a wagon and a steam-engine. These combinations are, however, paralleled to a certain extent in nature by the symbiosis of certain fungi and algae into lichens, or by the complex interactions of hosts and parasites.

Finally, it is not generally recognized that the human mind is, on the whole, such a successful device of Nature because it embodies to a high degree the anticipatory qualities which are essential to all life.

However, the resemblances between natural and human inventions are probably deceptive if they lead us to impute anthropomorphic qualities to Nature.

THE SEPARATION AND PROPERTIES OF THE ISOTOPES OF HYDROGEN[1]

By Professor **HAROLD C. UREY**

DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY

As all chemists know, the atoms of the elements are not all precisely identical. Most of the elements consist of mixtures of two or more varieties of atoms having similar chemical properties but different atomic weights. In most cases, the chemical and physical properties of these isotopes, as they are called, are so nearly identical that it is very difficult indeed to detect any differences except those which depend upon mass directly. In the case of the hydrogen isotopes, however, the mass ratio is one to two, and this large difference gives rise to very appreciable differences in the physical and chemical properties. Because of these outstanding differences it has seemed desirable to name each of the isotopes, and we have proposed the name protium for the isotope of hydrogen having an atomic weight of one, and deuterium for that of atomic weight two. The exact atomic weights are 1.00778 and 2.01356, based upon a standard of O^{16} having an exact atomic weight of sixteen.

Since the heavier isotope of hydrogen was discovered about two years ago, some seventy-five papers and notes have been published dealing with its properties. It would be difficult to give an adequate review of the subject in the time available for this talk, and therefore I shall confine myself to a few topics which have interested us at Columbia, giving them in detail and referring only briefly to other interesting and valuable work. I shall discuss methods of separation and the properties of the hydrogens. The method of discovery is history now and need not be reviewed.

THE SEPARATION OF THE ISOTOPES OF HYDROGEN

Because of the large mass ratio of the two isotopes of hydrogen, all methods for separating isotopes should be more effective when applied to these isotopes than when applied to any others. In the past, isotopes have been separated slightly by fractional evaporation and fractional diffusion through porous solids. Mass spectrographs have separated very minute amounts of the isotopes of many elements, but the complete separation of two isotopes in any quantity has only recently been accomplished in the cases of neon and hydrogen. In the case of neon, the separation was secured by Hertz, using a diffusion method. The separation and properties of the hydrogen isotopes is the subject of the present discussion.

The first appreciable increase in concentration of the hydrogen isotopes was secured by the distillation of liquid hydrogen near its triple point. Calculations by Dr. Murphy and myself, based on the third law of thermodynamics and the Debye theory of the solid state, showed that such a distillation should be effective. The ratio of vapor pressures of H^1_2 and H^1H^2 over their pure solids at 13.95° A should be 2.37. How closely this was the case is not known, for the hydrogen used was electrolytic hydrogen and the isotopic composition unknown, but the effect was appreciable but probably smaller than expected from theory. In this way, samples containing the heavy isotope to the extent of about 1 part in 1,000 were prepared by Dr. F. G. Brickwedde, of the U. S. Bureau of Standards. At that time distillation of hydrogen seemed to be a logical method for concentrating the isotope, but due to the low surface tension of liquid hydrogen, it is difficult to prevent its escape as mist in a fractionating column. Such methods have not been successful.

Last year Dr. D. MacGillavry and I attempted the separation of the hydrogen isotopes by diffusing hydrogen gas across a flowing stream of mercury vapor. This gave a fractionation factor of 2.5. This is rather high, but the speed of the process is too low to make this method effective as compared with other methods.

The progress which has been possible during this year on the hydrogen isotopes is due to the discovery by Washburn and myself of the electrolytic method of separation. Dr. Washburn suggested the possibility

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[1] Address before the New York Section of the American Chemical Society, December 8, 1933.

of separation by this method and we showed that the solutions in electrolytic cells contained higher concentrations of deuterium than natural water. Our first test was made spectroscopically, but subsequent density determinations showed that the density was greater than that of ordinary water by 60 parts per million, indicating a concentration of .0005 above the concentrations in ordinary water. Since this latter concentration is now known to be .0002, the concentrations in these electrolytic solutions is .0007 and the concentration has been increased by a factor of 3.5. In some cases the increase is even greater.

It is obvious, of course, that, by electrolyzing a large volume of water down to a small residual volume, the concentration of the deuterium can be increased without limit. The formula governing this electrolysis, if we assume that the fractionation factor does not change with the concentration of deuterium oxide, will be exactly that of the Rayleigh distillation formula:

$$\left(\frac{1-N_O}{1-N}\right)^{\frac{1}{\alpha-1}}\left(\frac{N_O}{N}\right)^{\frac{\alpha}{\alpha-1}} = \frac{W_O}{W}$$

where N_0 and N are the mole fractions of deuterium oxide in the initial water and the final residue, respectively, and W_0 and W are the initial and final volumes.

The following table shows the concentrations of deuterium oxide which can be secured by electrolyzing the water containing .0007 per cent. deuterium oxide down to different volumes, assuming that α, the fractionation ratio, is 6, as we have found for our laboratory cells. It will be seen that the method is quite effective for the separation of the isotopes.

N Mol. fract. of H^2_2O	W_0/W
.01	24.4
.10	393.5
.50	3054.0
.90	8531.0
.999	24280.0

This method was used by Dr. Washburn to secure samples of water containing a few per cent. of deuterium. It was on these samples that he discovered the difference in melting point and boiling point of the waters. This is also the method which Professor G. N. Lewis, of the University of California, has used for preparing the deuterium oxide in a practically pure state. This method has also been used by a number of other workers in the United States, and it is this method which is now being used by approximately ten or fifteen universities in the United States as well as a number in Europe.

The process which we are using at Columbia for carrying through this concentration is as follows. The first stages involve large-scale operations. We were fortunate to secure the cooperation of the Ohio Chemical Company who concentrated on a large scale the residual liquors which they have in their electrolytic cells. This work was carried on during the summer months and resulted in the preparation of water containing about ½ of 1 per cent. deuterium oxide. This help by the Ohio Chemical Company and particularly Mr. Rohrer, who carried it through, decreased the work which we must do in the further concentration, by about 75 per cent. and made available for other laboratories in the United States some 150 gallons of this water. Following this, Columbia University bought 50 gallons of the water, and Professors Zanetti, La Mer and myself and our coworkers have continued the concentration of the water in laboratory size cells.

The cells consist of a glass vessel with nickel tubing electrodes, so that the cell can be cooled by running water. In this way, it is possible to keep our cells operating at about 20° C., even with fairly high current densities flowing through the cell. The cells contain about 300 cc of potassium hydroxide solution and are operated at about 25 amp. current. Some 30 of these cells are placed in series across the 110 v. line. After the electrolysis has been carried down until the volume is about one third of the initial volume, the residual electrolyte is removed, ⅔ of the water is distilled from the potassium hydroxide and combined with the undistilled hydroxide. This material is then changed into other cells, which again carry the volume down to one third. Beginning with the second stage, the hydrogen and oxygen gases recombine, giving a condensate containing approximately .3 to .4 per cent. of deuterium oxide, and from this stage on, recombination of this kind is necessary. The gases of hydrogen and oxygen are burned through a nozzle, with the velocity of the flow of gas greater than the velocity of the flame, so that the flame does not strike back and cause the cells to explode. Explosion traps are placed between the cells and the nozzles so that, if an accidental explosion does occur, it does not break the cells.

In these laboratory cells, we have found that the fractionation factor is approximately 5 to 7, using these nickel electrodes. It does not vary greatly with current density, but decreases as the temperature increases, as though the difference in activation energy for the formation of H^1H^1 and H^1H^2 were 1,100–1,500 calories per gram molecule. The first stage produces 1 per cent., the second 2.2 per cent., the third 6.5 per cent., the fourth 16 to 20 per cent. and the fifth 40 per cent. deuterium oxide. At the present time we are allowing this material to accumulate until we secure larger amounts before continuing the electrolysis. Since we are planning to produce about 400 cc of the heavy water, we do not wish to work with very small quantities of the water because of the ease of losing the material.

The cost of producing this heavy water in these high concentrations comes to about $15 or $20 per gram. This is in marked contrast to the quotations which we have seen in the public press of $150 a gram. Such prices are purely fictitious, for, at least using the methods which we have developed, the material can be prepared for much less than that. At present, we have approximately 280 cc of H^2_2O in various concentrations, ranging from 1 per cent. to 99 per cent., with very appreciable amounts of the 16 per cent. and 40 per cent. material.

I might have exhibited here a number of samples in different stages of concentration, having filled all the bottles with ordinary water, for it would be quite impossible for you to tell the difference, but I do have a sample in this tube, and I can demonstrate that its freezing point is distinctively different from that of ordinary water. In the first place, we immerse the tube containing this deuterium oxide in an ice and water bath. This bath of course maintains a temperature lower than the melting point of pure deuterium oxide and hence it should freeze in this way. Due to the fact that the liquid supercools rather easily, it will not freeze readily under these conditions. I start the process by touching it for an instant to a piece of dry ice. This starts the crystals growing, and if you were nearer, you could see the long needles immediately shoot through the liquid. We will now immerse it in the ice and water bath for a period of ten minutes, and I think we will find that the material is frozen solid. Thus this sample contains a higher concentration of deuterium oxide than that which occurs in ordinary water, and we see here one of the physical differences between the light and heavy water.

The method of analysis of this water, which has been used largely up to the present time, is the determination of the density of the water, for it is to be expected that the volumes of the two varieties of water may be very nearly the same and thus that the ratio of the density of pure deuterium oxide and protium oxide should be the ratio of their molecular weights. In this way, it is possible to estimate the concentrations to a rather high degree of accuracy.

The method, however, is long and laborious, requiring very careful temperature controls in the thermostats and very careful weighing. Since the refractive indices of the waters are different, it is possible to use this as a method for analyzing the samples of water. Thus we find that a Zeiss interferometer may be used for analyzing our samples as soon as a relationship is established between the index of refraction and the density of the water. This method has been used by us for several months as a rapid method for following the increased concentrations of our deuterium, for it is possible to make an analysis within a few hundredths of a per cent. on samples running up to about 20 per cent. concentration in the course of about one hour. In this way, we are able to analyze the materials which are placed in our cells or which are removed, and so follow the course of the materials through the cells.

Properties of the Compounds Containing Protium and Deuterium

For our present purposes of discussion, we may classify the differences in properties of the compounds of the hydrogen isotopes under thermodynamic, physical, kinetic and physiological properties. Shortly after the discovery of the isotopes of hydrogen by Dr. Brickwedde, Dr. Murphy and myself, we made calculations to see what possible differences there might be in the thermodynamic properties of the two hydrogens and their compounds. Such calculations can be made, using the methods which have been established during the past ten years for securing the free energy, heat contents and entropies of diatomic gaseous substances, and the exact understanding of the structure of diatomic molecules, as revealed by molecular spectra.

Such calculations made for the reactions of hydrogen and chlorine and hydrogen and iodine show that small but appreciable differences in the free energy changes of the reactions could be expected, depending upon which of the two isotopes was used. Thus the difference in standard free energy change for the reactions:

$$H^1_2 + Cl_2 = 2\,H^1Cl \quad \text{and} \quad H^2_2 + Cl_2 = 2\,H^2Cl$$

should be about 408 cal. per gram molecule, which corresponds to a ratio of equilibrium constants for the two reactions of about 2 to 1 and a difference in the standard electrode potentials of about 9 millivolts. This, of course, would not be the electrode potential for the formation of aqueous hydrogen chloride from hydrogen gas and chlorine gas, because we do not know what differences in the solubilities of the hydrogen chlorides may exist, but it does give us an idea of the order of magnitude of the differences to be expected for such potentials. Similar calculations for the hydrogen iodide reactions showed that the ratio of equilibrium constants should be 1.222 at 700° K.

This difference is sufficiently great to make possible a test of the theory. Such experiments have been carried on in our laboratories by Mr. D. Rittenberg. In addition to ordinary hydrogen, Mr. Rittenberg has used samples containing higher concentrations of deuterium, thus being able to check the theory. Within the limits of experimental error, theory and experiment agree exactly. This, of course, is not as interesting as it would be if the experiments disagreed with the theory, but it is a great satisfaction to find that such a calculation is made possible by the progress that has been made in the fundamental understanding of the structure of atoms and molecules during the past quarter of a century. The calculation of this equilibrium constant was made and published months before the deuterium was prepared in a pure state. We may never be able to exactly calculate the equilibrium constant for the hydrogen iodide reaction without making any ordinary measurements on this equilibrium, but such checks as this at least give us the feeling that we understand pretty well the fundamental principles underlying such phenomena.

We have also secured very interesting results on this in connection with our studies of the equilibrium between the three varieties of hydrogen molecules, H^1_2, H^2_2 and H^1H^2. If we think of a bag containing protium and deuterium atoms and draw atoms from this bag to make up pairs of atoms to be represented as hydrogen molecules, we can easily show that the equilibrium constant for the reaction $H^1_2 + H^2_2 \rightarrow 2\ H^1H^2$ should always be 4. Thus the chance of drawing two H^1 atoms in succession is N^2, where N is the fraction of the total number of atoms which are protium atoms; and the chance of drawing two H^2 atoms in succession is $(1-N)^2$; while the chance of drawing first an H^1 and then an H^2 atom is $N(1-N)$ and the chance of drawing first an H^2 and then an H^1 atom is $(1-N)N$. Thus the relative abundance of the three types of molecules, $H^1_2 : H^1H^2 : H^2_2$, is $N^2 : 2N(1-N) : (1-N)^2$, and you will easily see that the equilibrium constant becomes equal to 4. An exact application of statistical mechanics to quantized systems such as these molecules shows that the equilibrium constant should not be exactly 4, but in fact at ordinary temperatures should be considerably less than that. The following table shows the calculated values for this equilibrium constant and also the experimental checks on this theory which we have secured in collaboration with Dr. Walker Bleakney, of Princeton. He is able to determine the relative abundance of the three types of molecules in a sample of hydrogen gas. He has been so kind as to analyze in this way samples of hydrogen which are the residual gases from the decomposition of our hydrogen iodide samples used to determine the equilibrium constants of the hydrogen iodide reactions. The third column gives the results of his determinations on these samples which we supplied to him.

EQUILIBRIUM CONSTANTS FOR THE REACTION
$H^1_2 + H^2_2 \rightleftarrows 2\ H^1H^2$

T	K (calc.)	K (obs.)
298.1	3.269	3.28
400.0	3.494	
575.0	3.710	
671.0	3.77	3.73
700.0	3.800	
741.0	3.82	3.75

It will be noticed that his equilibrium constants agree with the calculated values within the experimental limits of error in every case. Thus this check with the theory shows that we have secured equilibrium for our hydrogen iodide reaction at high temperature, for undoubtedly this equilibrium is established by the reaction of the hydrogen with the iodine to form hydrogen iodide molecules, and then these hydrogen iodide molecules react to give us hydrogen and iodine again. The whole system comes to equilibrium both with respect to the hydrogen iodide-iodine reaction and also with respect to the three varieties of hydrogen molecules. The second interesting point about this arises from the fact that Oliphant in England claims that heavy hydrogen gas confined over water disappears in the course of six weeks, showing that part of the heavy hydrogen has reacted with the light water, resulting in a mixing up of the hydrogen atoms in the gas and the hydrogen atoms in the water. This particular reaction was tried by Dr. Crist and Mr. Dalin at Columbia University about a year ago with negative results, though it may be of course that Oliphant had a catalyst present so that the reaction took place more rapidly. However, in the equilibrium between the three varieties of hydrogen molecules, such an exchange does not take place in the course of a few weeks because the samples of hydrogen which we prepared at 671° and 741° A were enclosed in glass flasks for several weeks at ordinary temperatures before Dr. Bleakney analyzed them. His tests showed that the equilibrium constant was still that characteristic of the high temperature and thus no very rapid exchange of atoms between the three types of hydrogen molecules had taken place in this length of time. At least we can say that not all exchange reactions involving the hydrogen atoms are so very rapid.

I think it is safe to predict that these calculations and experimental verifications indicate the order of magnitude to be expected in the differences of thermodynamic properties of the hydrogens and their compounds. Thus very appreciable differences in equilibrium constants, small differences in standard electrode potentials and in the standard free energy changes are to be expected through the whole field of chemical reactions involving hydrogen.

The differences in physical properties of the waters were not predicted by theory. Washburn first showed that the melting points and boiling points of a sample of water containing somewhat more than 1 per cent. of deuterium oxide had a distinctly higher melting point and boiling point than natural water. The differences were sufficiently large to be unmistakable. He further showed that the refractive index of this enriched water was distinctly less than that of natural water. Moreover, he followed this up by a distillation showing that the isotopes of hydrogen could be separated by fractional distillation. Following this, Lewis prepared what he considered to be practically pure deuterium oxide and determined its melting point as 3.8° C. and its boiling point as 101.4° C. He reports that the differences in the heats of vaporization of the two pure waters was about 269 cal. per gram molecule, the protium oxide having the lower value. In later work he has also shown that the separation of the isotopes by distillation effects a partial separation of the oxygen isotopes as well as the hydrogen isotopes. One can only admire the energy with which Lewis has attacked this problem and the skill he has shown in working with these minute samples. His values are undoubtedly of the right order of magnitude, but Professor La Mer and Dr. Eichelberger, from preliminary work in our laboratories, believe that the melting point given by Lewis is probably too low by about 0.5° and I think it probable that other constants reported must be revised.

It is interesting to consider one obvious but easily overlooked difficulty in working with this water. It must be very hygroscopic. Hygroscopic water! This is really something new! But you will see that nearly every molecule of atmospheric water that hits the surface of deuterium oxide will stick and, since this water is nearly pure protium oxide, will dilute it. The problem of overcoming this difficulty has prevented us from determining the density of our most concentrated samples, and our work on the purer material will be delayed until we have much larger samples, to avoid errors due to this effect. We are even considering a desiccated laboratory and the use of gas masks to prevent contamination of our water.

The following table records some of the differences in physical properties of H^2_2O observed so far:

PROPERTIES OF THE PROTIUM AND DEUTERIUM OXIDES

	H^1_2O	Mixture	(Per cent.)	H^2_2O
(1) Density D^4_{20}	0.9982			1.1056
(2) Refractive index n^D_{20}	1.33293	1.32849	(92)	(1.3281)
n^C_{20}	1.33044	1.32683	(92)	(1.3265)
(1) Molar refraction	3.711			(3.677)
(2) Viscosity	10.87	13.7	(92)	(14.2)
(2) Surface tension	72.75	88.1	(92)	(67.8)
(2) Mag. susceptibility	−0.72	−0.65	(92)	
(2) Molar susceptibility	−13.0	−13.0	(92)	
(3) Equivalent conductances				
(H^{1+} in H^1_2O)	315.2	(H^{2+} in H^2_2O)		213.7
K+	64.2			54.5
Cl−	65.2			55.3
(1) B.P.	100° C.			101.42° C.
(1) M.P.	0° C.			3.8° C.
(1) $\triangle H_v$	x			x + 259

(1) Lewis and MacDonald, *Jour. Am. Chem Soc.*, 55: 3057, 1933.

(2) Selwood and Frost, *Jour. Am. Chem. Soc.*, 55: 4335, 1933.

(3) Lewis and Doody, *Jour. Am. Chem. Soc.*, 55: 3504, 1933.

In addition to this, Taylor, Caley and Eyring have investigated the differences in solubilities of inorganic substances in 92 per cent. deuterium oxide, and they find that the solubility of these substances is markedly decreased by amounts of from 10 to 15 per cent. These investigations undoubtedly show something of the differences to be expected in physical properties of the hydrogens and their compounds. They are not large, but it is interesting indeed that we have here examples permitting us to see how they depend upon the mass of the hydrogen atoms present in the compounds. We may certainly expect that there will be a better understanding of both the solid and the liquid states resulting from a study of these properties, both experimentally and theoretically.

Up to the present time, sufficient work has not been done on the kinetic properties of the hydrogen isotopes to make possible anything but a brief discussion of theoretical arguments leading us to expect marked differences in the kinetics of the reaction. Undoubtedly the electrolytic separation of the hydrogen isotopes is itself an example of such a kinetic process. Unless the differences in electrode potentials are very much greater than those which are indicated by the calculations by Mr. Rittenberg and myself, we can not believe that the separation of the hydrogen isotopes is due to this cause.

Experiments which we have made on the temperature coefficient of the fractionation factor which are very preliminary indicate that the energy of activation for the process of the escape from the electrodes differs by approximately 1,100 to 1,500 cals., depending on whether it is an H^1_2 or H^1H^2 molecule which escapes. Eyring has suggested that the cause of this fractionation is due to this difference in the energy of activation, and the results which we have secured are of about the order of magnitude to be expected on the basis of his theory.

Newer theories in regard to the velocity of chemical reactions postulate with Arrhenius that there is a certain minimum energy of activation which is necessary for chemical reactions to go with finite velocity. Thus the average molecule at ordinary temperatures or the average pair of molecules at ordinary temperatures will not react, but must be raised to higher energy states before they will do so. In the case of the hydrogen isotopes, we could not at present say very much about the differences in energy between the activated molecules containing H^1 and those containing H^2. Thus the details of the excited states are beyond us at present, or at least this is certainly true so far as any detailed satisfactory discussion is concerned, but we do understand fairly well the unactivated energy states.

The principal difference between the compounds containing the heavy hydrogen and the light hydrogen will be in the zero point energies. This is a residual vibrational energy which the molecule does not lose, even at the absolute zero. It amounts to $\frac{1}{2}$ hν per molecule, where h is Planck's constant and ν is the frequency of vibration of the two atoms of a diatomic molecule relative to each other. The frequency ν depends upon the mass of the atoms of the molecule. Thus the ν's for the H^1_2 and H^2_2 molecules are in the inverse ratio of the square roots of the atomic weights. Hence, it must follow that the residual vibrational energy of the H^2 molecule is less than that of the H^1 molecule, and the calculated difference amounts to 1788.9 cals. per gram molecule. In order for the H^2_2 molecule to react, it must acquire this amount of energy more than the amount required for the H^1_2 to react, on the assumption that no other differences enter in, which is probably not exact. This difference alone will lead us to expect that the relative velocities will be in the ratio $\exp \frac{1788.9}{RT}$, which amounts at 700° K to 3.6. In addition to this effect, there are fewer collisions between the heavy molecules of a gas, other things being equal, which also favors the higher velocity of the reaction of the H^1_2 molecules.

The physiological differences between the compounds of the two hydrogens may be of very great importance in physiological studies. Professor Lewis has found that tobacco seeds did not sprout in this water, and Professor Taylor and his coworkers at Princeton have found that animals will not live when placed in the higher concentrations of the deuterium oxide.

The causes for these effects are not entirely clear, but from our own studies in regard to the differences in equilibrium constants, we believe it possible that the ionization constant for the deuterium oxide may be quite different from that of protium oxide. This would have a very marked effect upon living organisms.

In addition to this, the velocities of reactions within living organisms involve hydrogen atoms to a large extent, and since the velocities of chemical reactions may be markedly different, depending upon which isotope is used, it would not be at all surprising if the nice balance of chemical reactions taking place in living organisms would be disturbed to such an extent that life would be impossible. It will be interesting indeed to see whether animals can be acclimatized to the new water.

As to the question of possible industrial uses, no safe predictions can be made. Witness the uses for such substances as neon and argon! New methods of concentrating deuterium may be discovered, materially reducing its cost. The intense research activity here and abroad is likely to result in uses for it. Perhaps it will be as valuable as a by-product of the hydrogen and oxygen electrolytic plants as argon and neon are of the liquid air plants.

OBITUARY

FREDERICK LINCOLN CHASE

FREDERICK LINCOLN CHASE was born at Boulder, Colorado, on June 28, 1865, the son of George Franklin and Augusta Anne (Staples) Chase. He was graduated, A.B., at the University of Colorado in 1886 and was called to Yale Observatory as assistant astronomer in 1890. In 1910 after the retirement of Dr. Elkin from the directorship on account of ill health, Chase succeeded him with the title acting director; but his own health failed soon thereafter, and in 1913 he resigned his post and retired to his farm in Colorado, where he lived until his death on November 9 of this year.

Chase was an unusually able observer. In collabo-