and D_2 and an equilibrium mixture of H_2, HD and D_2 of the same atomic composition. For the ratio of the vapor pressures of hydrogen and hydrogen deuteride at 13.92°K, Scott, Brickwedde, Urey and Wahl have calculated a value of 2.42, which had led them to conclude that the enrichment secured by Urey, Brickwedde and Murphy[10] in the fractional distillation of liquid hydrogen is approximately that required by the theory, considering the experimental difficulties of such a fractionation.

b. Water and water-d_2. For the sake of convenience we have tabulated the properties of water and water-d_2 in Table VIII.

Several measurements of the refractive index of water containing deuterium have been reported. Luten,[53] in particular, has made an extensive investigation of the refractive indices of water containing 0.02, 44.4 and 95.6 percent deuterium oxide for several wavelengths and temperatures and also of the relation between the molecular volume of water and its isotopic composition. The equation thus obtained for expressing the molecular volume at 25°C as a function of the mole fraction of deuterium is*

$$V=18.069+0.065N_2-0.016N_2^2. \qquad (39)$$

Luten found that the maximum refractive index of water-d_2 lies at 6°C, and since the maximum occurs at -1 or -2°C for ordinary water, it occurs about 5 or 6° below the points of maximum density of both waters. At 25° the refractive index is a linear function of the mole fraction of deuterium. Even when corrections are made for the different gram molecular volumes of water and water-d_2 the molar refractivities of the two waters differ.

The molar refractivity is related to the characteristic frequencies of the molecules and the frequency of the light by the relation

$$R=\frac{4\pi}{3}N\sum\frac{e^2}{m}\frac{f_i}{\nu_i^2-\nu^2}, \qquad (40)$$

where N is the Avogadro number, f_i the oscillator strength, ν_i the ith characteristic frequency and ν the frequency of the light. The lower refractivity of water-d_2 thus means that the effective frequencies of D_2O are greater than those of H_2O. This is in agreement with the observations of Franck and Wood[131] who find that the long wavelength absorption limit of water-d_2 lies farther to the violet than this limit of H_2O. Since this spectrum is due to a transition from the normal state to a repulsive excited state, the ultraviolet absorption frequencies of the water-d_2 should be larger than those of water by about the difference in the zero point energies. This difference is about 1200 cm^{-1} which is perhaps one percent of the mean ν_i and hence would decrease the molar refraction of water-d_2 relative to that of water by about two percent. This is in fair agreement with the observed difference. Since the absorption bands of ammonia-d_3 are of shorter wavelength than those of ammonia, a similar difference in molar refractivities of these substances is to be expected.

The equivalent conductances listed in Table VIII were calculated from the ratio of the resistances of a conductivity cell containing solutions of HCl and KCl in water and water-d_2, respec-

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* This equation has been derived from Luten's by correcting for $d_{25}^{25}=1.1079$ for water-d_2 and by use of the molecular volume of water at 25° instead of at 4°C.

TABLE VIII. *Properties of H_2O and D_2O.* References to sources of data are given in last column.

Property		H_2O	D_2O	Ref.
Density$_{25}^{25}$		1.0000	1.1079	118
T of maximum density		4.0°C	11.6°C	119
Molar volume at temperature of maximum density		18.015 cc	18.140 cc	119
Lattice constants of ice	a	4.525A	4.505A	120
	b	7.39A	7.36A	
Volume of the ice cell		131.0A^3	129.3A^3	120
Mole volumes of the ices 0°C		19.65 cc	19.32 cc	120
Dielectric constant		81.5	80.7	121
Surface tension		72.75 dynes/cm	67.8 dynes/cm	122
Viscosity 10°C		13.10	16.85	130
in 20°C		10.09	12.60	
millipoises 30°C		8.00	9.72	
Molar magnetic susceptibility liquid at M.P.		12.93	12.66	124
solid at M.P.		12.65	12.54	
at 20°		12.97	12.75	
Refractive index 20°C NaD line		1.33300	1.32828	125
Molar refraction 20°C NaD line		3.7121	3.665	125
Verdet constant $\lambda = 5893A$		0.013067	0.012556	126
Min./gauss-cm $\lambda = 5460.7A$		0.015395	0.014793	126
M.P.		0.0	3.802	119, 127
B.P.		100.0	101.42	119
Heat of fusion		1436 cal.	1510 cal.	127
Heat of vaporization 25°C		10484 cal.	10743 cal.	128
Equivalent conductance at 18°C		H^+ in H_2O 315.2	D^+ in D_2O 213.7	123
K^+		64.2	54.5	
Cl^-		65.2	55.3	
Solubilities, molalities				
NaCl 25°C		6.145	6.145×0.92	129
$BaCl_2$ 20°C		1.72	1.72 ×0.88	

tively. The assumption was made that the ratios of the equivalent conductances at infinite dilution to those at the concentrations used are the same for both solvents and that the ratio of the equivalent conductances of K^+ and Cl^- is the same for both solvents. Though this assumption may not be quite exact, it should give results of the correct order of magnitude. The ratios of K^+ and Cl^- in water and water-d_2 are 1.178 and 1.179, respectively. These ratios are nearly but not exactly equal to the ratio of the viscosities of the two waters. Exact agreement would not be expected since the slight difference in the dielectric constants of the waters should affect the mobilities.

It is a noteworthy fact that the ratio of the molecular volumes of solid water-d_2 and ordinary ice near the melting point is 0.987 while the ratio of the molecular volumes of the liquid waters is greater than unity. Also water-d_2 has a greater viscosity than has ordinary water. The surface tension, however, is lower for water-d_2 than for water. In the case of the vapor pressures, the lower value is shown by water-d_2.

Fowler[132] has discussed these properties of the waters in their relationship to a theory of the constitution of ordinary water previously derived by Bernal and Fowler.[133] According to this theory, the above differences of the molecular volumes are correlated with a more rigid crystal structure in solid water-d_2 than in ice and a greater persistence of the ice structure in liquid water-d_2. The greater rigidity is considered as due to a greater strength of the "deuteron bond" as compared to the "proton bond." The greater viscosity and lower vapor pressure of water-d_2 may also be correlated with the greater strength of the deuteron bond. The difference in the surface tensions, however, appears to be in the opposite direction from that expected.

The postulates of Bernal and Fowler's theory indicate an impossibility of proton or deuteron bonds such as those of water in the case of the ammonias. It is therefore of some interest to note that the vapor pressures, melting points and heats of vaporization of the ammonias differ by amounts of the same order of magnitude as the differences in these quantities for the waters. Also the vapor pressure of H_2O^{18} is appreciably less than that of H_2O^{16}, as has been shown by Lewis and Cornish.[96] Wahl and

TABLE IX. *Comparison of various constants of compounds of hydrogen and deuterium.*

	M.P.	B.P.	ΔH Vaporization	ΔH Sublimation	ΔH Fusion	$\frac{p_2}{p_1}$	T_e	Ref.
NH_3	195.2	239.75	5797			$(L)^*$ $1.32 \exp -\frac{193}{RT}$	342	140
ND_3	199	242.3	5990					
HF	−83	293.07	6023			(L) $0.674 \exp \frac{254.4}{RT}$	325	141
DF		291.81	5768					
H_2O	273.18	373.18	10726	12162	1436	(L) $1.35 \exp -\frac{259}{RT}$	435	119
D_2O	277.00	374.60	10985	12495	1520			
HCl	158.9	188.1	4081	4557	476	(L) $1.189 \exp -\frac{70}{RT}$	204	142
DCl	158 2	191.6	4151	4292	141	$(S)^*$ $0.410 \exp \frac{265}{RT}$	150	
HCN	259	298.5	6618	8585	1967	(L) $0.794 \exp \frac{123.5}{RT}-\frac{800}{RT^2}$	263	143
DCN	261	299.2	6501	8722	2221	(S) $1.27 \exp -\frac{137}{T}$	289	

* (*L*) and (*S*) refer to the ratio of vapor pressures for the liquids and solids, respectively.

Urey[134] have found that this difference at 11°C is 1.4 percent and, though smaller than the vapor pressure difference of water and water-d_2, is not negligible and cannot be explained as due to a difference in the proton or deuteron bonds.

The freezing point of water as a function of the deuterium content has been investigated by La Mer and his co-workers.[135] They find that the freezing point follows the equation:

$$t=4.213N_2-0.411N_2^2. \qquad (41)$$

This gives 3.802°C as the melting point of pure D_2O (specific gravity 1.1079 at 25°C). From the mole fraction freezing point depression constant obtained by using KCl as the solute, they find a heat of fusion of 1510 cal. per mole of 99.5 percent D_2O. This variation in melting point will depend on the heats of fusion of H_2O, HDO and D_2O and on the equilibrium between these three molecules.[136]

Doehlemann, Lange and Voll[137] have found that the integral heat of dilution of dilute heavy waters (up to 5 percent deuterium content) is negative and linear in the mole fraction of HDO. This heat of dilution for a sample containing 10 mole percent of HDO is −0.40 calorie.

Stewart[138] finds that the curves of the diffraction of x-ray by water and water-d_2 are very similar except that the peaks for the latter are somewhat sharper. Also, Froman[139] has found that the coefficients of absorption of water and water-d_2 for x-rays of wavelengths 0.5–0.6A are the same within ±3 percent.

c. Vapor pressures and other properties of other hydrogen and deuterium compounds. In Table IX we list the melting points, boiling points, heats of transition and formulae for the ratios of vapor pressures for a number of pairs of isotopic compounds as functions of the temperature. Since the vapor pressure of a substance is related to the heat of evaporation and entropy of vaporization from the liquid or solid in its standard state to the vapor at one atmosphere pressure by the equation

$$\ln p=-\frac{\Delta H^0}{RT}+\frac{\Delta S^0}{R}, \qquad (42)$$

these formulae have the form

$$\frac{p_2}{p_1}=\exp\left[\frac{\Delta S_2{}^\circ-\Delta S_1{}^\circ}{R}\right]\exp\left[-\frac{\Delta H_2{}^\circ-\Delta H_1{}^\circ}{RT}\right]. \qquad (43)$$

And since the heat capacity of the isotopic substances in the vapor state or in the condensed states can reasonably be expected to be very closely the same, the quantities $\Delta S_2{}^\circ-\Delta S_1{}^\circ$ and $\Delta H_2{}^\circ-\Delta H_1{}^\circ$ should be quite constant. This appears to be true except in the case of the $\Delta H_2{}^\circ-\Delta H_1{}^\circ$ of liquid HCN and DCN and of liquid CH_3COOH and CH_3COOD and even here the variations are not large. We shall refer to the term $\exp\,(\Delta S_2{}^\circ-\Delta S_1{}^\circ)/R$ as the entropy factor and $\Delta H_2{}^\circ-\Delta H_1{}^\circ$ as the heat content difference.

It will be noted that if the entropy factor is greater than unity, the heat content difference is positive and if it is less than unity, the heat content difference is negative. This means that at some temperature the vapor pressures will be equal and the vapor pressure curves cross each other. The absolute temperatures for which this occurs are listed in Table IX as T_e. These values are secured by setting $p_2/p_1=1$ in the equations and solving for T. Often this involves a considerable extrapolation, but in the case of HCl and DCl the experimental values extend nearly to the calculated values of T_e for both the liquids and solids and, in the case of HCN and DCN, T_e for the liquid lies within the experimental range, while the value of T_e for the solid lies above the melting point.

Water, ammonia and hydrogen fluoride are very similar liquids, but while the vapors of ammonia and water are monomolecular, that of hydrogen fluoride is polymerized. The different behavior of the hydrogen and deuterium fluorides as compared to that of the ammonias and of the waters is probably due in part to this difference in the vapors, as suggested by Claussen and Hildebrand.[141] The vapor pressures of the liquid cyanides differ only slightly, due to the entropy factor being nearly the reciprocal of the exponential factor, so that T_e falls only slightly above the melting point. Thus the vapor pressure curves cross just in the region of measurement and differences in vapor pressures will be small. The vapor pressures of the chlorides also differ but slightly and for similar reasons, except that the entropy factors and heat content differences do not run parallel to those of the cyanides at all. In the case of the chlorides, the deuterium chloride has the lower vapor pressure between 150° and 203°K, but outside this range has the higher vapor pressure.

Lewis and Schutz[144] have measured the vapor pressures of CH_3COOH and CH_3COOD and find that the deuterium compound has the higher vapor pressure between 50 and 94°C. This higher vapor pressure is believed by these authors to be due to association in the gaseous state. However, the plot which they publish indicates that the vapor pressure curves would cross at higher temperatures.

These differences in vapor pressures cannot be explained on the basis of the dependence of the free energy on the Debye vibrations if their contributions to the heat capacities are near the classical value of $3R$, which must be true for all the compounds discussed above with the exception of the hydrogens.

Neopentyl deuteride, or mono deuterio tetramethyl methane, a complex and interesting organic compound, has been prepared and its properties studied by Whitmore[145] and his coworkers. It is found that the melting point is raised slightly and the boiling point lowered by the introduction of the one deuterium atom. The Raman spectrum showed the presence of a displacement, $\Delta\tilde{\nu}=2150$, which can be assigned to the carbon deuterium bond. The refractive index of the deuterio compound was lowered slightly.

d. Equilibrium constants in condensed phases. Equilibrium constants differing from those expected from simple statistical distribution of the atoms between molecules are certainly to be expected for reactions in liquid phases. Halford, Anderson and Bates[146] have reported such an example. They find that the equilibrium constant for the reaction

$$CH_3COCH_3+HDO=CH_2DCOCH_3+H_2O$$

is approximately 2, so that the deuterium is concentrated in the acetone. It seems probable that in all cases in which isotopic equilibrium is established between water and an organic compound there will be at least slight deviations from a simple statistical distribution of deuterium between the components.

Approximate values for the ionization constant of deuterium oxide, $K=[D^+][OD^-]$, have been secured by Topley and Wynne-Jones[147] and by Abel, Bratu and Redlick.[148] Their results are in agreement and indicate that this constant is about one-third the corresponding constant for water, namely, 1.04×10^{-14} at 25°C.

Lewis and Schutz[149] have secured approximate values for the ionization constants of deuterio acetic acid, CH_3COOD, chlorodeuterio acetic acid, $CH_2ClCOOD$, and deuterio ammonium deuteroxide, ND_4OD, using conductivity meth-

TABLE X. *Ionization constants for hydrogen and deuterium compounds.*

	Hydrogen compound	Deuterium compound	Ratio (approximate)
H_2O-D_2O	1.04×10^{-14}	0.33×10^{-14}	3
$CH_3COOH-CH_3COOD$	1.84×10^{-5}	$0.45–0.59\times10^{-5}$	3.5
$CH_2ClCOOH-CH_2ClCOOD$	$1.71–1.74\times10^{-5}$*	0.63×10^{-5}	2.7
NH_4OH-ND_4OD	1.82×10^{-5}	$1.1–1.4\times10^{-5}$	1.5

* This value does not agree with previous values given in the International Critical Tables.

ods. The values for hydrogen and deuterium compounds are given in Table X. These differences in equilibrium constants are undoubtedly due to differences in the free energies between the ionized substances and the neutral substances similar to those calculated and observed in the case of gaseous substances and described above.

Hall, Wentzel and Smith[150] have studied the upper consolute temperature of phenol and water and the lower consolute temperature of nicotine and water as functions of the deuterium content of the water. The first of these increased with increasing deuterium concentration and by extrapolating to 100 percent D_2O, they find a total rise of 11.8°. The second was studied only with water up to 10.6 percent deuterium content, and for this concentration the consolute temperature was lowered 0.72°. Thus the solubilities of phenol and nicotine in water-d_2 are less than they are in water. This is also true of sodium and barium chlorides, as recorded in Table VIII.

The differences in vapor pressures suggest that distribution coefficients differing from 1 may be expected in other equilibria between two phases. Bruni[151] has found no detectable fractionation of hydrogen and deuterium in the fractional crystallization of ice. Gilfillan[152] finds that the fractionation changes the density by 0.1 part per million when one-half of the body of water is frozen. Thus the separation is certainly small.

Day, Hughes, Ingold and Wilson[153] have found that only slight fractionation occurs in the crystallization of $Li_2SO_4\cdot H_2O$, $SrCl_2\cdot 6H_2O$, $CuSO_4\cdot 5H_2O$, $Li_2SO_4\cdot H_2O$, $Na_2CO_3\cdot 10H_2O$ and $K_2Cr_2O_4\cdot H_2O$, indicating that the molecules of water are held in the lattices with energies of about the same kind as those in ice or liquid water and not of the chemical valence type.

V. Chemical Kinetics of Hydrogen and Deuterium

1. Theoretical considerations

Differences in the rates of analogous reactions of isotopic compounds should arise from several factors dependent on mass. We may consider first the possible effect of the relative number of collisions of hydrogen and deuterium with a third molecule (like or unlike) in the gas. Other factors being equal, the number of collisions is inversely proportional to the square root of the reduced mass of the colliding pair, since the collision radii should be the same in either case.* We have also to consider the dependence of the activation energy of a reaction on mass. The activation energies, that is, the differences in the average energies of the reacting molecules and of all the molecules, must differ for isotopic molecules principally because of the difference in zero point energies of such molecules, but possibly also because of different energies in the excited states. In the case of electrolytic solutions, the dielectric constant plays an important part and since the dielectric constant of deuterium oxide differs from that of hydrogen oxide, important though probably small effects on the kinetics of the reactions may be expected. The order of magnitude of such effects is indicated by the decreased solubilities of electrolytes in water-d_2.

Tolman[154] has given formulae for the velocity constants of chemical reactions derived from general considerations. It is not our purpose to review this subject, since this has been done in several outstanding treatises, but only to point out certain applications to the relative velocities of the hydrogen and deuterium reactions. For definiteness we shall discuss the hydrogen-iodine

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* See, however, footnote p. 64.

reaction. This is a representative bimolecular gaseous reaction between diatomic molecules for which the velocity of arrival of molecules in the activated states is large compared to the rate of reaction and should serve to bring out the factors to be considered in many other reactions. The following symbols will be used:—

$\mu_1(\mu_2)$ = the reduced mass for the collision between hydrogen (deuterium) and iodine molecules;

$\bar{\mu}_1(\bar{\mu}_2)$ = the reduced mass of the hydrogen (deuterium) molecule, or, in the more general case, of a diatomic molecule containing hydrogen (deuterium);

$E_1(E_2)$ = the internal rotational and vibrational energy of the hydrogen (deuterium) molecule or of a diatomic molecule containing hydrogen (deuterium);

E_x = the internal energy of the iodine molecule or of a molecule not containing hydrogen or deuterium;

E_R = the relative energy of the two molecules due to the relative velocity of the colliding molecules along the line joining them;

E_S = the relative energy of the two molecules due to the relative velocities of the colliding molecules perpendicular to the line joining them;

$k_1(k_2)$ = the specific velocity constant for the reaction involving hydrogen (deuterium);

p_1, p_2, p_x = the statistical weight factors for hydrogen, deuterium and the iodine (or other molecule);

$n_1(n_2)$ = the number of molecules of hydrogen (deuterium) per cm³;

n_x = the number of molecules of iodine per cm³;

σ = the distance of nearest approach between a hydrogen or deuterium molecule and an iodine molecule.

The velocity of the bimolecular reaction can be written as,

$$-\frac{dn}{dt}=k_1n_1n_x=n_1n_x\frac{2\pi^2\sigma^2}{(kT)^{3/2}}\left(\frac{2\pi}{\mu_1}\right)^{1/2}\frac{\sum\sum\int\int K_1'(E_1,\,E_x,\,E_R,\,E_S)p_1p_xe^{-(E_1+E_x+E_R+E_S)/kT}dE_RdE_S}{\sum p_1e^{-E_1/kT}\cdot\sum p_xe^{-E_x/kT}}. \tag{44a}$$

The constant $K_1'(E_1, E_x, E_R, E_S)$ is the probability of a reaction occurring due to a collision between a hydrogen molecule of internal energy E_1 and an iodine molecule of internal energy E_x, with relative translational energies between E_R and E_R+dE_R and E_S and E_S+dE_S. The summations are to be taken over all the internal degrees of freedom of the hydrogen and deuterium molecules, and the integrations from 0 to ∞. It is instructive to consider the reverse reaction as well, and the requirements on the velocity constants which must obtain when equilibrium conditions are approached. The ratio of the forward and backward velocity constants at equilibrium must equal the equilibrium constant of the reaction, and this is (see Section IV)

$$\frac{k\ \text{(forward)}}{k\ \text{(backward)}}=K=\frac{M_{\mathrm{HI}}{}^3}{M_{\mathrm{H_2}}{}^{3/2}M_{\mathrm{I_2}}{}^{3/2}}\,\frac{Q_{\mathrm{HI}}{}^2}{Q_{\mathrm{H_2}}Q_{\mathrm{I_2}}}e^{-\Delta E/kT},$$

where the Q's are the summations of state, $\Sigma pe^{-E/kT}$, and ΔE is the energy difference of the vibrationless hydrogen iodide molecules and of the vibrationless hydrogen and iodine molecules. In order that this equation should hold, the velocity constants of the forward and reverse reactions must be inversely proportional to $1/\mu^{\frac{3}{2}}$. Then,

$$k_1=\frac{(2\pi)^{5/2}}{2(kT)^{3/2}}\,\frac{1}{\mu_1{}^{3/2}}\,\frac{\sum\sum\int\int K_1(E_1,\,E_x,\,E_R,\,E_S)p_1p_xe^{-(E_1+E_x+E_R+E_S)/kT}dE_RdE_S}{Q_1\cdot Q_x}, \tag{44b}$$

where K_1 now is $K_1'\mu_1\sigma^2$. We can now say that the quantity represented by the double summation and double integral is the same for both the forward and backward reactions. Since a similar equation should hold for deuterium, the ratio of the velocity constants becomes

$$\frac{k_1}{k_2}=\left(\frac{\mu_2}{\mu_1}\right)^{3/2}\cdot\frac{\sum\sum\int\int K_1(E_1,\,E_x,\,E_R,\,E_S)p_1p_xe^{-(E_1+E_x+E_R+E_S)/kT}dE_RdE_S}{\sum\sum\int\int K_2(E_2,\,E_x,\,E_R,\,E_S)p_2p_xe^{-(E_2+E_x+E_R+E_S)/kT}dE_RdE_S}\cdot\frac{\sum p_2e^{-E_2/kT}}{\sum p_1e^{-E_1/kT}}=A\cdot B\cdot C, \tag{45}$$

where A, B and C refer to the three factors in the equation.

If the concentration of activated molecules is not approximately that when equilibrium obtains, Eq. (44a) should not hold and it is necessary to consider the relative speeds of activation since this would be the determining factor. Tolman has derived an equation for the monomolecular reactions for this case. The final equation can be put in the form of three factors, the first and last being the same as in the case given above, while the factor corresponding to B depends on the relative rates with which molecules enter the activated states and leave by reaction to form the products or by deactivation to form the original reactants. The factor B in this case, just as in the simpler case, cannot be exactly estimated.

A and C can be calculated exactly for the hydrogen iodide reaction and also for many other reactions. The factor A takes account of the requirements of the mass ratios at equilibrium. We may consider the following special cases: (1) the probability factors, K_1 and K_2, may not depend on the rotational energy; (2) K_1 and K_2 may not depend on the vibrational energy, so that all vibrational effects cancel, including the effect of zero point energy; (3) and finally, K_1 and K_2 may not depend on the translational energy. The factor, C, at ordinary and somewhat higher temperatures is approximately

$$C=(\bar{\mu}_2/\bar{\mu}_1)\exp\left[(E_1{}^\circ-E_2{}^\circ)/kT\right], \qquad (46)$$

where $E_1{}^\circ$ and $E_2{}^\circ$ are the zero point energies of hydrogen and deuterium in the example we have chosen. If K_1 and K_2 do not depend on the rotational energy, the factor $\bar{\mu}_2/\bar{\mu}_1$ is cancelled by the inverse of this factor coming from the B factor, and if they do not depend on the vibrational energy, the exponential factor of (46) is cancelled in a similar way. We shall discuss the experimental data in terms of these possibilities. The values of K_1 and K_2 cannot be estimated without an exact theory of the reaction process. However, it is evident that the K's are zero unless the total energy available at a collision is greater than the energy of reaction.

The two reasons which have been suggested for expecting the factor B to differ from unity are: first, penetration of a potential barrier by the hydrogen or deuterium atoms should favor an increased velocity of the hydrogen reaction relative to that of deuterium and, second, the occurrence of "zero point activation energies," as suggested by Polanyi,[156] might favor either one or the other of the isotopes. The possible effects of penetration of barriers first discussed in connection with deuterium by Cremer and Polanyi,[28] have been investigated by Bawn and Ogden[155] using a very simple example. They calculate values of the factor B for the passage of hydrogen and deuterium atoms over a symmetrical barrier, devised by Eckart,[157] for which the potential energy $V(x)$ is

$$V(x)=4We^{2\pi x/l}/(1+e^{2\pi x/l})^2, \qquad (47)$$

where W is the height of the barrier, $2l$ is its width and x is the distance from the midpoint of the barrier. The K's of Eq. (45) depend only on the translational energy, since there is no internal energy of rotation and vibration for the atoms, and the factor C can be omitted. K is then given by the expression

$$K(E_t)=\frac{\cosh 4\pi\alpha-1}{\cosh 4\pi\alpha+\cosh 2\pi\delta}, \qquad (48)$$

where

$$\alpha=(l/h)(2\pi E_t)^{\frac{1}{2}}, \quad \delta=\tfrac{1}{2}\left[32E_m l^2/h^2-1\right]^{\frac{1}{2}}$$

and E_t equals the translational energy. They have further calculated the numerator and denominator of B separately. Their calculations apply strictly only for their simple problem but may indicate the order of magnitude of this effect for other reactions such as are considered here. Table XI summarizes the results of their calculations. A high and narrow barrier favors a large effect on the relative velocities of hydrogen and deuterium reactions. As yet it is not at all certain whether this effect is of importance in reactions which have been investigated, for the shape of the hill determines the magnitude of the effect and the width, height and shapes of these barriers are not well known, though the calculation of potential energy hills by Eyring and his co-workers indicates that they are broad and flat so that this effect should be small.

The "zero point energy in the activated state," which has often been mentioned in the literature, has quite varied features that may appropriately

TABLE XI. *Ratio of velocity constants k_1/k_2 for various barrier widths and temperatures.*[155]

Kcal./mole	Width of barrier $2l$	Temperature	k_1/k_2
14.5	2A	273°K	23.1
		473	2.3
14.5	3A	273	3.6
		473	1.4
6.5	1.5A	273	4.1
		473	1.7
15.0	1.5A	273	74.1

be considered in connection with chemical kinetics. Many chemical reactions proceed by the system passing through a saddle-shaped potential energy pass, in which there may be a depression representative of a metastable intermediate product. If the system passes through a long potential energy trough, the energy associated with the translational degree or degrees of freedom will have continuous energy values, while the internal degrees of freedom are discretely quantized. For exact quantization of the energy, the trough must be infinitely long, and since this is not the case, the quantization for real systems will not be sharp.

A picture of this possible effect and of the general behavior of molecules with energies just above the dissociation energy can be secured by considering the predissociation phenomenon, which is the reverse process of a recombination reaction. The vibrational bands of some molecules, particularly polyatomic molecules, in absorption are sharp down to a certain wavelength and beyond this are diffuse. The diffuse character may appear very sharply at some band or the successive bands may become gradually more and more diffuse. This is due to transitions from the sharp normal level to diffuse excited levels. These excited levels are diffuse because of spontaneous dissociation of the molecules into two fragments and the more diffuse the level, the shorter the life of the molecule in this level. The lives are, in fact, so short that predissociation bands cannot be observed in emission spectra. The energy levels of the molecules follow a smooth formula through the predissociation limit with no evidence of marked irregularity in position such as would be expected if a zero point energy of $\frac{1}{2}h\nu$ above the potential energy hill was even approximately required. It may be that the last sharp level of one isotopic molecule lies just below the predissociation limit so that the next level lies about $h\nu$ higher than the limit, or it may be that the first diffuse level lies just above the limit and the first diffuse levels of the other isotopic molecule may fall in either of these positions relative to the limit. An example of this sort is furnished by the H_2, HD and D_2 molecules as described in Section VII.

The internal degrees of freedom may be qualitatively separated into two classes. In the first place, the K's of Eq. (45) may not depend appreciably on many of the degrees of freedom, particularly if the molecule is large. A high energy "localized" in one part of a large molecule may have little effect on the probability of a reaction involving another distant part of the molecule. In this case if we assume the internal vibrational energy to consist of a sum of terms in the $(v+\frac{1}{2})$'s and neglect cross product terms, these terms can be removed from the summation-integrals of factor B and summed by themselves and will cancel similar factors from C, including the zero point energy for these degrees of freedom. This effect may be expected to be present qualitatively even if the cross product terms in the energy cannot be neglected; and it has just the effect on the relative velocities of hydrogen and deuterium reactions that a "zero point energy of the activated state" predicts, namely, it contributes to an increased velocity of the deuterium reaction relative to the hydrogen reaction over that expected if this effect were neglected. It would not, however, cause the deuterium reaction to be faster than the hydrogen reaction, though this conclusion might be the result of the neglect of the cross product terms in the energy equation.

Then there are the translational, vibrational and rotational degrees of freedom more intimately involved in the chemical change. In the case of predissociation of a molecule, such as water, the energy occurring in three translational, three vibrational and three rotational degrees of freedom must, after dissociation into, let us assume, OH and H, be redistributed in one vibrational, two rotational and six translational degrees of freedom. Though the details of such a simple reaction have not been adequately described, it seems possible, but not evident, to the writers that the K's of Eq. (45) may be such that the ratio of velocities of the hydrogen and deuterium reactions may be decreased if this factor were calculated exactly and, in fact, that the deuterium reaction might actually be the faster of the two. Perhaps some light on this question can be secured by returning to the predissociation phenomena. Thus, if the dissociation reaction proceeded mostly through the first diffuse level in both the hydrogen and deuterium cases, the factor B might be appreciably smaller than one if the first diffuse level of the hydrogen system were far above the predissociation limit and that of the deuterium system immediately above the limit, or B might be considerably larger than one if the relative positions of the diffuse levels of the two systems were reversed. If dissociation did not occur mainly through these lowest diffuse levels, all effects due to this "chance" arrangement of levels in the neighborhood of the limit should become unimportant. The present inadequacy of the theory and the lack of data, however, make a more detailed discussion of this point impossible at this time.

If the reaction proceeds through a well-defined intermediate product, stable at least for times considerably longer than the reciprocals of its vibration frequencies and in equilibrium with the reacting molecules, this intermediate will have fairly well defined zero point energy and its concentration could be calculated from statistical theory, given the necessary data (see Section IV). The deuterium intermediate may exist in higher concentrations than the hydrogen intermediate under comparable conditions and hence it is argued that the deuterium reaction may be the faster. However, this argument fails to include a consideration of the relative rates with which the intermediate products pass to the final products, and it appears possible that the reactions of the more stable intermediate may be sufficiently slow to counterbalance the effect of the higher concentration. This, of course, brings one back to a consideration of the same problems relative to the passage of the system over a barrier that have been discussed above.

No satisfactory comparison can be made of the theory and experiment since, on one hand, the theory is very approximate and, on the other, most reactions studied are chain or surface reactions, and hence are more complex than assumed above. However, the discussion will perhaps have some value in calling to mind some of the factors that must be considered in explaining experimental results such as those reported below.

2. Gaseous reactions

The simplest reaction which has been studied so far is the dissociation of hydrogen and deuterium into atoms due to collisions with mercury atoms in the 6^3P_1 state,

$$\mathrm{Hg}' + \mathrm{H}_2 = \mathrm{Hg} + 2\mathrm{H},$$
$$\mathrm{Hg}' + \mathrm{D}_2 = \mathrm{Hg} + 2\mathrm{D}.$$

Evans[158] finds from quenching experiments that the rates of these two reactions are equal. Since the energy of the mercury atom is 112 kcal. and the dissociation energies of hydrogen and deuterium are 101 and 103 kcal., respectively, it seems probable that the K_1 and K_2 will not depend on the vibrational, rotational or translational energies and hence the factor C will be completely cancelled by the inverse of this factor from B. Moreover, the number of collisions between hydrogen and mercury is greater than between deuterium and mercury by the factor $(\mu_2/\mu_1)^{1/2}$, but the duration of the collisions have the ratio $(\mu_1/\mu_2)^{1/2}$ and if the probability of dissociation is proportional to the time of "contact," the effect of the greater number of collisions would be cancelled by the lower probability of reaction.*

Evans finds that the ratio of quenching efficiencies of water and water-d_2 vapors on the 2537 line of mercury is 1 : 0.46, and this ratio for ammonia and ammonia-d_3 is 3.00 : 1.09. These molecules are not dissociated in the quenching process as hydrogen and deuterium are, and hence the same reasoning does not

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* Professor I. I. Rabi (private communication) has found that the collisional areas of deuterium molecules and sodium and potassium atoms are larger than these areas for hydrogen molecules and the same atoms.

There is also some evidence from the vapor pressure equations of hydrogen and deuterium that the latter is a less perfect gas than the former (see H. C. Urey, Les Prix Nobel, 1934).

apply. It appears that the difference between the waters and the ammonias is due to the difference in spacing of the levels of the isotopic molecules. The energy difference between the $^3P_1$ and $^3P_0$ levels of mercury is 0.218 electron volt, while the vibrational energy differences of the molecules which most nearly coincide with this value are in the same units: NH_3, 0.202; ND_3, 0.29; H_2O, 0.197; D_2O, 0.15. The greater quenching efficiency when exact coincidence is approached is in accord with observations on other molecules.

Bonhoeffer, Bach and Fajans[159] have investigated the thermal reaction of hydrogen and deuterium with bromine at 578°K and find a ratio of reaction rates of 3.3. And more recently, Bonhoeffer[160] has reported the results of a more extensive investigation showing the ratio to be 5.0 at 581°K. These reactions belong to the group of chain reactions in which the velocity of the reaction is determined by the number of chains started per unit time and the length of the chains. The length of the chains depends on the mechanism which terminates them. Assuming that this mechanism is as efficient in one case as in the other, the relative rates will depend on the probability of the individual links occurring per unit time. The starting process is undoubtedly the dissociation of bromine molecules to form atoms and the chain consists of the reactions, $Br+H_2 \rightarrow HBr+H-14{,}500$ calories, and $Br_2+H \rightarrow HBr+Br+41{,}300$ calories, the reaction chain being terminated by the reaction $2Br \rightarrow Br_2$ taking place as a result of triple collisions.[161] The second reaction occurs so rapidly for both hydrogen and deuterium that it is a negligible factor in controlling the rate of the total reaction. The first reaction, however, is endothermic to the extent of 14,500 calories per mole. The temperature coefficient indicates an activation energy of 17,640 calories per mole, which is somewhat greater than the energy required for this reaction. The inverse ratio of the mean times required for the individual reactions $H_2+Br \rightarrow HBr+H$ and $D_2+Br \rightarrow DBr+D$ to take place should equal the ratio of the observed overall rates of the reactions. The *C* factor of Eq. (45) can easily be calculated using the ratio of the summation of state for D_2 and H_2. The calculation of the *A* and *C* factors of Eq. (45) gives approximately

$$k_1/k_2 = 2^{5/2}e^{1795/RT} = 5.6\times 4.74 = 26.5,$$

where the factor 4.74 is due to the zero point energy difference. These results indicate that the observed ratio of velocities may be due to the zero point energies only. The reaction is complicated by the many factors characteristic of chain reactions and the theory we have used is, of course, incomplete.*

Rollefson[162] and Farkas and Farkas[163] have investigated the velocity of the hydrogen-chlorine and deuterium-chlorine reactions. Rollefson finds that the ratios of velocities at 0°C and 32°C are 13.4 and 9.75, respectively, from a study of the relative amounts of phosgene and hydrogen chloride formed when hydrogen (or deuterium), chlorine and carbon monoxide are illuminated by light absorbed by chlorine. The latter authors find the ratio at 30°C for hydrogen and a hydrogen-deuterium mixture containing 29 percent deuterium to be 3.3. This is another chain reaction, the slow reaction being

$$H_2 \text{ (or } D_2) + Cl \rightarrow HCl \text{ (or } DCl) + H \text{ (or } D),$$

and, as before,

$$k_1/k_2 = 2^{5/2}e^{1795/RT} = 5.64\times e^{1795/RT}.$$

At 273 and 303°K this gives $5.64\times 27.4 = 154$ and $5.64\times 18.4 = 104$, respectively. In this case the zero point energy alone gives results which are about twice the observed ratios. However, the temperature coefficient of the reaction velocity is exactly that required by the theory. The numerical values require that the *B* factor be about $2^{-7/2}$ but it should be noted that this reaction is not simple at all. The disagreement may be due to differences in the mechanism terminating the chains or other factors.

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* Recently Bach, Bonhoeffer and Moelwyn-Hughes (Zeits. f. physik. Chemie **B27**, 71 (1934)) have investigated the velocities of this reaction and find that the velocities of the hydrogen and deuterium reactions are

$$K_1 = 6.92\times 10^{10}\times e^{-17{,}740/RT},$$

and

$$K_2 = 8.34\times 10^{10}\times e^{-19{,}870/RT},$$

respectively. The difference in activation energies is approximately 2.1 kcal. and thus is nearly equal to the difference in the zero point energies, namely, 1.8 kcal., though the experimental error in this difference may be 1 kcal. This indicates that the factor *B* is not equal to 1 and in fact that it is approximately the reciprocal of the factor *A*.

The reactions of hydrogen and deuterium with iodine would seem to be the most important reactions which could be studied at the present time for the hydrogen-iodine reaction is known to be homogeneous and bimolecular. Thus many of the complications arising in the cases considered above should not appear and the possible contributions of the factors A, B and C of Eq. (45) might be estimated more satisfactorily.

The oxygen-hydrogen and oxygen-deuterium reactions have been compared in several respects by Hinshelwood, Williamson and Wolfenden,[164] by Melville[165] and by Frost and Alyea.[166] The results of such experiments have been reported in greatest detail by the first authors. Two pressure explosion limits have been observed for the oxygen-hydrogen reaction. The low pressure explosion limit is determined by the branching of the reaction chains and the upper limit is reached when the effective branching is balanced by deactivating ternary collisions in the gas phase so that a chain is terminated for every branch formed. The upper explosion limit is raised in the case of deuterium and this is interpreted as being due to the higher pressures required for sufficient ternary collisions to terminate the chains. It is found that a plot of the logarithm of the pressure above which explosion just does not occur against the reciprocal of the temperature gives parallel straight lines for hydrogen and deuterium, the ratio of the limiting pressures of the deuterium and hydrogen reactions being 1.31.

Grant and Hinshelwood[167] have given a simple theory for the upper explosion limit. It is assumed that there is a probability ν that branching occurs in the collision of two particles X and Y, which take part in the reaction chain, and that branching is prevented if a molecule collides with these two molcules during the time of their collision. This leads to the following condition for the upper limit,

$$\nu k[X][Y]=Z_{\mathrm{H}_2}[X][Y][\mathrm{H}_2]+Z_{\mathrm{O}_2}[X][Y][\mathrm{O}_2],$$

the Z factors being proportional to the collision frequencies of the collision complex XY with hydrogen or oxygen. This gives, $Z_{\mathrm{H}_2}P_{\mathrm{H}_2}+Z_{\mathrm{O}_2}P_{\mathrm{O}_2}=C$. If the chain mechanism is the same for both hydrogen and deuterium, the constant C is the same for both, and since hydrogen (or deuterium) and oxygen in their experiments are always used in the ratio of 2 to 1, i.e., P_{H_2} equals $2P_{\mathrm{O}_2}$, the ratio of the pressures at which explosion occurs is

$$\frac{P_{\mathrm{H}_2}+P_{\mathrm{O}_2}}{P_{\mathrm{D}_2}+P_{\mathrm{O}_2}}=\frac{2Z_{\mathrm{D}_2}+Z_{\mathrm{O}_2}}{2Z_{\mathrm{H}_2}+Z_{\mathrm{O}_2}}.$$

In order to calculate the relative number of collisions of hydrogen (or deuterium) and of oxygen with collision complexes, it is necessary to make some assumption in regard to collision areas and reduced masses. The authors assume that the number of collisions is proportional to $\sigma^2/\mu^{\frac{1}{2}}$; σ, assumed to be the same for the hydrogen and deuterium collisions, is the sum of the molecular radii of the reaction complex XY and of the third molecules which are assumed to be hydrogen (or deuterium) and oxygen. μ is taken equal to

$$\frac{(M_{\mathrm{H}_2}+M_{\mathrm{O}_2})\cdot M_{\mathrm{H}_2}}{2M_{\mathrm{H}_2}+M_{\mathrm{O}_2}} \quad \text{and} \quad \frac{(M_{\mathrm{D}_2}+M_{\mathrm{O}_2})\cdot M_{\mathrm{O}_2}}{2M_{\mathrm{D}_2}+M_{\mathrm{O}_2}}.$$

The identity of the molecules XY is not known, but in calculating the μ's by these formulae it is assumed that the value of M_{XY} is equal to the sum of the masses of the oxygen molecule and the hydrogen (or deuterium) molecule. In this way 1.29 is secured for the ratio of the upper limiting pressures as compared to the experimental value of 1.31. However, the equal collisional areas for the hydrogen and deuterium cases cannot be assumed without reservations.

The value of the activation energies for the branching processes is, within an experimental error of 1000 calories, about the same for hydrogen and deuterium. This factor indicates that the slow reactions of the chain do not involve the hydrogen and deuterium molecules, or the breaking of O–H or O–D linkages, for otherwise we might expect a difference in the activation energies equal to the difference in zero point energies of such molecules.

On the other hand, it is found that the velocity of the steady gas reactions at about 560°C, 150 mm of oxygen and 300 mm of hydrogen (or deuterium) are markedly different with a maximum ratio of the velocities of approximately $2\frac{1}{2}$. The authors suggest that this difference may be due to different zero point energies of some molecules occurring in the reaction chains. Hinshelwood, Williamson, Wolfenden[164] have investigated the relative rates of hydrogen-oxygen and deuterium-oxygen reactions at 525°C on quartz surface. The velocity of the deuterium reaction is less than that of the hydrogen reaction in the ratio of 0.66 in a 2 : 1 mixture of hydrogen (or deuterium) and oxygen at total pressures of 300 and 450 mm.

3. Surface reactions

The theory of the velocity of reactions on surfaces depends largely on the fundamental concepts of surface adsorption stated by Langmuir. The reacting substances are adsorbed on the surface, the reaction takes place between the adsorbed molecules and atoms and this is followed by desorption of these products. Whether a gas is adsorbed in the atomic or molecular condition can only be deduced from postulates in regard to the kinetics of these reactions and since the measured velocity of a reaction may be the net result of many elementary processes, it has been, and still is, difficult to be certain that the postulates which account for the observations are unique. However, the data thus far obtained for surface reactions in which the hydrogen isotopes are used are very suggestive and give promise of greatly clarifying the problems in this field.

Gould, Bleakney and Taylor[51] have investigated the condition of adsorbed hydrogen and deuterium by the simple method of observing whether isotopic exchange with the production of HD molecules occurs in a mixture of pure hydrogen, H_2, and pure deuterium, D_2, in the presence of certain catalysts. The occurrence of such exchange on a solid is regarded as proof of activated (atomic) adsorption of hydrogen whereas non-occurrence must mean that the hydrogen is adsorbed as molecules. It was found that soft and Pyrex glasses, stopcock grease and mercury do not effect such an exchange, and, moreover, deuterium, in the absence of metals, does not become contaminated by hydrogen from these surfaces. Though from other work[105] it is known that charcoal at liquid air temperatures is an efficient catalyst for the ortho-para conversion of hydrogen and deuterium (see Section VI), these authors and also Farkas, Farkas and P. Harteck[168] have observed no isotopic exchange to occur between H_2 and D_2 molecules adsorbed, under similar conditions, on this solid. The adsorption is therefore of the molecular type. However, for palladium at 270°C and for chromium oxide and also nickel catalysts at $-190°$ to 110°C the exchange occurs and, hence, the adsorption on these solids must be of the atomic type.

The velocities of adsorption of hydrogen and deuterium on chromium oxide, zinc oxide, chromium oxide, and nickel catalysts, as observed by Pace and Taylor,[169] are the same, within experimental limits of error, at all the temperatures investigated. This means that the zero point energies of H_2 and D_2 are not concerned in these processes, for, neglecting the possible contributions of relative numbers of collisions with the surfaces, the ratio of the velocities of adsorption (due to this cause alone) would be 8.5 at 420°K. If it were a matter of the number of collisions, the ratio of the velocities should be $\sqrt{2} : 1$, and if the controlling velocity were a diffusion process, the ratio of rates should be about 1.2 : 1. Pace and Taylor have suggested that the controlling factor must be associated with the condition of the catalytic surface and not with the hydrogen or deuterium at all, and that there may be some necessary spacing of atoms on the surface which determines the rate. The velocity and its change with temperature would thus be correlated with the rate at which atoms in the catalytic surface arrive in states permitting adsorption.

In a number of reactions on surfaces, processes which were previously unknown and unsuspected are found to take place. Thus hydrogen and deuterium gases exchange with these elements held, probably in the form of water, in chromium oxide gel and zinc oxide catalysts. Taylor and Diamond[170] report that very large dilutions of deuterium gas with hydrogen may occur because of exchange with the hydrogen held in the catalyst. Further saturation finally can be secured and then hydrogen samples brought in contact with the catalyst are diluted with deuterium. Two very interesting examples of this kind have been observed by Horiuti, Ogden and Polanyi[171] and by Farkas, Farkas and Rideal.[172] The former have observed that the exchange reaction

$$HD+C_6H_6=C_6H_5D+H_2$$

takes place on platinum black and nickel catalysts and occurs much more readily than the hydrogenation of benzene. The latter authors find that the exchange reaction

$$C_2H_4+HD=C_2H_3D+H_2$$

takes place at 120°C on nickel at a speed comparable to that of the reaction

$$C_2H_4+H_2=C_2H_6.$$

The authors suggest that it is the $=C=C=$ radical which is adsorbed and, since hydrogen and deuterium atoms are present on the surface, the exchange takes place as the C_2H_4 or C_2H_3D molecule is reformed. It may be of course that the adsorbed molecule is C_2H_3- and that the adsorbed molecule, in the case of benzene, is C_6H_5-. Or, possibly, ethylene and benzene may be adsorbed as whole molecules with exchange occurring because of existence of a high concentration of hydrogen atoms on the surface, the mechanism being similar to that originally suggested by Eyring and Polanyi[173] in connection with the ortho-para hydrogen conversion and other reactions. Such points can only be decided by further study of these reactions.

Urey and Price[174] have reported that the reaction of aluminum carbide with H_2O is twenty-three times the velocity of its reaction with D_2O. However, Hughes, Ingold and Wilson find that water containing 2.20 percent D_2O produces methane containing only 1.11 percent deuterium, indicating a ratio of velocities of only 2.* It appears that an exchange of hydrogen and deuterium between methane molecules must occur probably through surface catalysis, as observed in other cases.

Melville[175] has compared the velocities of reaction of hydrogen and hydrogen-deuterium mixtures (30 percent D and 66 percent D) with oxygen, nitrous oxide and ethylene in the presence of a nickel catalyst. He concludes that the ratio of velocities observed can be explained by a difference in zero point energies of the Ni−H and Ni−D bonds only and that these energies differ by about 700 calories.

Bonhoeffer, Bach and Fajans[159] have compared the velocities of the ortho-para hydrogen conversion and the velocity of the formation of hydrogen deuteride from hydrogen and deuterium on the same nickel catalyst. They find that the plots of the logarithms of the velocity constants against the reciprocal of the temperature are straight lines and that the heats of activation differ by 1360 calories per mole.

4. Photochemical reactions

The decomposition of ammonia and ammonia-d_3 by light alone and by light in the presence of mercury vapor has been studied by Taylor and Jungers[177] and by Evans and Taylor.[178] In the presence of mercury vapor illuminated by the λ2537 line of mercury, the course of the reaction can be described by the following reactions, which are probably not unique:

$$\begin{aligned}
&Hg+h\nu=Hg', && K,\\
&Hg'+NH_3=Hg+\text{decomposition}, && k_1,\\
&Hg'+H_2=Hg+2H, && k_2,\\
&Hg'=Hg+h\nu, && k_3,\\
&Hg'+NH_3=NH_3'+Hg, && k_4.
\end{aligned}$$

The first four equations are given by Melville and the last one is added, following a suggestion made by Taylor and Evans, in order to account for the ratio of the $K/(1+k_4/k_1)$ for the two ammonias.

The constants K, k_1, k_2, k_3 and k_4 are velocity constants for these reactions. K should depend on the light intensity and mercury vapor pressure only, except possibly for a small effect due to pressure broadening of the absorption line. Thus in the steady state,

$$\frac{d[Hg']}{dt}=K-(k_1+k_4)[Hg'][NH_3]-k_2[Hg'][H_2]-k_3[Hg']=0$$

and

$$-\frac{d[NH_3]}{dt}=k_1[Hg'][NH_3]=\frac{k_1K[NH_3]}{(k_1+k_4)[NH_3]+k_2[H_2]+k_3}. \tag{49}$$

Or letting

$$-\frac{d[NH_3]}{dt}=R, \qquad \frac{1}{R}=\frac{1+k_4/k_1}{K}\left\{1+\frac{k_2[H_2]+k_3}{(k_1+k_4)[NH_3]}\right\}.$$

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* Dr. Price has secured a fractionation factor of 1.2 in this laboratory.

This equation holds well in the region of low pressures, but at higher pressures $[NH_3]$ in Eq. (49) must be replaced by $[NH_3](1+x[NH_3])$, according to Evans and Taylor. The constant x is small and its kinetic origin is unknown. k_1+k_4 is the quenching constant for the resonance light in the presence of ammonia and k_2 is the same constant in the presence of hydrogen. In experiments using the pure gases it is found that k_2 is the same for hydrogen and deuterium and that k_1+k_4 is three times as large for pure ammonia as in the case of ammonia containing 80 percent deuterium. The kinetics of the reactions using pure ammonia and ammonia containing 80 percent deuterium are consistent with the values of about 4 to 1 for the ratio of the (k_1+k_4) constants as compared to 3 to 1 from the quenching experiments, about 5 to 1 for the ratio of the $K/(1+k_4/k_1)$ constants and the same value of x for these two gases, respectively. It is not possible to solve for k_1 and k_4 separately for each sample of ammonia. Taylor and Evans ascribe the differences in these velocities to the zero point energy differences of ammonia and ammonia-d_3.

Photochemical decomposition occurs when ammonia is illuminated with light of 2100A. Though the details of this reaction are less satisfactorily understood than those of the sensitized photochemical reaction, certain points have been clarified by the use of deuterium. The primary reaction is, undoubtedly,

$$NH_3+h\nu=NH_2+H.$$

The quantum yield at ordinary temperatures is 0.25. Thus reverse reactions must be present and many intermediate ones may also be postulated. Taylor and Jungers have shown that the reaction

$$NH_2+H \text{ (or D)}=NH_3 \text{ (or } NH_2D)$$

takes place by illuminating a mixture of ammonia, deuterium and mercury vapor with light from the zinc spark (2100A) and a mercury lamp (2537A). Under these conditions NH_2, D and H should be present and, if the above reactions take place, the deuterium in the ammonia should increase with time, as was found experimentally. On the other hand, the reaction

$$NH_3+D=NH_2D+H$$

does not occur, since the deuterium content of the ammonia increased only slightly when the conditions were kept the same except for the elimination of the 2100A radiation.*

5. Kinetics of reactions in solutions

In the case of reactions in solutions it is necessary to consider factors in addition to those discussed above. Thus, the viscosity and the dielectric constant of the solution may be expected to play important roles, the first factor influencing the number of collisions per unit time and the last being related to large effects that are produced by the charges of the reacting molecules or of ions in solution and by catalysis by neutral or ionized substances. Brönsted and others in recent years have established the general nature of acid-base equilibria and have applied these ideas to acid and base catalysis. Substances which donate protons to other substances are to be regarded as acids, while those that accept protons are bases. Thus H_3O^+ and $OH-$ are an acid and base, respectively, having properties similar to those of many other substances, and water itself is both an acid and a base. Many reactions in solution are catalyzed by acids and bases, the reaction proceeding by the addition of a proton at one time and the removal of another proton in a following step of the reaction.

Wynne-Jones[179] has studied the reaction of nitroethane with hydroxyl and deuteroxyl ion to form water and ions of the type $CH_3CH:NO_2^-$. Pedersen[180] has given reasons for believing that such reactions proceed through the steps

$$\text{(a)}\quad \begin{array}{l} CH_3\cdot CH_2\cdot NO_2+OH^-\rightarrow CH_3\overline{C}H\cdot NO_2+H_2O \\ \qquad CH_3\cdot\overline{C}H\cdot NO_2\rightarrow CH_3\cdot CH:NO_2^- \end{array}$$

and that the slow reaction is the first of these, so that the observed velocity is due to this reaction. The velocity of this reaction is compared with the velocities of the following reactions (b), (d) and (f):

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* That the first of these reactions takes place has been demonstrated by Farkas and Harteck (Zeits. f. physik. Chemie **B25**, 257 (1934)) using the ortho-para conversion as an indicator. However, these authors concluded that the last reaction should be possible which is in disagreement with the results of Taylor and Jungers.

(b) $CH_3 \cdot CH_2 \cdot NO_2 + OD^- \rightarrow CH_3CH : NO_2^- + HOD$,
(c) $CH_3CH : NO_2^- + D_3O^+ \rightarrow CH_3CHD \cdot NO_2 + D_2O$,
(d) $CH_3CHD \cdot NO_2 + OD^- \rightarrow CH_3CD : NO_2^- + HOD$,
(e) $CH_3CD : NO_2^- + D_3O^+ \rightarrow CH_3CD_2 \cdot NO_2 + D_2O$,
(f) $CH_3CD_2 \cdot NO_2 + OD^- \rightarrow CH_3CD : NO_2^- + D_2O$.

The OD^- ion was supplied as $Ba(OD)_2$ in a solution in water-d_2 and the course of the reaction was followed by the changing conductivity of the solution. When reaction (b) was complete, D_2SO_4 was added so that reaction (c) took place; then adding more $Ba(OD)_2$, reaction (d) took place, the velocity being followed again by the changing conductivity. Subsequent to another neutralization with D_2SO_4, the $Ba(OH)_2$ solution was again added so that the velocity of reaction (f) could be followed. It was found first that reaction (a) proceeds ten times as rapidly as reaction (f); second, reaction (b) is faster than (a) by about 50 percent, so that the removal of a proton by the OD^- ion is more probable than the removal of a proton by the OH^- ion; third, reaction (d) proceeds with 60 percent of the velocity of reaction (b); and fourth, reaction (f) is about 15 to 25 percent as fast as reaction (b). The large ratio of velocities of reactions (a) and (f) is of the magnitude observed in the case of gaseous reactions such as the hydrogen- or deuterium-chlorine reactions and is to be explained in a similar way.

The second conclusion above is similar to the results observed by Moelwyn-Hughes and Bonhoeffer[181] on the hydrolysis of sucrose, namely, that the reaction proceeds some 60 percent faster in water-d_2 than in water. Also, Schwarz[182] has found that the hydrolysis of ethyl and methyl acetates in 0.5 N HCl solution proceeds about 50 percent faster in 90 percent D_2O than in natural water. Moelwyn-Hughes and Bonhoeffer explain their results by assuming that the velocity is proportional to the concentration of a fairly stable complex of sucrose and hydrogen ion or of sucrose and deuterium ion. Then the velocity constant k equals $(C_{H^+}/K) \cdot k'$, where C_{H^+} is the concentration of H^+ and K and k_1 are, respectively, the dissociation and the velocity constants for the complex. Hence

$$\frac{k_{H_3O^+}}{k_{D_3O^+}} = \frac{K_{(D_2O)}}{K_{(H_2O)}} \cdot \frac{k'_{(H_2O)}}{k'_{(D_2O)}}.$$

Thus $k_{H_2O^+}/k_{D_3O^+}$ may be less than one, even if $k'_{(H_2O)}/k'_{(D_2O)}$ is greater than one, if K_{D_2O}/K_{H_2O} is sufficiently small. On the other hand, Wynne-Jones suggests that this case of the hydrolysis of sucrose and the case cited as the second conclusion of the proceeding paragraph are due to large zero point energies in the activated states, so that the energy of activation of the deuterium ion-sucrose complex is larger than that of the hydrogen ion-sucrose complex. In view of the fact that a small value of $K_{(D_2O)}/K_{(H_2O)}$ must at least partially depend on such a difference in zero point energies, it seems that there is little real difference in these views.

The velocity of mutarotation of glucose has been studied by Pacsu,[183] Wynne-Jones,[179] Moelwyn-Hughes, Klar and Bonhoeffer[184] and by Hammill and La Mer.[185] The results of these authors are in substantial agreement. The latter authors have studied the reaction at different concentrations of D_2O up to 60 percent and Wynne-Jones has given values for the velocity constants in 100 percent D_2O. These results differ somewhat from those of Pacsu and Moelwyn-Hughes and Bonhoeffer. The reaction, when the hydrogen ion concentration lies between 10^{-4} and 10^{-6}, is slightly catalyzed by water alone, and if hydrogen or hydroxyl ions are present, the reaction velocity is greatly increased. The velocity of the reaction in water can be written

$$v = (k_1 + k_2 + k_3) \times \text{concentration of glucose},$$

where the k's are given by the relations:

$$k_1 = k_{H_2O} N_{H_2O} + k_{HDO} N_{HDO} + k_{D_2O} N_{D_2O},$$

$$k_2 = k_{H_3O^+} N_{H_3O^+} + k_{HD_2O^+} N_{HD_2O^+} + k_{H_2DO^+} N_{H_2DO^+} + k_{D_3O^+} N_{D_3O^+},$$

$$k_3 = k_{OH^-} N_{OH^-} + k_{OD^-} N_{OD^-}.$$

The N's are concentrations in mole fractions.

Hammill and La Mer find that the constant k_1 varies with the concentration of deuterium in the water and that this variation can be explained as due to different catalytic constants for H_2O, HDO and D_2O. They find that these three constants are 0.01037, 0.00498 and 0.00273, respectively. It will be noted that the constant for HDO is nearly the geometric mean of the other two.

Moreover, the ratio of the constants for H_2O and D_2O is much smaller than would be expected on the assumption that it is due to the zero point energy difference of H_2O and D_2O, namely, about 3400 cal./mole. The constants for the hydrogen ion and deuterium ion catalysis have the ratio 1.33.

The iodine ion catalysis of the decomposition of hydrogen peroxide in heavy water (60 percent) has been studied by Abel, Redlich and Stricks,[186] who observed a decrease in the velocity constant of 20 percent as compared to that for ordinary water.

Farkas, Farkas and J. Yudkin[187] have investigated the decomposition of sodium formate in heavy water caused by the action of palladium black and the enzyme hydrogenlyase of Bacterium coli. It was thought that the reaction might be

$$CHCOOD \rightarrow HD + CO_2.$$

However, it was established that the hydrogen which was evolved was in equilibrium according to the equation

$$H_2 + D_2 = 2HD.$$

Additional experiments showed that the gas was in isotopic equilibrium with the water from which it was evolved and that both the above catalysts effected an exchange between heavy hydrogen in contact with ordinary water. The equilibrium constant for the exchange reaction

$$H_2O + HD = HOD + H_2,$$

catalyzed by platinum black, was determined to be 3.58. The authors conclude that the catalysis of the formate decomposition reaction by these catalysts occur by atomic reactions and that the H and D atoms exchange with water before combining to form hydrogen molecules.

The relative velocities of the reactions of metals with water containing varying concentrations of deuterium have been investigated by Hughes, Ingold and Wilson[188] by Davis and Johnston,[189] by Farkas and Farkas[19c] and by Horiuti and Bzabo.[190] The results are often contradictory and it appears, especially from the results of Hughes and his co-workers, that slight impurities may make marked differences in the relative velocities. In view of the fact that the experimental results of these three groups of workers disagree by large amounts, it seems that any detailed discussion of the results would best be delayed. The variation in results may be due to the exchange reaction between hydrogen and water being catalyzed more or less by the reacting metal or by impurities. Also diffusion processes must play an important part in such reactions, and in such cases the experimental conditions must be carefully arranged in order to enable one to satisfactorily interpret the results. In particular, Hughes, Ingold and Wilson find that zinc couples give the highest ratios of velocities, the values being approximately equal to those observed in the case of electrolysis, indicating that the mechanism is the same in the two cases, as is to be expected.

For some metals the relative velocities are less than 3, which is the value expected for equilibrium conditions, while for others it is greater than this. If the hydrogen-water reaction is catalyzed in any way under the conditions of these reactions, all relative velocities will be brought nearer to the value 3.

6. General exchange reactions

A number of observations on exchange reactions have been made; for the most part, they show whether the reaction does or does not take place. The results are listed in Tables XII and XIII. Bonhoeffer and Brown[191] first showed that the hydrogen of the $-OH$ groups of sucrose exchange with water while the hydrogens attached to the carbons do not. From the tables we see that the hydrogens of $-NH_2$ groups exchange immediately with water; the hydrogen of the aldehyde group, $-CHO$, exchanges slowly; those on the carbons linked to the carbon of the ketone group all exchange with water, rapidly in alkaline solutions, less rapidly in acid solutions, and very slowly in neutral solutions; the hydrogens of acetylene exchange in the presence of alkalies. The hydrogens of saturated hydrocarbon groups, whether aliphatic or aromatic, do not exchange with the hydrogen of water. All these observations are in accord with the expectations of organic chemists, though the confirmation of many points and the velocity observations are interesting.

The exchange in the case of $-OH$ groups

TABLE XII. *Exchange reactions between water and organic compounds.*

Compound	Observation	Reference
CH_3COONa	No exchange	192
CH_3COOH	" "	144
C_6H_6	" "	192
CH_3CHO	1 hydrogen atom exchanges slowly	192
CH_2O	2 hydrogen atoms exchange slowly	192
CH_3COCH_3	Very slow exchange in neutral solution	192, 193, 146
	Faster exchange in acid solution	
	Very fast exchange in alkaline solution	
$CH_3COCH_2COCH_3$	All hydrogens exchange	192
C_2H_2	Exchange in alkaline solution	194
Glucose and Cane Sugar	Hydroxyl hydrogens exchange immediately	191
$(CH_2OH)_2$	One-third of hydrogens exchange immediately	195
Egg albumen	All hydrogens attached to N atoms exchange	112
Cellulose	All hydroxyl hydrogens exchange	112

TABLE XIII. *Inorganic exchange reactions.*

Reaction	Observation	Reference
$H_2(g) \rightleftarrows H_2O(l)$ and (g)	Exchange in presence of platinum	91, 112
	Exchange observed in 6 weeks without addition of catalyst	198
	No exchange observed in 19 days without catalyst	51
	Exchange in 1–9.5 hours under 340–370 atmospheres pressure	195
	Exchange observed without catalyst in Pyrex and quartz vessels at 800°A	113
$H_2(g) \rightleftarrows HI(g)$	Exchange observed at 400°C and above	26
$H_2(g) \rightleftarrows HCl(g)$	Exchange in presence of palladium at 180°C	196
$H_2O(l) \rightleftarrows NH_4'(\text{sol.})$	All hydrogen atoms exchange	191
$H_2O(l) \rightleftarrows NH_3(l)$	All hydrogen atoms exchange	197
$H_2(g)+D_2(g) \rightleftarrows 2HD(g)$ see Sections IV and V	Exchange at high temperatures and on catalytic surfaces. Ni, chromium oxide, Pd, Hg, Pyrex and soft glass, and charcoal at liquid air temperatures do not promote exchange.	
$KH_2PO_2 \rightleftarrows H_2O$	No exchange.	195
$[Co(NH_3)_6](NO_3)_3 \rightleftarrows H_2O$	All hydrogens exchange	199

probably occurs through the addition of water, or weak ionization and in the case of $-NH_2$ through the reversible formation of $-NH_3^+$. In the case of the CH_2O and the $-CHO$ groups, the exchange takes place through the reaction

$$H-CHO+H_2O \rightleftarrows H-CH(OH)_2.$$

The ketones exist in enol- and keto-forms, as for example,

$$\underset{\text{enol}}{CH_3COH=CH_2} \rightleftarrows \underset{\text{keto}}{CH_3COCH_3}$$

and the exchange takes place while in the enol form since in this form it behaves as an alcohol. Acetylene behaves as a weak acid so that the exchange takes place because of the formation of small amounts of C_2H^- in alkaline solutions.

The variation of the observations on the hydrogen-water exchange is probably due to the chance presence of catalytic substances in some cases, though there may be a slow uncatalyzed reaction.

It seems likely that the study of these exchange reactions will furnish some simple examples of reaction kinetics. Such simple examples are needed to secure an understanding of many details of reactions of general interest. The equilibrium constants of simple gaseous reactions can be calculated from theory and it is to be hoped that similar theoretical calculations of the velocities of reactions can be made in the near future.

VI. NUCLEAR SPINS AND MOMENTS AND THE ORTHO-PARA CONVERSIONS

1. Spins and moments of the proton and deuteron

The nuclear spins of the proton and the deuteron have been determined from the alternating intensities of spectral lines. The characteristic functions for the positional coordinates of the nuclei of the hydrogen or deuterium molecule are symmetric or antisymmetric according as the rotational quantum number, *J*, is even or odd, respectively, in the normal $^1\Sigma_g{}^+$ state. If the nuclear spin is 1/2, three nuclear spin characteristic functions are symmetric and one is antisymmetric. If the proton is a simple particle, we expect that only those states which are antisymmetric in the protons, including both positional and spin functions, shall exist. Thus the even states are symmetric in the positional coordinates and antisymmetric in the spin coordinates, and the odd states antisymmetric in the positional and symmetric in the spin coordinates. Hence the *a priori* probability of the even (para) states is $2J+1$ and of the odd (ortho) states $3(2J+1)$. The even states are characterized by the nuclear spins being antiparallel so that the resultant magnetic moment of the protons is zero, while the odd states have parallel nuclear spins so that the resultant magnetic moment is twice that of the proton.

In the case of deuterium, it is commonly assumed that there are two (an even number) particles in the deuteron and that the characteristic function should be antisymmetric in each of these particles, so that the function for the composite deuterons in the molecule should be symmetric in the positional and spin coordinates. These assumptions are in accordance with observation (see Section VII) as has been shown by Lewis and Ashley[200] and, moreover, like considerations, when applied to the N^{14} nucleus, which may be composed of three alpha-particles plus the particles of the deuteron, lead to similar conclusions agreeing with experiment. Lewis and Ashley also showed that the deuteron spin is not zero, since in this case alternate rotational lines of the D_2 spectrum should be missing. And, more recently, Murphy and Johnston[201] have shown that the alternating intensity ratio is 2 : 1, corresponding to the statistical weights $6(2J+1)$ and $3(2J+1)$ for the even (ortho) and odd (para) states, respectively. The ratio of 2 in these statistical weights indicates a spin of one unit for the deuteron.

The para states of statistical weight 3 have a resultant mechanical nuclear moment of $h/2\pi$ and a resultant magnetic moment equal to that of the deuteron itself, while the ortho states consist of a state of statistical weight 5 with resultant nuclear mechanical moment of $2h/2\pi$ and magnetic moment of twice the deuteron moment and a state of statistical weight 1 with zero mechanical and magnetic moments. Thus neither the ortho nor para states of deuterium correspond to antiparallel spins only, and neither lack a magnetic moment due to the nuclei. In addition to the nuclear magnetic moments a magnetic moment arises from the rotation of the molecule as a whole since electrons do not rotate at the same distance from the center of mass on the average as the nuclei do, and hence the two fields do not exactly cancel; moreover, the electrons lag behind the nuclei in the rotation, making the calculation of this magnetic moment difficult and unreliable.

Stern and Estermann[202] have used the deflection of H_2 and D_2 molecules in inhomogeneous magnetic fields to determine the magnetic moments of the proton and deuteron. The deflections depend on the resultant magnetic moments of the nuclei and the molecular rotation. The latter magnetic moment was measured using para hydrogen, so that the entire deflection was due to the rotational moment; by assuming that this magnetic moment is proportional to J/I, the deflection in other cases could be corrected for this effect. If the proton follows Dirac's theory, its moment must be equal to one nuclear Bohr magneton, $eh/4\pi Mc$, just as that of the electron is $eh/4\pi mc$. However, according to Stern and Estermann, the moments of the proton and deuteron are equal, respectively, to 2.5 ± 10 percent and 0.7 Bohr magneton.

Rabi has determined these magnetic moments by use of a deflection method depending on a coupling of the nuclear and electron spins of the hydrogen or deuterium atom. As the magnetic field increases a Paschen-Back effect takes place. The energy of the unexcited hydrogen or deuterium atom in a magnetic field of strength H, is

$$W=-\frac{\Delta W}{2(2i+1)}\pm\frac{\Delta W}{2}\left(1+\frac{4m}{2i+1}x+x^2\right)^{\frac{1}{2}} \qquad (50)$$

where $x=8\mu_0 H/W$, W is the hyperfine structure splitting for zero field, i is the nuclear spin, g is the Landé factor and equals 2 for this case, μ_0 is the electronic Bohr magneton and m is the magnetic quantum number.

For hydrogen, $i=1/2$ and $m=1$, 0, 0, -1, while for deuterium, $i=1$ and $m=3/2$, $1/2$, $1/2$, $-1/2$, $-1/2$, $-3/2$. The ambiguous sign gives the values for the pairs of equal values of m; for the maximum values of m the positive sign is used, and for the minimum value of m, the negative sign. In an inhomogeneous field the force is

$$F=-(dW/dH)(\partial H/\partial x).$$

For hydrogen, this gives

$$F=\left(1,\ \frac{x}{(1+x^2)^{1/2}},\ -\frac{x}{(1+x^2)^{1/2}},\ -1\right)\mu_0\frac{\partial H}{\partial y},\qquad (m=1,\ 0,\ 0,\ -1),\tag{51}$$

and for deuterium

$$F=\left(1,\ \frac{x+1/3}{(1+2/3\,x+x^2)^{1/2}},\ -\frac{x+1/3}{(1+2/3\,x+x^2)^{1/2}},\ \frac{x-1/3}{(1-2/3\,x+x^2)^{1/2}},\ -\frac{x-1/3}{(1-2/3\,x+x^2)^{1/2}},\ -1\right)\mu_0\frac{\partial H}{\partial y},\tag{52}$$

$$(m=3/2,\ 1/2,\ 1/2,\ -1/2,\ -1/2,\ -3/2).$$

The atoms are passed through a weak magnetic field having high inhomogeneity so that appreciable deflection is secured without breaking down the coupling. Traces of the deflected and undeflected beams are recorded on a molybdenum oxide plate on which the atoms impinge. Due to the Maxwell distribution of velocities, all the components cannot be separated and only two components are recorded. The relation of blackening of the oxide to the intensity of the atomic beam is not known and, hence, two points of equal intensity, i.e., equal blackening, on each component are selected, their distances are measured and values of ΔW which agree with these distances for equal intensity are selected. Knowing ΔW, it is then possible to calculate the nuclear magnetic moment, μ, from the relation,

$$W=8\pi\mu\mu_0\psi^2(0),$$

where $\psi(0)$ is the value of the Schrödinger wave function at the nucleus. In this way, Rabi, Kellogg and Zacharias[203] have secured 3.25 ± 0.33 and 0.77 ± 0.2 for the magnetic moments of the proton and deuteron, respectively, in nuclear magneton units.

The results of Stern and Estermann and of Rabi, Kellogg and Zacharias do not agree within the limits of error given by them. However, considering the great difference in the methods of investigation, the approximate agreement between their results is to be regarded as very satisfactory. The experimental technique is difficult in both experiments. The results of Rabi, Kellogg and Zacharias depend on the validity of the cosine law of coupling between the nuclear and electronic spins and those of Stern and Estermann on the validity of a similar law of coupling between the nuclear and rotational moments; either of these assumptions may not be exactly correct.

2. The conversion of ortho and para deuterium

The ortho-para conversion has been extensively studied in recent years and has been shown to occur thermally, photochemically, and to be produced catalytically by paramagnetic substances and by adsorption on certain solids.[105] It is to be expected, of course, that the conversion of ortho and para deuterium will proceed by similar means; thus far, however, the only available experimental data on the deuterium conversion are those of Farkas, Farkas and Harteck,[106] which concern the catalysis by solid surfaces of glass and carbon and by the paramagnetic gas, oxygen.

In this work the analysis was by the thermal conductivity method previously used in the case of ortho and para hydrogen. The method depends on the different heat capacities of ortho and para deuterium and follows the same reasoning as that applied to the analysis of hydrogen-deuterium mixtures (Section II) except that the molecular weights need not be considered since they are the same.

Experiments carried out in the presence of charcoal at liquid air temperatures showed that para deuterium under such circumstances is converted rapidly to ortho deuterium. A glass tube acted as a less active catalyst and the slower rates of conversion resulting from its use made possible a comparison of the half-periods of the conversions of ortho to para hydrogen and of para to ortho deuterium. The values thus obtained were 11 and 19 minutes, respectively.

The above authors' recent experiments on the catalysis of the deuterium conversion by the paramagnetic molecule oxygen are entirely similar to those first carried out for hydrogen by Farkas and Sachsse.[204] The reactions are, in both cases, reversible and may be represented by the equations

$$p-\mathrm{H}_2+\mathrm{O}_2\rightleftarrows o-\mathrm{H}_2+\mathrm{O}_2$$

and

$$o-\mathrm{D}_2+\mathrm{O}_2\rightleftarrows p-\mathrm{D}_2+\mathrm{O}_2.$$

The experimental procedure consisted in introducing a small quantity of oxygen into a sample of hydrogen (or deuterium) containing an increased concentration of para hydrogen (or ortho deuterium) and subsequently determining the composition of the gas after freezing out the oxygen, from time to time, with liquid hydrogen. The partial pressure of para hydrogen (or ortho deuterium) as a function of the time is given by the usual formula for a bimolecular reversible reaction with the concentration of one constituent (O_2) remaining constant. Thus

$$P_t-P_\infty=(P_o-P_\infty)\exp-(k_{p\to o}+k_{o\to p})[\mathrm{O}_2]t, \quad (53)$$

where P_t, P_o and P_∞ are the partial pressures at the times t, zero and infinity, respectively, $[\mathrm{O}_2]$ is the concentration of oxygen and $k_{p\to o}$ and $k_{o\to p}$ are the rates of the para to ortho and ortho to para reactions. Under similar experimental conditions, the values of $(k_{p\to o}+k_{o\to p})$ obtained by use of this equation and the measured partial pressures are 9.16 and 0.57 liters per mole minute for hydrogen and deuterium, respectively. The separate velocities may be obtained from the above values since their ratio, $k_{p\to o}/k_{o\to p}$, must equal 3 and 2 for hydrogen and deuterium, respectively. This follows from the fact that under equilibrium conditions and at ordinary temperatures, or above, the concentrations of molecules in ortho and para states are in the ratio 3 : 1 for hydrogen and 2 : 1 for deuterium.

From these experiments and others it is evident that the reorientation of the nuclear spin vectors in hydrogen or deuterium molecules occurring during an ortho-para conversion may be effected by interaction between strong and highly inhomogeneous magnetic fields and the fields due to the nuclear moments of protons and deuterons. By considering this problem theoretically, Wigner[205] has been able to derive an expression for the velocities of conversion. He finds that the probability of a molecule in a para state passing to one in an ortho state by collision with paramagnetic molecules, is[206]

$$W_{J,\,J+1}=\frac{2\pi^2\mathrm{I}\mu_{\mathrm{O}_2}{}^2\mu^2}{27h^2a_s{}^6kT}\,\frac{J+1}{2J+1}\,\frac{(i+1)(2i+1)}{i^2}\exp\left(\frac{E_{J+1}-E_J}{kT}\right)$$

or

$$W_{J,\,J-1}=\frac{2\pi^2I\mu_{\mathrm{O}_2}{}^2\mu^2}{27h^2a_s{}^6kT}\,\frac{J}{2J+1}\,\frac{(i+1)(2i+1)}{i^2}. \quad (54)$$

μ_{O_2} is the magnetic moment of the oxygen molecule, μ is the magnetic moment of the proton or deuteron, a_s is an effective collision radius, which we shall assume to be the same for hydrogen and deuterium. The exponential factor appears because the transition from the Jth to the $(J+1)$th state occurs with the absorption of the energy $E_{J+1}-E_J$. The probabilities for transitions from the ortho to the para states are the same as for the reverse transitions except the factor containing the nuclear spins is $(2i+1)/i$ instead of $(i+1)(2i+1)/i^2$. Then if T is the same for the experiments with hydrogen and deuterium, we have

$$W_{J,\,J+1}=c\mu_{\mathrm{H}}{}^2I_{\mathrm{H}}\frac{J+1}{2J+1}\exp-\left(\frac{E_{J+1}-E_J}{kT}\right)\cdot 12\,\{\text{or } 4\}$$

$$W_{J,\,J-1}=c\mu_{\mathrm{H}}{}^2I_{\mathrm{H}}\frac{J}{2J+1}\cdot 12\,\{\text{or } 4\}$$

for hydrogen, where the factor 12 is to be used for the $p \rightarrow o$ transitions and the factor 4 for the $o \rightarrow p$ transitions, and

$$
\begin{aligned}
W_{J,\,J+1} &= c\mu_{\mathrm{D}}{}^2 I_{\mathrm{D}} \frac{J+1}{2J+1} \exp -\left(\frac{E_{J+1}-E_J}{kT}\right) \cdot 6\{\text{or } 3\}, \\
W_{J,\,J-1} &= c\mu_{\mathrm{D}}{}^2 I_{\mathrm{D}} \frac{J}{2J+1} \cdot 6\{\text{or } 3\}
\end{aligned}
\qquad (55)
$$

for deuterium, where the factors 6 and 3 apply to the $p \rightarrow o$ and $o \rightarrow p$ transitions, respectively.

Letting the partial pressure of molecules in the Jth steady state be P_J, we have

$$P_J/P_{\mathrm{even}} = (2J+1)e^{-E_J/kT}/(1+5e^{-E_2/kT}+9e^{-E_4/kT}+\cdots), \qquad J \text{ even},$$

and

$$P_J/P_{\mathrm{odd}} = (2J+1)e^{-E_J/kT}/(3e^{-E_1/kT}+7e^{-E_3/kT}+\cdots), \qquad J \text{ odd}. \qquad (56)$$

Therefore,

$$k_{o\rightarrow p}+k_{p\rightarrow o} = [\sum P_J/P_{\mathrm{even}}(W_{J,\,J+1}+W_{J,\,J-1})+\sum P_J/P_{\mathrm{odd}}(W_{J,\,J+1}+W_{J,\,J-1})] \times \qquad (57)$$

the number of collisions between hydrogen (or deuterium) and the oxygen molecules.

Making the necessary substitutions for hydrogen and deuterium and remembering that $1+5e^{-E_2/kT}+\cdots = 3e^{-E_1/kT}+7e^{-E_3/kT}+\cdots$ at ordinary and higher temperatures, we get

$$\frac{(k_{o\rightarrow p}+k_{p\rightarrow o})_{\mathrm{H}}}{(k_{o\rightarrow p}+k_{p\rightarrow o})_{\mathrm{D}}} = \frac{\mu_{\mathrm{H}}{}^2 I_{\mathrm{H}}}{\mu_{\mathrm{D}}{}^2 I_{\mathrm{D}}} \cdot \frac{16}{39} \left[\frac{e^{-E_1/kT}+2e^{-E_2/kT}+3e^{-E_3/kT}+\cdots}{1+5e^{-E_2/kT}+9e^{-E_3/kT}+\cdots}\right]_{\mathrm{H}} \left[\frac{1+5e^{-E_2/kT}+9e^{-E_3/kT}+\cdots}{e^{-E_1/kT}+2e^{-E_2/kT}+3e^{-E_3/kT}+\cdots}\right]_{\mathrm{D}} \cdot \qquad (58)$$

The ratio of the moments of inertia is 1/2. By introduction of the experimental values of $k_{p\rightarrow o}+k_{o\rightarrow p}$ and the calculated values of $E_J = BhcJ(J+1)$, using the B's given in Section VII, it is possible to calculate the ratio $\mu_{\mathrm{H}}/\mu_{\mathrm{D}}$. The value thus obtained is 4.1, in good agreement with that secured from deflection experiments by Rabi and Stern and their co-workers.

It should be emphasized that the theory of Wigner is approximate and, hence, the ratio secured by it cannot be final. Kalchar and Teller[206] state that more reliable results could be secured by comparing the velocity constant for hydrogen at T with that for deuterium at $T/2$. Thus far, however, the details of their theory have not been published and also further experimental data are required for its use.

VII. The Spectra of Deuterium and Its Compounds

1. The atomic spectrum of deuterium

The positions of the lines of the atomic spectrum of deuterium may be accurately calculated from the usual Balmer formula by introduction of a Rydberg constant for deuterium derived from the relationship:

$$\frac{R_{\mathrm{H}}}{R_{\mathrm{D}}} = \frac{M_{\mathrm{H}}}{M_{\mathrm{D}}} \frac{m+M_{\mathrm{D}}}{m+M_{\mathrm{H}}}, \qquad (59)$$

where M_{H}, M_{D} and m represent the masses of the proton, deuteron and electron, respectively. If R_{H} is taken equal to 109,677.759±0.05 cm^{-1}, R_{D} is found equal to 109,707.62. The values thus calculated are in reasonably satisfactory agreement with those obtained experimentally by Urey, Brickwedde and Murphy,[10] for the Balmer lines and by Ballard and White[207] for the lines of the Lyman series, as can be seen in Table XIV. Measurements by Rank[14] on the separation of Hγ and Dγ are in substantial agreement with the above values. In agreement with the theory of line broadening due to the Doppler effect, the deuterium lines have been found narrower than the hydrogen lines.[10, 208, 209, 210]

TABLE XIV. *Displacements of atomic spectral lines of D from lines of H.*

λ(H) vac. calc.	λ(D) vac. calc.	Δλ calc.	Δλ obs.
Balmer series			
6564.686	6562.899	1.787	1.79
4862.730	4861.407	1.323	1.33
4341.723	4340.541	1.182	1.19
4102.929	4101.812	1.117	1.12
Lyman series			
1215.664	1215.334	0.330	0.330
1025.718	1025.439	0.279	0.276
972.533	972.269	0.264	0.266
949.739	949.481	0.258	0.262
937.800	937.545	0.255	0.274*
930.744	930.491	0.253	0.258

* This value is probably inaccurate, because of difficulties in measuring it.

A much less satisfactory situation exists in regard to the fine structure of the atomic lines. Until recently, work on the fine structure of lines in the Balmer series had led to the conclusion that the positions of the individual components of the lines are those predicted by Dirac's relativistic theory of the hydrogen atom. On the basis of this theory an alkali-like spectrum is expected, with the positions of the components identical with those predicted by the Sommerfeld formula when the selection rules are modified to include the requirements of electron spin. Discrepancies that were observed between the calculated and experimental values for the relative intensities of the components of each doublet were generally attributed to a lack of knowledge of the excitation conditions. However, it appears evident from recent work that a definite discrepancy exists between the theory and experiment, although the exact magnitude of the difference is somewhat uncertain.

Microphotometer tracings of the fringe systems given by Hα and Dα when photographed through an etalon interferometer with auxiliary dispersion[210] indicate the presence of a third component $(n=3\rightarrow 2,\ j=\frac{1}{2}\rightarrow\frac{1}{2})$. In the case of deuterium, the dissymmetry in the microphotometer curves is particularly evident between the two major components and close to the short wave one. Williams and Gibbs[208] have made an analysis of the fine structure of Hα and Dα by an examination of the intensity curves of interferometer fringes obtained by photographing the lines with an etalon. These authors conclude that methods used previously in determining "doublet" intervals are in error due to the failure of workers to distinguish clearly between the intensity maximum of the complex of components and its center of gravity and that corrections have been erroneously applied to measurements. Their analyzed intensity curves indicate the presence of four components, the analysis not being sufficiently critical to decide as to the existence of the weak fifth component predicted by the theory. The interval found between the two chief components is 0.321 cm^{-1} for Dα and 0.308 cm^{-1} for Hα whereas 0.328 cm^{-1} is the expected value. Thus the values are lower than the theoretical ones by approximately 6 percent in the case of Hα and 2 percent in the case of Dα. This discrepancy is in only approximate agreement with the results of Houston and Hsieh,[211] who, using an accurate and new method, have measured the separation of the centers of gravity of the doublets of Hβ, Hγ, Hδ and Hε and have found discrepancies of about 4 percent. The measurements of Kopfermann[210] indicate values for Dα that are too low by 2 to 3 percent, while the work of Spedding, Shane and Grace[210] pointed to a discrepancy of only 0.5 percent.*

That the above discrepancies are due to the use of too large a value of the fine structure constant $\alpha(=2\pi e^2/hc)$ seems definitely excluded, for it seems impossible that the constants could be so greatly in error and, also, because such an explanation would require the discrepancy between the observed and theoretical values to be the same for hydrogen and deuterium. The lack of agreement of observed and calculated doublet separations therefore may be due to a deficiency in the theory of fine structure.

It seems likely[204] that levels with high electron densities near the nuclei may be affected by deviations from a Coulomb field. In the case of certain heavier nuclei this is known to be true, and Kemble and Present[212] believe it to occur for the hydrogen isotopes also. By

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* In a recent paper Spedding, Shane and Grace (Phys. Rev. **47**, 38 (1935)) find that the fine structure separations of *Hα* and *Dα* are very nearly the same and that they agree with the expected theoretical values very closely. They find that the intensities of the components depart markedly from the theoretical values, but that the same intensities can be assumed for the *Hα* and *Dα* components.

assuming a Coulomb field down to a finite radius a and then another type of law with the potential approaching a limit equal to e^2/a, these authors were enabled to compute the displacement of the energy levels as a function of a. The S levels are raised by an amount $2a^2e^2/3n^3r_0^3$, which is equivalent to the introduction of a quantum deficiency $n-n^*=a^2e^2/3Rhr_0^3$, where R is the Rydberg constant and r_0 is the radius of the innermost Bohr orbit. This results in a narrowing of the "doublet" separation by an amount in approximate agreement with the measurements of Houston and Hsieh on the H lines. The value of a in this case must be taken equal to 5×10^{-12} cm, which is surprisingly large in view of the fact that the classical electron radius is 2×10^{-13} cm. On the basis of this theory, the proton and deuteron may have different radii and to account for the discrepancy in the doublet separation of deuterium, the deuteron radius, a, must be 3.5×10^{-12} cm.

Houston and Hsieh report a suggestion made to them by Professors Bohr and Oppenheimer that the effect they observed may be due to a displacement of the levels by interaction between the electron and the radiation field. Thus there may be a relative displacement of the levels of the order of the product of the fine structure constant and the fine structure separation which is comparable to the observed effect. They are more inclined, however, to an explanation involving the natural width of the lines. The $2p$ level, which has the shortest lifetime of any of the levels involved, has a life of 0.16×10^{-8} sec. By the uncertainty principle a width of 0.02 cm^{-1} is indicated, which is larger than any of the observed discrepancies.

By introduction of Houston's value of $\nu(\text{H}\alpha)$ and the measured interval between the components of Hα and Dα arising from the $3d\,{}^2D_{5/2}\rightarrow 2p\,{}^2P_{3/2}$ transitions into the equation

$$\frac{\nu(\text{H}\alpha)}{\nu(\text{D}\alpha)}=\frac{M_\text{H}/(m+M_\text{H})}{M_\text{D}/(m+M_\text{D})},$$

it becomes possible to calculate the electronic atomic weight and the ratio e/m. Using the masses found by Bainbridge[24] for the hydrogen and deuterium nuclei, Gibbs and Williams[208] find the electronic atomic weight equal to $(5.491\pm0.002)\times10^{-4}$. Dividing the value of the Faraday given by Birge[213] by this value of m results in the ratio $e/m=(1.757\pm0.001)\times10^7$ e.m.u./gram. This is in agreement with earlier and similar measurements of Spedding, Shane and Grace, who concluded that the ratio e/m is less than 1.758×10^7 e.m.u.* It is also in good agreement with those recently obtained by magnetic deflection methods used by Dunnington[214] and Kretschmar[215] as well as with that obtained by Kinsler and Houston[216] from a study of the Zeeman effect in hydrogen. This value of the electronic atomic weight and Bainbridge's values for the atomic weights of hydrogen and deuterium have been used in calculating the value of R_D and the values of Table XIV.

Photographs of the Stark effect in a mixture of the hydrogen isotopes have been obtained by Foster and Snell.[217] The displacements found are not in agreement with those expected on the basis of the Epstein theory, even when the second order effect is included. The discrepancies are made particularly evident by variations in the separation of H–D pairs of Stark components since in the spectra the hydrogen and deuterium lines are about equally intense. The irregularities are more pronounced in the case of the π components and available evidence seems to indicate that the irregularities vary for different field strengths. According to measurements on Hγ and Dγ the variations appear too large to be explained completely by differences in the fine structure separation for the two isotopes, though it does seem probable that both are due to the neglect of the same factor in the theory or to the same uncertainty in the experimental conditions.

It is observed that in a given mixture of the isotopes at zero field, the deuterium line is always stronger in the H–Dγ pair than in the H–Dβ pair. In a mixture in which Hγ was much stronger than Dγ at zero field, the Dγ line was favored by the application of even a weak field and at a maximum field became practically as intense as Hγ. Foster and Snell[217] suggest that the origin of such variations may be in the occurrence of collisions of the second kind, the probability of such collisions being greatest when

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* Shane and Spedding (Phys. Rev. **47**, 33 (1935)) report a new value for e/m, namely, $1.7579\pm0.0003\times10^7$.

the H atom is the one excited. The relative intensities of corresponding components of Hγ and Dγ and also of Hβ and Dβ are not constant. Such variations may be due to a selective action whereby certain pairs of isotopic states are preferred in energy transfers. This is, as these authors have pointed out, equivalent to saying that there are departures from the theoretical intensities and that such departures are different for the two isotopes.

2. Diatomic molecular spectra

By examining the atomic spectra of hydrogen and deuterium, we have seen that the isotope effect, which is an electronic one, is a relatively small, though measurable, effect. It seems probable that the electronic effect in band spectra will also be quite small generally and very nearly negligible in comparison to the large effects observed in the rotational-vibrational bands of isotopic molecules. In this latter case, the influence of nuclear mass is very great since both the moment of inertia and the vibrational frequency are affected. The differences in the moments of inertia of two isotopic molecules are attributable almost wholly to differences in the reduced masses since the internuclear distances depend on the nuclear and electronic interactions. While differences in such interactions are, as indicated above, quite small usually, they may be expected to be largest for molecules involving the hydrogen isotopes, and are perhaps not entirely negligible in certain specific cases.

The rotational vibrational energy levels of a diatomic molecule in a specified electronic state are given (in cm^{-1}) by the following equation:

$$\begin{aligned}\frac{E_{v,\,J}}{hc} &= \tilde{\omega}_e(v+1/2) - x\tilde{\omega}_e(v+1/2)^2 \\ &\quad + y\tilde{\omega}_e(v+1/2)^3 + z\tilde{\omega}_e(v+1/2)^4 \\ &\quad + [B_e - \alpha_e(v+1/2) + \gamma(v+1/2)^2 \\ &\quad - \delta(v+1/2)^3]J(J+1) + [D_e + \beta(v+1/2)] \\ &\quad \times J^2(J+1)^2 + F_e J^3(J+1)^3, \qquad (60)\end{aligned}$$

where J and v are, respectively, the rotational and vibrational quantum numbers. In most cases the terms in $(v+\frac{1}{2})^3$ and $(v+\frac{1}{2})^4$ can be neglected. This equation has been shown in a number of instances to agree well with experiment and the form satisfies the requirements of quantum-mechanical theory.

$\tilde{\omega}_e$ is a constant for a given electronic state of the molecule and has a relatively large value for molecules involving the hydrogen isotopes, since it is the frequency (in wave numbers) of vibrations of infinitesimal amplitude about the equilibrium positions. The other constants are fairly small ones, except in the case of B_e, which is related to the moment of inertia by the equation,

$$B_e = h/8\pi^2 cI_e.$$

The other constants are related to B_e and $\tilde{\omega}_e$; the exact relationships are given elsewhere.[218]

For isotopic diatomic molecules in which the electronic effect is negligible, the ratios of the constants of Eq. (60) for the two molecules are equal to powers of the ratio of the reduced masses. A function ρ may therefore be defined by the equation

$$\rho = (\mu_1/\mu_2)^{1/2},$$

where μ_2 and μ_1 are the reduced masses of the two molecules. Since the constants appearing in the energy level equation are all interrelated, the equation for the XH molecule is easily transformed into one for the XD molecule by multiplication of the various constants by ρ taken to the same power as the order in v and J of the term in which the respective constants appear.[218]

a. The spectra of HD and D_2 and the spin of the deuteron. In the last few years, the molecular spectrum of hydrogen has been analyzed in great detail by Richardson, Dieke, their coworkers and others.[219, 224] There still remain, however, a great many problems connected with a complete analysis of this very complex spectrum; it seems likely that the study of the analogous spectra of the HD and D_2 molecules will be a very important factor in their solution.

Recently, Jeppesen[220] and Beutler and Mie[221] have photographed lines in the extreme ultraviolet emission spectra of hydrogen-deuterium mixtures and have identified several bands as belonging to the HD molecule. Jeppesen used the usual hydrogen discharge while Beutler and Mie observed the spectrum in a discharge containing a large proportion of argon and only a small amount of hydrogen and deuterium. Jeppesen identified twelve bands as belonging to the $1s\sigma 2p\pi\ {}^1\Pi_u \rightarrow 1s\sigma^2\ {}^1\Sigma_g{}^+$ system of the HD molecule[*] and Mie observed several doublets of this system excited by argon and originating in the $v'=0$ level of the $1s\sigma 2p\pi\ {}^1\Pi_u$ state. In addition to these doublets, which Mie believes may be due to a fluorescence involving the 1048.28A argon line and the $v''=1$ level of the lower electronic state, he has also observed a very simple series of equally spaced pairs of doublets originating in the $J'=1$ and 2, $v'=3$ rotational-vibrational levels of the $1s\sigma 2p\sigma\ {}^1\Sigma_u{}^+$ state and ending in the various vibrational levels of $1s\sigma^2\ {}^1\Sigma_g{}^+$ state. These latter doublets are resonance lines similar to the type observed in iodine and are thought to be due probably to collisions of the second kind between argon atoms and HD molecules.

Though the HD lines photographed in the argon-hydrogen discharge were frequently five times as intense as the H_2 lines, indicating an equilibrium concentration of D_2 about 1.5 times that of HD, no lines were obtained for D_2. Mie shows that this is probably due to the slight probability of excitation of D_2 by argon atoms because of the unfavorable relative positions of the energy levels of argon atoms and D_2 molecules.

The results of the above two investigations are in good agreement and comparison of the molecular constants obtained for the various states with those previously obtained for H_2[220] indicates that the usual theory for isotopic molecules holds. The experimental data for the normal $1s\sigma^2\ {}^1\Sigma_g{}^+$ state of the HD molecule agree with equations of the type given above if the constants in Table XV are used. The data as given here apply only to low values of v; the constants for higher values of v may, however, be obtained by reference to the original papers. The values of the constants of the D_2 molecule, given in the third column, are calculated from those given for H_2 and HD since experimental data on the symmetrical heavy molecule are not yet available.

TABLE XV. *Molecular constants of hydrogen isotopes.*[*]
$1s\sigma^2\ {}^1\Sigma_g{}^+$ state.

	H_2	HD	D_2
$\tilde{\omega}_e$	4415.64	3824.99	3124.07
$x\tilde{\omega}_e$	131.203	98.36	65.67
$y\tilde{\omega}_e$	3.1169	2.0252	1.103
$z\tilde{\omega}_e$	0.19000	0.10694	0.04758
B_e	60.848	45.6549	30.459
α	3.0670	1.9928	1.0858
γ	0.06840	0.03850	0.01713
δ	0.0065	0.00317	0.00115
$-D_e$	0.04648	0.02602	0.01121
β	1.34×10^{-3}	6.58×10^{-4}	2.39×10^{-4}
F_e	5.1806×10^{-5}	2.19×10^{-5}	6.49×10^{-6}

[*] The values of the constants given in this table, though derived from Jeppesen's data, differ slightly from this authors' values because of his use of $(J+\frac{1}{2})^2$ in the energy equation instead of $J(J+1)$ as used here.

In the visible region of the spectrum, the HD and D_2 molecules yield emission spectra of relatively simple structure that are entirely analogous to the Fulcher bands of H_2. These spectra are due to transitions from the $1s\sigma 3p\pi\ {}^3\Pi_u$ upper state and to the $1s\sigma 2s\sigma\ {}^3\Sigma_g{}^+$ lower state. The shifts of lines in these spectra due to rotational and vibrational isotopic effects have been found by Ashley[222] and by Dieke and Blue[223] to be in agreement with those predicted by the simple theory, referred to above, relating the constants of isotopic molecules. The results of Dieke and Blue are very well summarized in Table XVI. In this table are given the values of the chief constants of H_2, HD and D_2 for the $3p\pi\ {}^3\Pi_u$ and $2s\sigma\ {}^3\Sigma_g{}^+$ states. In the columns headed "Ratio" are the observed ratios of the constants of HD and D_2 to corresponding ones of H_2, i.e., the value of column 1 divided by that of 2 and 3, respectively. The values of the ratios given in the next two columns are those expected theoretically, calculated from the known values of the reduced masses. In computing constants from the observed data terms up to v^4 and J^6 were used. The authors state that the slight discrepancies that appear in the above table are due to the use of an inadequate formula in calculating the constants, rather than to an inadequacy of the theory.

As might be expected for isotopic molecules for which the mass ratios are very large, the spectra of H_2, HD and D_2 show marked electronic effects. Miss Ashley found an electronic isotope shift of 2.4 cm^{-1} in the Fulcher system as compared to 5 cm^{-1} indicated in the work of Dieke and Blue.

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[*] The designations g and u do not apply to the states of a heteronuclear molecule. However, we have retained them for the HD molecule to indicate more definitely the relation between the states of the H_2, HD and D_2 molecules.

TABLE XVI. *The constants of the Fulcher bands.*

	1	2	3	Ratio				
	H_2	HD	D_2	2 : 1	3 : 1	ρ_{12}^n	ρ_{13}^n	n
$\tilde{\omega}'$	2371.58	2054.59	1678.22	0.86634	0.70764	0.86616	0.70744	1
$\tilde{\omega}''$	2664.83	2308.44	1885.84	.86626	.70768			
$x'\,\tilde{\omega}'$	66.27	49.74	32.94	.7506	.4970	.7502	.5005	2
$x''\,\tilde{\omega}''$	71.65	53.77	35.96	.7505	.5018			
B'	30.364	22.810	15.200	.7512	.5006			
B''	34.216	25.685	17.109	.7507	.5000			
α'	1.545	1.020	0.5520	.660	.357	.650	.354	3
α''	1.671	1.099	0.606	.658	.363			
$-D'$	0.0191	0.0116	0.0049	.61	.26	.563	.250	4
$-D''$	0.0216	0.0128	0.0055	.59	.25			
$y'\,\tilde{\omega}'$	0.88	0.58	0.24	.66	.27			
$y''\,\tilde{\omega}'$	0.92	0.60	0.34	.65	.36			
ν_0	16793.87	16788.86	16783.92					

Mie[221] finds values of 15±10 cm^{-1} and 12±10 cm^{-1}, respectively, for the electronic isotope effect of the $1s\sigma\,2p\pi\;{}^1\Pi_u \rightarrow 1s\sigma^2\;{}^1\Sigma_g^+$ and $1s\sigma 2p\sigma\;{}^1\Sigma_u^+ \rightarrow 1s\sigma^2\;{}^1\Sigma_g^+$ systems of the H_2 and HD molecules. According to Mie, the former value for the $1s\sigma 2p\pi\;{}^1\Sigma_u \rightarrow 1s\sigma^2\;{}^1\Sigma_g^+$ system is in agreement with the recalculated data of Jeppesen.

Beutler[221] has found additional resonance bands of H_2 in which the transitions are to the vibrational states 13 and 14 of the normal electronic state, and in this way he has secured a better extrapolated value for the dissociation energy of H_2. Using this value and the zero point energy of H_2, HD and D_2, he has secured more exact values for the dissociation energies of the two latter molecules. In this way he secures the values: H_2, 102.68±0.12 kcal.; HD, 103.50±0.12 kcal.; D_2, 104.48±0.12 kcal.

Anharmonic binding may result in different positions of perturbing and perturbed levels in isotopic molecules and thus lead to differences in the details of the perturbations. In the case of the $1s\sigma 2p\pi\;{}^1\Pi_u$ state of the HD molecule, Jeppesen finds evidence for a perturbation of a few wave numbers in the $K=3$, $v=2$ level similar in character to the perturbation of -7.4 cm^{-1} in the corresponding level of H_2. All of the lines of the P and R branches of bands of HD having $v=3$ as the initial level are perturbed by about 4.3 cm^{-1}. This latter perturbation thus appears similar to the 10.4 cm^{-1} perturbation for the same level of H_2. The level of HD with $v=3$ has more nearly the same energy as the level of H_2 with $v=3$ than has any other vibrational level of HD in this electronic state, so that the perturbations seem to come at the same total value of the energy.

All three molecules of hydrogen are found by Dieke and Blue to show perturbations of the component of the initial $1s\sigma 3p\pi\;{}^3\Pi_u$ state that gives P and R branches. In H_2 the $v'=1$ level is the one most strongly affected, whereas in HD it is quite regular and the $v'=0$ is very irregular. The authors believe that this is due to the effect of anharmonic binding which changes the relative positions of the perturbing and perturbed vibrational levels in the two molecules.

In agreement with the results of Richardson and Das on H_2, Dieke and Blue find that for HD all P and R branches in the $1s\sigma 3p\pi\;{}^3\Pi_u \rightarrow 1s\sigma 2s\sigma\;{}^3\Sigma_g^+$ system are absent for $v'>4$. For D_2 however, the P and R branches are normal for $v'=4$, but are absent for $v'>5$. Dieke and Blue attribute the disappearance of these branches to predissociation. The predissociation limit should be practically independent of the masses of the molecules and dependent only on the shape of the potential energy curves. From these facts it is possible to conclude that the predissociation limit must lie between 0.93 to 1.02 volts above the origin of this ${}^3\Pi$ state.

From the observation of Lewis and Ashley[200] that an alternation of intensities occurs in the alpha-bands of D_2, the lines involving transitions from even states being more intense, than those involving transitions from odd states, it could be concluded that the nucleus of deuterium obeys the Einstein-Bose statistics, and that the spin cannot be zero. By the application of methods of spectrographic photometry to P, Q and R branches of five bands of the $\Delta v=0$ sequence of the Fulcher spectrum of D_2, Murphy and Johnston[201] have checked the above results and have determined the ratio

$$g_s/g_a=1.97\pm0.03,$$

where g_s and g_a are, respectively, the statistical weights of the symmetric and antisymmetric states. From this value of the g_s/g_a ratio, which was obtained as the weighted average from four plates, one concludes that the spin of the deuterium nucleus is 1.

b. The infrared spectrum of DCl. The first investigation made on the molecular spectrum of a molecule involving deuterium was that of Hardy, Barker and Dennison[225] who measured nineteen lines in the fundamental absorption band of DCl^{35} and seventeen in the band of DCl^{37}. By introduction of constants derived from Meyer and Levin's[226] measurements of infrared lines of HCl into the equation developed by Fues[227] for the energy levels of a rotating dipole, these authors obtained an equation relating the lines of DCl to those of HCl:*

$$\begin{aligned}\tilde{\nu}=(2989.24\rho^{1/2}-103.40\rho-0.076\rho^{3/2})\\+(21.1678\rho-0.6060\rho^{3/2}-0.0005\rho^2)J\\-0.3030\rho^{3/2}J^2-0.0020\rho^2J^3.\quad(61)\end{aligned}$$

The value of ρ was found by a method of successive approximations involving the assumption of a value, calculation of the frequencies of DCl and comparison with the experimental data. The final equation, corresponding to $\rho=0.514430$, is

$$\begin{aligned}\tilde{\nu}=2090.78+10.666J\\-0.1118J^2-0.00056J^3.\quad(62)\end{aligned}$$

Very good agreement between the calculated and observed values of the wave numbers is secured.

The effective moving charge to be associated with the vibrating dipole is 1/5 electron.[228] The reduced mass is M_1M_x/M_1+M_x where M_1 and M_x are the effective masses of the vibrating particles, that is, the masses of the hydrogen atom minus 1/5th of an electron and of chlorine plus 1/5th of an electron. From the value of $\rho=0.514430\pm0.000004$, and the equation,

$$\rho=\mu_1/\mu_2=M_1(M_2+M_x)/M_2(M_1+M_x)$$

or

$$M_2=M_1/[\rho-(M_1/M_x)(1-\rho)].$$

M_2 may be calculated to be 2.01356 ± 0.00010, thereby resulting, after 1/5th of the atomic weight of the electron is added, in a value for the mass (O = 16) of the deuterium atom equal to

$$2.01367\pm0.00010.$$

This value agrees satisfactorily with that obtained by Bainbridge[24] using the mass-spectrograph, namely, 2.01363 ± 0.00008.

c. The ND and NH molecules. Recently there have been observed in an electrical discharge in a mixture of nitrogen with hydrogen and deuterium two very simple bands at 3240A and 3235A, corresponding to the $^1\Pi\rightarrow{}^1\Delta$ systems of the NH and ND molecules. The NH band was discovered and analyzed independently by Pearse,[229] and by Dieke and Blue.[230] The latter authors have also reported results on the corresponding band of ND. The bands are both 0→0 vibrational transitions. In Table XVII, we give values of the constants both for NH and ND, taken from the work of Dieke and Blue. Due to Λ-type doubling of the upper ($^1\Pi$) state, the values of B_0 are effective ones for the two components. The Λ-type doubling for the $^1\Delta$ state was found entirely negligible. Though it was necessary to include the term $FJ^3(J+1)^3$ in the computation of the constants of NH, it was negligible in the case of ND. In the fourth column are the observed ratios of the corresponding constants of

TABLE XVII. *Constants of the $^1\Pi\rightarrow{}^1\Delta$ bands of NH and ND.*

	NH	ND	Ratio (obs.)	Ratio $=\rho^n$ (calc.)	n
B_a'	14.154	7.639	1.8529	1.8726	2
B_b'	14.171	7.640	1.8555	1.8726	2
B''	16.446	8.836	1.8614	1.8726	2
D'	2.44×10^{-3}	6.54×10^{-4}	3.72	3.5113	4
D''	1.74×10^{-3}	5.05×10^{-4}	3.45	3.5113	4
ν_0	30755.61	30849.00		Difference 93.39	

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* This differs from Eq. (60) since $(J+1/2)^2$ is used in place of $J(J+1)$. The effect on the HCl and DCl band constants will be small. In any case the difference between the observed ρ and calculated ρ cannot be as great as in the case of the AlH and AlD bands discussed below.

the two molecules, and in the fifth column their theoretical values. It is readily seen that they do not agree.

This is in agreement with the fact that the relations derived from the ratio of the reduced masses of isotopic molecules are for molecules without rotational or vibrational motion, whereas in the zero vibrational state they still have a half quantum of vibrational energy. Since publication of the above values of the constants of the levels Dieke and Blue have succeeded in photographing and analyzing the 1→0 band of NH and the 1→0 and 1→2 bands of ND. From the analysis, which is yet unpublished, they are enabled to calculate the values of α and therefore values of B_e, the constant for the vibrationless state. The B_e ratios thus obtained agree satisfactorily with the theoretical value $\rho^2 = 1.8726$.

The Λ-type doubling should, according to theory, be proportional to $J(J+1)$ and have a transformation factor of ρ^4. The experimental results for the doublet separation when plotted against $J(J+1)$ show excellent agreement with the theory. The doublet separation is 3.511 times larger for NH than for ND. This was expected, for Λ doubling is due to the interaction of electronic and rotational motions, the doubling being greater for higher angular velocities of the molecule, and, since in isotopic molecules the electronic motions are practically the same, the doubling is greater for the lighter molecule, i.e., the one having the lower moment of inertia and therefore the higher angular velocity.

d. The spectrum of the neutral OD molecule. Recently photographs of the OD spectrum similar to that of OH near 3000A have been obtained and analyzed by Johnston and Dawson[231] and by Shaw and Gibbs.[232] The former authors have identified and assigned nearly 500 OD lines, which are distributed through eight bands (including the (3,1) and (3,2) bands). In the (0,0) bands the assignments extend beyond $K = 30$. It was found necessary to introduce corrections for isotope effects in spin coupling and in Λ-type doubling in the $^2\Pi$ (ground) level and to include γ_e terms in the equation for the rotational constants B_v for both upper and lower levels in the calculation of corresponding lines in the spectra of OD and OH. In Table XVIII we give the preliminary results of Johnston and Dawson for the isotopic displacement of three band heads. The constants of OH previously calculated[233] were used in obtaining the values in the table. The good agreement between observed and calculated displacements shows that previous vibrational analyses have been essentially correct.

TABLE XVIII. *Isotopic displacement for the OD molecule.*

v',v''	Vibration	Rotation	Spin coupling	Calc. sum	Obs. displacement
2,0	−1379.5	− 44.5	+ 8.7	−1415.3	−1417
1,0	− 697.3	− 63.4	+10.0	− 750.7	− 750
0,1	+1014.6	−167.7	+ 7.0	+ 853.8	+ 864

The OD and OH molecules are an interesting isotopic pair in which to study spin doubling. Contrary to the usual observance of a contraction between energy levels on going from a light molecule to a heavier one, the separation of the $^2\Pi$ levels, due to spin coupling, is found[231, 232] to be greater for OD than for OH. Though the theory of spin-coupling developed by Hill and Van Vleck[234] does not predict exactly the spin doublet spacing in either OH or OD, it accounts fairly well for the difference between the doublet spacings of the two molecules.

Johnston was unable to fit an expression for Λ-type doubling derived by Van Vleck[235] to the experimental data on the $^2\Pi$ levels of OH or to account, by means of the expression, for the differences in the doublet spacings of OD and OH. The Van Vleck equation for case "*b*" molecules, however, reproduced approximately the observed ratios of the doublet spacings for common values of the rotational quantum number. The Λ-type doublet separation for OD is 0.284 that for OH for equal values of K. The separation for OH is 17 cm^{-1} greater than that for OD at $K = 25$ in the case of the $^2\Pi_{3/2}$ level.

e. The AlH and AlD molecules. Several bands in the $^1\Pi - {}^1\Sigma$ system of the AlD as well as of the AlH molecule have been photographed and analyzed by Holst and Hulthen.[236] The results of AlH agree very well with a previous study of these bands[237] and two new levels of the $^1\Sigma$ state are included in the analysis. In order to study the marked pressure effect[238] related to the predissociation of the $^1\Sigma$ state, photographs of the spectrum were taken with the hydrogen atmosphere surrounding the source at the pressures 600 mm and 40 mm.

Vibrational terms up to $v''=3$ for $^1\Sigma$ and $v'=2$ for $^1\Pi$ appear in the AlD spectrum. Though the data do not allow confirmation of the nonoccurrence of an electronic isotope effect in the $^1\Pi$ state, the term values are calculated on this assumption. Within the limits of experimental error, the wave numbers of the band lines are represented by the computed term values by use of the selection rule ($\Delta K=0, \pm 1$). The vibrational term values are given by the usual polynomial in $(v+1/2)$.

The constants $\tilde{\omega}_e$ and B_e for these two molecules in the normal $^1\Sigma$ state are particularly interesting. These values are: $\tilde{\omega}_e=1682.57$ and $B_e=6.3962$ for the AlH, and $\tilde{\omega}_e=1212.02$ and $B_e=3.3185$ for AlD. Using these constants values of the isotopic factor can be secured. Thus,

$$\frac{B_e(\text{AlD})}{B_e(\text{AlH})}=\frac{\mu r_e^2(\text{AlH})}{\mu r_e^2(\text{AlD})}=0.51882,$$

and

$$\frac{\tilde{\omega}_e^2(\text{AlD})}{\tilde{\omega}_e^2(\text{AlH})}=\frac{\mu(\text{AlH})}{\mu(\text{AlD})}=0.51889.$$

Now if the equilibrium distances (r_e) and the restoring forces near the equilibrium point are equal, respectively, for AlH and AlD, then the above ratios should equal the value of ρ^2 calculated directly from the reduced masses obtained from the known atomic weights for Al($M=26.97$), H($M_1=1.00778$) and D($M_2=2.0136$). The direct computation, however, gives

$$\rho^2=0.51848\pm 0.00002,$$

where the limit of error is due to an uncertainty of 1 percent in the atomic weight of Al. As the ratios computed from the spectroscopic data can scarcely be so greatly in error as the above discrepancy, it may be concluded that the usual isotopic theory discussed above does not account for the experimental results.

Holst and Hulthén have suggested that the discrepancy may be accounted for by the inclusion in the usual expression for the moment of inertia of a rotating molecule of a term i_e, which is the moment of inertia of the electron cloud surrounding the Al nucleus. Calculation of i_e for Al by using the electron distributions of Thomas[239] leads to the value $\rho^2=0.51892$, which is in good agreement with the spectroscopic value. An explanation due to Kronig[240] is that the general assumption of identity of potential energy curves for isotopic molecules is justified only in certain molecules for which the resultant orbital angular momentum, L, considering the molecule as an atom in which the two nuclei have coalesced, is equal to zero. In AlH or AlD the ground state $^1\Sigma$ probably goes over to the lowest ^{1}D state of Si if the nuclei are imagined to coalesce. Use of $L=2$ in the equation derived by Kronig results in an expected difference of 2.8×10^{-12} cm in the equilibrium distance of AlH and AlD. This is less than the difference 6×10^{-12} cm found by Holst and Hulthén, but the deviation between the two values may reasonably be accounted for by a second term of Kronig's theoretical equation which cannot be calculated or possibly by a lower accuracy of the experimental results than that estimated by Holst and Hulthén.

On the basis of his theory, Kronig explains the failure of Hardy, Barker and Dennison[225] to observe similar discrepancies in ρ for HCl and DCl as being due chiefly to these molecules going to the $^1S(L=0)$ state of the argon atom if the two nuclei are imagined to coincide. It is suggested, also, that the distortion of the potential energy curves should be smaller for a small displacement Δr_e of the H nucleus for the argon-like configuration of HCl than for the silicon-like configuration AlH. This difficulty arises in the case of other hydride molecules to be considered shortly.

The Λ-type doubling of the $^1\Pi$ state of AlD is found to be smaller than for AlH. A plot of the doublet separation shows a linear variation with $K(K+1)$ and agrees with the formula

$$T_{dc}(K)=\gamma K(K+1),$$

where $\gamma(\text{AlH})=0.0072$ cm^{-1} and $\gamma(\text{AlD})=0.0020$ cm^{-1}. Use of these values of γ in the theoretical expression[240]

$$B_v^x=B_v-\frac{2B_v^2 l(l+1)}{\nu(\Pi\Sigma)},$$

where the correction to B_v is equal to γ, leads to

$B_e(\mathrm{AlH}) = 6.4040$ and $B_e(\mathrm{AlD}) = 3.3208$ for the excited $^1\Pi$ states and thus to $\rho^2 = 0.51855$ in good agreement with the calculated ρ^2 of 0.51848. However, the theory for γ is approximate and too great weight cannot be given to this result.

f. The CaH and CaD molecules. The B band systems of the CaH and CaD molecules have been photographed by Watson,[241] who has also analyzed the spectra and determined the rotational constants of the normal $^2\Sigma$ and excited $^2\Pi$ states. According to mass-spectrographic determinations of the atomic weights of Ca, H and D, ρ^2 should be 0.51276 if the usual isotope theory holds. Watson, however, finds the ratio of the B_e constants of the normal $^2\Sigma$ states which exhibit negligible interaction with other states, to be 0.51337, the difference in the theoretical and observed values being practically the same as that found by Holst and Hulthén in the case of the $^1\Sigma$ states of AlH and AlD. The discrepancy also is of the order of magnitude expected on the basis of Kronig's theory, discussed above, since the normal $^2\Sigma$ state passes into a ^2P state of scandium when the nuclei are united.

In the case of excited $^2\Sigma$ states, it is necessary to correct the experimentally determined B values because of the interaction of the excited $^2\Sigma$ state with the $^2\Pi$ state that lies near it. This correction is proportional to B^2 and for B_0 amounts to -0.067 in the case of CaH and to -0.017 in the case of CaD. Inclusion of the corrections increases the ratio of the B_e's from 0.50788 to 0.51365, which is in approximate agreement with the ratio obtained for the normal $^2\Sigma$ state.

g. The LiH, LiD, NaH and NaD molecules. Photographs by Crawford and Jorgensen[242] of the absorption spectrum of LiD, at temperatures up to 960°C, show it to be very rich in lines and considerably more so than is the spectrum of LiH. This is due, undoubtedly, to the fact that at equal temperatures LiD molecules are distributed through a greater number of energy states than are LiH molecules. Crawford and Jorgensen find that the recently observed spectrum of LiD extends from about 3175A to the absorption limit of the Li_2 molecule in the red.

The authors find discrepancies between the calculated and observed values of ρ^2 similar to those observed by Holst and Hulthén for AlH and AlD and by Watson for CaH and CaD.

Olsson[243] finds that the ρ^2 for the NaH and NaD molecules is 0.5222 ± 0.0003 for the normal states of these molecules, while the calculated value from the simple theory gives 0.52147, again in disagreement in the same direction and by approximately the same amount as in the case of the AlH and CaH and the deuterium compounds.

The effect considered by Kronig should be present in the case of AlH and AlD, and CaH and CaD but not in the case of LiH and LiD, NaH and NaD and HCl and DCl. The theoretical explanation of these facts is unsatisfactory at present.

3. Polyatomic molecular spectra

a. The H_2O, HOD and D_2O molecules. Much study has been given to the water molecule spectrum, but as yet only a partial analysis has been secured. The additional information obtainable by a further study of its isotopic forms should obviate the necessity of making certain more or less arbitrary assumptions regarding the force constants, and should thus aid in the satisfactory interpretation of the spectra of this important example of the non-linear triatomic molecule. Indeed, certain inferences may already be drawn from some recent Raman and infrared data on the isotopic forms of water vapor. In Table XIX, we give the Raman data of Rank, Larsen and Bordner[244] and Johnston and Walker[245] and also the infrared data of Bartholomé and Clusius[246] and Sleator and Barker,[247] as well as the fundamental frequencies calculated by Bonner.[248] In addition to the data

TABLE XIX. *Fundamental frequencies (cm^{-1}) of water vapor.*

Molecule	Raman data			Infrared data		
	$\tilde{\omega}_1$	$\tilde{\omega}_2$	$\tilde{\omega}_3$	$\tilde{\omega}_1$	$\tilde{\omega}_2$	$\tilde{\omega}_3$
H_2O (calc.)	3756.5*	3604.6	1595.5*	3756.5*	3604.6	1595.5*
H_2O (obs.)	3804^c	3646.1^a 3653.9^a	1648^b(?)	3742^d 3756.5^f		1596^d 1595.5^f
HDO (obs.)		2718^a		3720^e		1380^e
D_2O (obs.)		2666^a		2775^e 2784^d		1185^e 1179^d
D_2O (calc.)	2790	2655	1180	2790	2655	1180

* These frequencies were used by Bonner to establish his constants. The designation of the frequencies is that used by Bonner. The references are as follows: calculated values from (248); a, 244; b, 245; c, 249; d, 247; e, 246; f, 250.

listed in the table, Bartholomé and Clusius have observed a line at 2810 cm^{-1} in the absorption spectrum of heavy water vapor. Rosenthal[251] has discussed the relationship between the frequencies of water and water-d_2 which must obtain regardless of the character of the force fields.*

Sleator and Barker find the wave number differences between the first line in the positive branch corresponding to $\tilde{\omega}_3$, which represents one of the vibrations parallel to the symmetry axis of the molecule, and the first line of the negative branch are 22.7 for the heavy molecule as compared to 30.3 for the lighter one. They were able to detect changes in the relative intensities of the lines, indicating a change in the statistics of the molecule when hydrogen is replaced by deuterium. The $\tilde{\omega}_1$ bands appear to be similar for light and heavy water, though the distance between the maxima of the positive and negative branches is approximately 115 cm^{-1} for the heavy molecule as compared to 200 cm^{-1} for the ordinary one.

It is interesting to note that the data for HOD in Table XIX are in quite good agreement with the values $\tilde{\omega}_2 = 2720$, $\tilde{\omega}_3 = 1400$ and $\tilde{\omega}_1 = 3750$, calculated by Van Vleck and Cross[252] previous to the experimental observance of these frequencies.

In general, condensation of a vapor to its liquid causes a decrease in the vibrational frequencies of the molecule. In the case of ordinary water, the perturbations introduced by condensation are so great that the frequency is decreased by approximately 220 cm^{-1}. In the case of HOD and D_2O, the data now available indicate similar decreases of the vibration frequencies by approximately 100 cm^{-1} and 210 cm^{-1}, respectively. Though it is at present impossible to theoretically calculate the perturbations in a liquid such as water, it is evident that the difference in the vibrational frequencies in the gaseous and liquid states must cause differences in the zero point energies of the molecules in the two states and must contribute to the heats of vaporization of the liquids.

The Raman spectrum of water, water-*d* and water-d_2 have been investigated by Wood[253] and these infrared spectra by Ellis and Sorge[254] and Casselman.[255] The spectra of the liquids are very much more complex than those of the gases and no entirely satisfactory arrangement of the observed data has been secured.

b. The NH_3 and ND_3 molecules. For the symmetrical molecule YX_3, there are six modes of vibrational motion possible; since, however, two of them are doubly degenerate, only four fundamental frequencies may be expected to be observed experimentally. Of these, two represent vibrations of the electric moment parallel to the symmetry axis of the molecule and the two doubly degenerate ones represent vibrations of the electric moment perpendicular to the axis. All four of the frequencies are active and have recently been observed by Silverman and Sanderson[256] in the infrared spectrum of ND_3. Table XX gives their results, compared with previously obtained results on NH_3[207]. The four bands observed for ND_3 have similar structure to those of NH_3 and, in each case, the theoretically expected type of vibration is found.

TABLE XX. *The fundamental vibrational frequencies of NH_3 and ND_3.**

NH_3	3336	1631	950	4417(?)
ND_3	2421	1158	770	3287(?)

* The values given in the first and third columns are generally recognized as the parallel frequencies of ammonia. The ratio of the products of these frequencies for the NH_3 and ND_3, respectively, differ from the value required by Rosenthal's[251] general theory by about 8 percent.

Pure rotational lines of ND_3 and NH_3 have been observed by Barnes, Benedict and Lewis[258] in the far infrared. In the case of the ten lines of NH_3, observed from 168μ to 42.46μ and corresponding to rotational numbers 3 to 12, respectively, the frequencies agree quite well with the formula $\tilde{\nu} = 19.8801\ J - 0.00178 J^3$ calculated by Wright and Randall,[259] the average deviation being 0.12 cm^{-1}. The resolution was just sufficient to give clear indications of the doubling of the energy levels previously found by these latter authors. The six lines of ND_3 observed between 49μ and 68μ correspond to numbers 15 to 20. It is found that the usual formula, $\tilde{\nu} = 2BJ - 4DJ^3$, will fit the data only if 4D is nearly zero or negative. It is suggested that this may be due to the

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* It appears that Bonner's theoretical values for the frequencies of D_2O with zero amplitude do not agree exactly with the requirements of Rosenthal's theory, which should hold regardless of the force constants and angles assumed. However, the frequencies observed in the Raman and infrared spectra of H_2O and D_2O are consistent with the latter author's theory.

influence of rotations around one axis on the moment of inertia about another. Such interaction, which has been found in the Raman lines of NH_3,[260] should introduce a term $D_{JK}J(J+1)K^2$ into the usual energy equation and would cause a splitting of each line into J unresolvable components, corresponding to $0<K<J-1$. On taking into account the fact that the departure from the usual formula should be greater for the heavier ammonia molecule, the value of $2B=10.22\pm0.05$ cm^{-1} was found for ND_3, and this, in connection with $2B=19.88$ for NH_3, leads to 0.34±0.03A as the height of the ammonia pyramid as compared to 0.38A calculated directly from assumed potential functions.[261]

In addition to the above, photographs of the far ultraviolet absorption spectrum of heavy ammonia[140] show a shift of the lines of the heavier molecules towards shorter wavelengths. Also a richer spectrum is obtained than for ordinary ammonia.

c. The C_2H_2, C_2HD and C_2D_2 molecules. According to Dennison's selection rules, the symmetrical acetylene molecules C_2H_2 and C_2D_2 should have only two of their five fundamental vibrational frequencies that are capable of direct observation in the infrared spectrum. In the case of C_2H_2, these directly observed fundamentals are, in Sutherland's notation,[262] $\tilde{\omega}_3=3288$ cm^{-1}, and $\tilde{\omega}_4=730$ cm^{-1}. Randall and Barker[263] have recently observed the $\tilde{\omega}_4$ bands of C_2D_2 and C_2HD and also the $\tilde{\omega}_5$ band of C_2HD that is forbidden in the selection rules for symmetrical molecules, the positions being 520 cm^{-1} (19.2μ), 679 cm^{-1} (14.7μ) and 541 cm^{-1} (18.5μ), respectively.

In addition to these fundamentals that are directly observable, acetylene shows infrared absorption bands that may be interpreted as combination frequencies of the five fundamentals. In the case of ordinary acetylene, the additional fundamental frequencies that may be observed as combinations are:

$$\tilde{\omega}_1=1974\ \text{cm}^{-1};\quad \tilde{\omega}_2=3372\ \text{cm}^{-1};\quad \tilde{\omega}_5=605\ \text{cm}^{-1}.$$

Several of the combination bands of C_2HD and C_2D_2 in the near infrared have been photographed by McKellar and Bradley[264] and by Herzberg, Patat and Spinks.[265] The former authors find only one band for C_2HD between 6000 and 10,500A. This band, which was also studied by the latter authors, has its origin at λ10,302 or 9706 cm^{-1}. It has a single P and R branch. Bands of C_2HD at 9139 cm^{-1}, 8550 cm^{-1} and 8410 cm^{-1} and of C_2D_2 at 9641 cm^{-1} and 9835 cm^{-1} have also been observed by Herzberg, Patat and Spinks.

Glockler and Davis [270] found that the Raman line corresponding to the $C\equiv C$ vibration of acetylene is $\tilde{\omega}_1=1973.1$ cm^{-1} for C_2H_2 and $\tilde{\omega}_1=1761$ cm^{-1} for C_2D_2. The recent interpretation of the C_2HD infrared bands by Sutherland[266] gives very satisfactory agreement with his calculated values, $\tilde{\omega}_1=1858$ cm^{-1}, $\tilde{\omega}_2=3343$ cm^{-1}, and $\tilde{\omega}_3=2543$ and also the above Raman data are consistent with his calculations for the C_2H_2 and C_2D_2 molecules.

The rotational structure of the λ10,302 band was carefully measured by McKellar and Bradley and that of the λ10,302 and λ10,942 bands was studied by Herzberg, Patat and Spinks. They were thus enabled to calculate the B's and therefore the moments of inertia of the C_2HD molecule in the upper and lower states involved in the λ10,302 band. The results for the moment of inertia of the lower state are tabulated in Table XXI, together with internuclear distances in the acetylene molecules as calculated on the very probable assumptions that r_{CH} and r_{CD} are equal and r_{CC} is a constant in the isotopic molecules.

TABLE XXI. *Constants of the acetylene molecules.*

	C_2H_2	C_2HD	Reference
I_0 (g.cm$^2\times10^{40}$)	23.50	27.90	265
	23.509±0.040	27.412±0.043	264
r_{CC} (A)	1.205		265
	1.247±0.008		264
	1.22 ±0.08		267
$r_{CH}=r_{CD}$ (A)	1.062		265
	0.940±0.036		264

The values of r_{CC} thus calculated from the two sets of data are in good agreement with one determined by Wierl[267] from electron diffraction experiments in gaseous acetylene, though they do not agree so well between themselves. They are all slightly higher than 1.19×10^{-8} cm which Hedfeld and Mecke[268] computed by assuming $r_{CH}=1.08\times10^{-8}$ cm as calculated from the Raman data on CH_4 obtained by Dickinson, Dillon and Rasetti.[269]

Price[271] has recently observed acetylene to have a rich absorption spectrum extending from λ1520 to λ1050 in the far ultraviolet. The absorption is very strong, a pressure of only 0.001 mm of acetylene being required in the spectrograph, which has an optical path of about 1.5 meters, to make most of the bands appear. These bands are of two kinds, the first possessing P, Q and R branches and appearing as narrow doublets at low pressures. They have a sharp head and degrade towards the red. The bands of the second kind have a single head and contain only more diffuse P and R branches. Comparison of similar absorption bands of the C_2HD molecule with the above show a small shift of one band of each electronic transition attributable solely to zero point energy differences; these serve to identify the transitions in which the vibrational quantum number does not change. The bands thus found were arranged in two Rydberg series containing more than ten terms and agreeing approximately with the following equations:

$$\bar{\nu}=92{,}000-R/(n-0.95)^2,$$
$$\bar{\nu}=92{,}000-R/(n-1.5)^2,$$

where $n=3, 4, \ldots.$

The double bands agree with the first equation and the single bands with the second equation. The evidence indicates that the series are due to excitation of one of the valence electrons between the carbon atoms, the two series being the result of different coupling of the orbital momentum of the excited electrons with the internuclear axis. The analysis of the vibrational transitions, there being as many as ten for some electronic transitions, is greatly aided by consideration of the isotopic shifts for the two molecules.

Price has observed that predissociation appears in a band system of C_2H_2 at 1340A. If it is assumed that the predissociation is due to interaction with the normal state, then the heat of dissociation of C_2H_2 is less than 8.1 electron volts, and if the dissociation is to 2CH the energy of the triple carbon bond is less than 187 kcal./mole.

A similar predissociation is observed in the case of ethylene and the results show that the energy of the dissociation of C_2H_4 into $2CH_2$ is less than 162 kcal./mole. These bond strengths are in agreement with chemical data.

d. The Raman spectra of tetramethyl methane-d, methane-d and benzene-d_6. Rank, Bordner and Larsen[272] have examined the Raman spectrum of neopentyl deuteride, that is, tetramethyl methane in which one deuterium atom replaces one of the hydrogens in a methyl group, and have found the degeneracy of the molecule decreased.

The isotopic methane molecules are particularly interesting cases for investigation. Because of its high degree of symmetry, methane has only four frequencies for its nine vibrational degrees of freedom and only two of these are active and thus appear as fundamental absorption bands, each of these two being triply degenerate. Substitution of a deuterium atom for one of the hydrogens to give methane-*d* decreases the degeneracy, thus increasing the number of active vibrations from two to six. This makes it possible to learn more of the force constants and dimensions of the molecule than was possible from a study of the symmetrical methane. Barker and Ginsburg[272] have observed all six of the active fundamental bands of methane-*d*. Dennison and Johnston[272] have recently published a note on the theoretical vibrational frequencies of the five methanes and secure values for the frequencies which agree with those of Barker and Ginsburg except that one band reported by them is probably due to CH_2D_2.

Murray, Squire and Andrews[273] have observed a Raman frequency of hexadeuterio benzene at 943 cm^{-1}, which they believe is due to the symmetrical vibration in which all carbons and deuterium atoms move toward the center of the ring, and is of the same character as the 992.5 cm^{-1} of benzene. Two doubtful frequencies at 1600 and 2290 cm^{-1} are also reported.

VIII. CONCLUSION

In this review, particular emphasis has been placed on the molecular spectra work since it appears that the study of molecular spectra has been the most fruitful source of knowledge of the detailed characteristics of molecules necessary in interpreting their macroscopic physical and chemical properties. This seems especially evident from the fact that in almost every attempt to give an explanation of the experimental observations, the information furnished by molecular spectra has been used. It seems quite certain that the further study of this subject will contribute much to the theoretical interpretation of the results discussed above and also greatly increase the general utility of spectral data.

At the risk of suggesting the obvious, we wish to point out that one problem which challenges chemists and physicists is the separation of the isotopes of other light elements. Already orientation studies have been made on the methods which may be used. The most promising of these methods is undoubtedly the distillation of isotopic compounds. Lewis and Cornish have shown that there is a difference in the vapor pressures of the O^{16} and O^{18} waters. At ordinary temperatures the difference amounts to about 1.4 percent, and though this is small, the use of modern fractionating columns should make possible an effective separation of the oxygen isotopes by this method. Further, this difference in the vapor pressures of the O^{16} and O^{18} waters leads us to expect a similar difference in the vapor pressure of the N^{14} and N^{15} ammonias, and hence that these may be also separated by distillation. Klar and Krauss[274] and Smith [275] have shown that a slight concentration of O^{18} occurs in the technical fractionation of liquid oxygen. There may be other cases in which distillation may be used effectively.

Recent studies by Urey and Greiff[276] show that the equilibrium constants for exchange reactions involving oxygen, carbon, nitrogen and lithium may lead to small but appreciable separations of the isotopes of these elements. Countercurrent scrubbing methods may be applied in certain cases and the method is at least promising for separating certain of these isotopes, particularly those for which distillation for some reason or another is not successful.

In the third place, Taylor and Gould[277] have reported a fractional separation of the oxygen isotopes by the decomposition of hydrogen peroxide. Such differences in velocity can hardly be as useful as the first two methods proposed, but are certainly worthy of consideration.

Up to the present time, Hertz, using his diffusion method has made a separation of the oxygen isotopes, and Polanyi and Szabo[278] have shown one example of how samples of O^{18} thus obtained can be useful in chemical study. Also Oliphant, Shire and Crowther[279] have obtained practically pure samples of Li^6 and Li^7 by use of the mass spectrograph. These two methods, though satisfactory for producing small amounts to be used in transmutation reactions, can scarcely be expected to give the larger quantities required for effective chemical and physical experimentation.

With the separation of the isotopes of the light elements, we may expect further developments in chemistry and physics of the same order of magnitude as those that have been opened by the successful separation of the hydrogen isotopes. It appears, therefore, that the work reported in this review may be considered as only the beginning of a very great development of chemistry and physics in non-nuclear fields.

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