minutes, it is cooled and hydrolyzed with dilute hydrochloric acid. The ether layer is washed again with dilute hydrochloric acid and evaporated. The crude toluidide is purified by crystallization from dilute alcohol.

Table I summarizes the results obtained in this laboratory. The method failed when applied to the following dibasic esters: benzyl succinate, ethyl malonate, methyl oxalate, and methyl phthalate.

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RECEIVED APRIL 3, 1933
PUBLISHED JULY 6, 1933

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# COMMUNICATIONS TO THE EDITOR

## PLATINUM OXIDE AND CARBON MONOXIDE

*Sir:*

In a previous publication [THIS JOURNAL, **54,** 4498 (1932)] it was shown that the reduction of palladium oxide by carbon monoxide requires a higher temperature than is necessary for reduction by hydrogen. A cause was found in the exceptional adsorption of carbon monoxide and dioxide by the palladium oxide. Since Langmuir [*ibid.*, **40,** 1398 (1918)] and also Taylor and Burns [*ibid.*, **43,** 1282 (1921)] found a much stronger adsorption of carbon monoxide and oxygen on platinum than on palladium it was reasonable to suppose that platinum oxide might reduce in the usual manner.

We have prepared samples of platinum oxide using the procedure and apparatus previously described and have established that platinum oxide reduces with carbon monoxide at 0°. The reaction is autocatalytic in type, having an induction period, and is similar in all ways to the reduction of copper oxide described by Jones and Taylor [*J. Phys. Chem.*, **27,** 623 (1923)]. A powdery 2-g. sample at 0° in a tube of 1 cm. diameter at a flow rate of 20 cc. of carbon monoxide per minute had an induction period of twelve minutes followed by an extremely rapid reaction. A sample first washed free of air by nitrogen gave no reaction in one hour at 0°, nothing at 10° in thirty minutes, but at 25° reacted immediately. A layer of recently reduced platinum practically eliminated the induction period. Platinum oxide thus shows none of the exceptional behavior found in the case of palladium oxide.

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EDWIN F. MORFIT

RECEIVED MAY 15, 1933 PUBLISHED JULY 6, 1933

## THE CHEMICAL ACTION OF AUDIBLE SOUND

*Sir:*

While investigating the bactericidal action of intense audible sound, a wide variety of interesting chemical reactions have been observed to take place. These have been produced using both the Gaines modification of the Pierce magnetostriction oscillator with a nickel tube[1] and a modified electro-magnetic oscillator with a stainless steel diaphragm of a type used by the Submarine Signal Company of Boston.

Solutions of Merck egg albumin, of four times recrystallized egg albumin and of synthetic plastein are almost instantly coagulated, at 30°. Solutions of agar and of starch, free from electrolytes, produce a little dextrin and reducing sugar. Sucrose in neutral solutions is hydrolyzed to glucose about twice as fast at 5° as ordinarily at the boiling point, while with a trace of acid the hydrolysis is complete and almost instantaneous. The hydrolysis of ethyl acetate is also accelerated and *n*-tetradecane and vegetable oils containing olein are cracked.

Inorganic halides in solution are oxidized to free halogen and hydrogen sulfide rapidly to sulfur by dissolved oxygen. In the former case the hydrolysis of the hypochlorite formed results in an increase of the *P*H. Even with an initial excess of acid, after five minutes of sonic vibration, hydroxides of Cu, Mn, Ni, Al and Cr are precipitated from their chlorides. In the presence of oxygen but in the absence of an excess of acid, ferrous chloride is rapidly oxidized and precipitated as ferric hydroxide which is thereby rendered unavailable for reduction by the nickel of the vibrator. In the presence of an excess of acid ferric ions are reduced by the nickel in spite of the fact that free chlorine is detectable. After cessation of vibration, any free chlorine remaining in solution is consumed in oxidizing ferrous ions. Mercuric chloride is rapidly reduced by the nickel to calomel, free chlorine and free mercury, the latter producing a rather permanent sol. Gold is precipitated from gold chloride. In general, with oxygen present, the anion in the metallic halides and sulfides is oxidized although, depending upon the relative position in the electromotive series, displacement or reduction of nickel by the metallic ion will also take place at a highly accelerated rate.

During the exposure to sound, a trace of nickel or stainless steel is dispersed. But the organic reactions are not due to metallic catalysis, since they progress in the presence of hydrogen sulfide, carbon disulfide, mercury salts and metallic mercury. The reactions may be due to a conversion of the sound energy into heat energy, which hypothesis we propose to test. The catalytic influence of the cavitation surfaces produced within the liquids can be excluded because at 4 to 10 atmospheres, where cavitation is suppressed, the reactions still progress.

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(1) Newton Gaines, *Physics*, **3**, 209–229 (1932).

It should be emphasized that these effects are produced by audible sound, the frequencies (1000–15,000) being of a far different order than any hitherto reported as influencing chemical reactions. Because of the relative ease of producing high energy densities in this range, it seems likely that such methods will prove to be useful.

THE JOHNSON FOUNDATION FOR MEDICAL PHYSICS
THE DEPARTMENTS OF BACTERIOLOGY AND PEDIATRICS
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RECEIVED MAY 20, 1933 PUBLISHED JULY 6, 1933

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## THE FORMULAS OF ANTIMONIC ACID AND THE ANTIMONATES

*Sir:*

In my recent discussion of antimonic acid [THIS JOURNAL, **55,** 1895 (1933)] I stated that its formula had not been previously recognized to be $HSb(OH)_6$. I have just learned that this statement is incorrect, for in 1929 Professor L. P. Hammett, in an interesting discussion of amphoteric hydroxides ["Solutions of Electrolytes," McGraw-Hill Book Co., New York, 1929, p. 108], wrote: ". . . the sodium antimonate whose crystallization is used as a test for sodium has exactly the right content of water so that it can be written $NaSb(OH)_6$."

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LINUS PAULING

RECEIVED JUNE 2, 1933 PUBLISHED JULY 6, 1933

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## EXPERIMENTAL EVIDENCE FOR ACTIVATED ADSORPTION OF HYDROGEN BY CHARCOAL

*Sir:*

It was shown recently by Kingman [*Trans. Faraday Soc.*, **28,** 269 (1932)] and by Burstein and Frumkin [*ibid.*, **28,** 273 (1932)] that hydrogen is slowly sorbed by charcoal at higher temperatures (above 100°), whereas at room temperature only van der Waals adsorption is observed. The experiments described below give in our opinion a direct proof that hydrogen sorbed at higher temperatures remains on the charcoal surface and is not dissolved in the interior of the solid, as it was suggested for similar cases by Steacie and Ward.

Burstein and Frumkin [*Z. physik. Chem.*, **141,** 158 (1929)] found that charcoal heated in hydrogen to 1000° and cooled to room temperature adsorbs small quantities of alkali from an aqueous solution if protected from contact with oxygen. The mechanism of this process consists in an ionization of the hydrogen, the negative charge of the charcoal surface attracting the cations of the solution.

In connection with the problem of activated adsorption, it appeared worth while to investigate under what conditions adsorbed hydrogen acquires the property of passing into the ionic state. The experimental method has been described in a previous paper [*Z. physik. Chem.*, **150,** 421 (1930)]. The charcoal[1] was outgassed at 950° for forty-eight hours and then cooled to the temperature of hydrogen adsorption. After a certain quantity of hydrogen had been adsorbed, the charcoal was brought at room temperature into contact with an outgassed solution of sodium hydroxide and after five hours the change of concentration determined. These experiments showed that hydrogen adsorbed at low temperatures (20–100°) is not exchanged against sodium ions, whereas hydrogen adsorbed in the temperature region of activated adsorption (300° and 800°) readily reacts with the alkaline solution. In this case, if the quantity adsorbed is small, the whole of the adsorbed hydrogen is exchanged. In one experiment 1 g. of charcoal adsorbed 0.100 millieq. of hydrogen at 300° and afterward, 0.090 millieq. of alkali; in another (temperature of hydrogen adsorption 800°) the corresponding quantities were 0.064 and 0.066. If the amount of adsorbed hydrogen becomes larger, only a part of it is exchanged.

The adsorption of alkali depends only on the quantity of hydrogen adsorbed at high temperature. An excess of hydrogen in the gaseous phase during the interaction between the charcoal and the solution has not the slightest influence on the results of the experiments and if the charcoal has not been previously heated in hydrogen until activated adsorption sets in, the adsorption of alkali is nil.

The fact that hydrogen adsorbed at high temperatures can be exchanged at room temperature quantitatively against sodium ions seems to prove definitely that the hydrogen remains on the charcoal surface (probably in an atomic form) and does not diffuse into the interior of the solid.

(1) We used activated sugar charcoal prepared as described by Bruns and Frumkin [*Z. physik. Chem.*, **141**, 145 (1929)]. It contained 0.05% ash. A control experiment carried out with a charcoal specimen with an ash content of only 0.005%, which was prepared from distilled materials [*cf.* Low, *Phys.*, **2**, 505 (1932)] gave the same results.

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R. BURSTEIN
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RECEIVED JUNE 9, 1933 PUBLISHED JULY 6, 1933

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## AN ARRANGEMENT OF ATOMIC NUCLEI AND THE PREDICTION OF ISOTOPES

*Sir:*

The regularities observed in the existence and abundance of atomic nuclei have been commented on by Harkins, Beck, Barton, Latimer, Johnston, Urey and others.[1] From such regularities attempts have been

(1) Harkins, THIS JOURNAL, **39,** 859 (1917); **42,** 1976 (1920); **43,** 1050 (1921); *Phys. Rev.*, **15,** 85 (1920); *Phil. Mag.*, **42,** 305 (1921); *Chem. Rev.*, **5,** 371 (1928); Beck, *Z. Physik*, **47,** 407 (1928); Barton, *Phys. Rev.*, **35,** 408 (1930); Latimer, THIS JOURNAL, **53,** 981 (1931); Johnston, *ibid.*, **53,** 2866 (1931); Urey, *ibid.*, **53,** 2872 (1931).

made to predict the existence of isotopes. In his book, "Constitution of Atomic Nuclei and Radioactivity," Gamow, also, publishes a series of

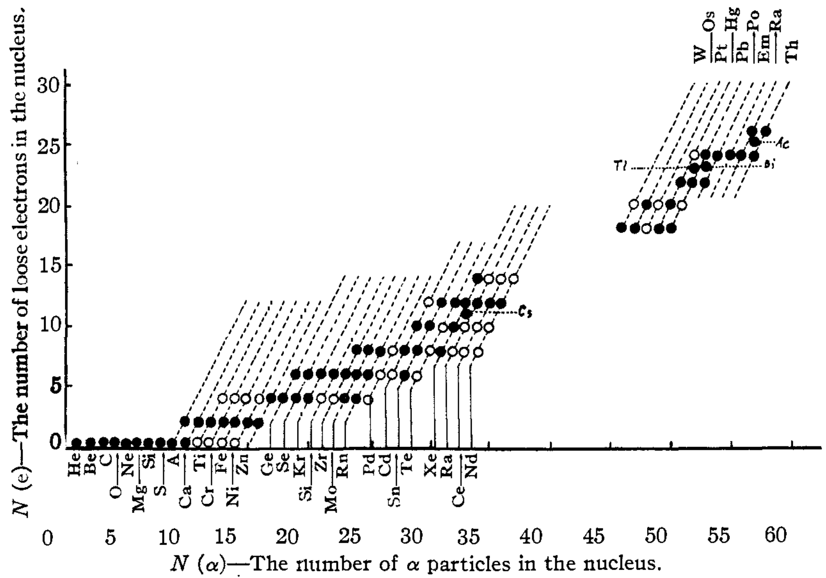

Fig. 1.—Arrangement of the nuclei of the 4 $N$ type.

figures, and, like Johnston, he classifies all the known nuclei into the four well-known types $4n$, $4n + 1$, $4n + 2$ and $4n + 3$, and shows the number of loose electrons in each nucleus.

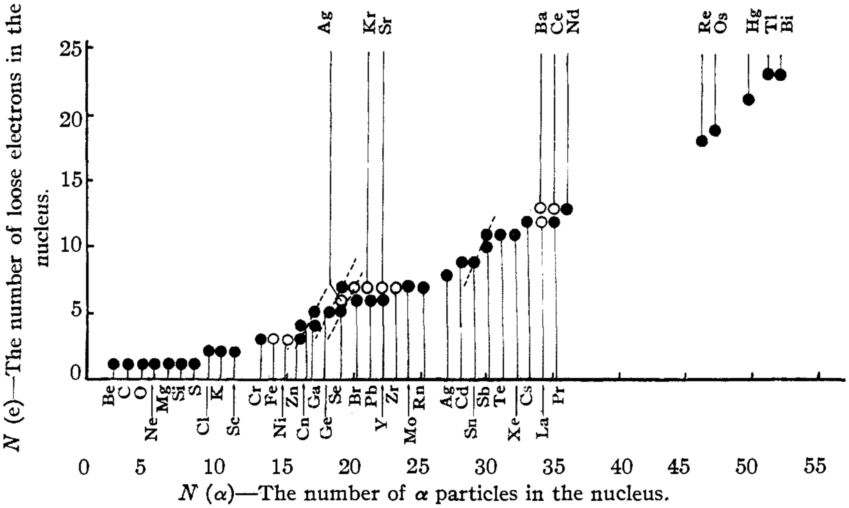

Fig. 2.—Arrangement of the nuclei of 4 $N$ + 1 type.

In the following, Gamow's figures have been reproduced after putting in the nuclei that have been recently reported to have been discovered.

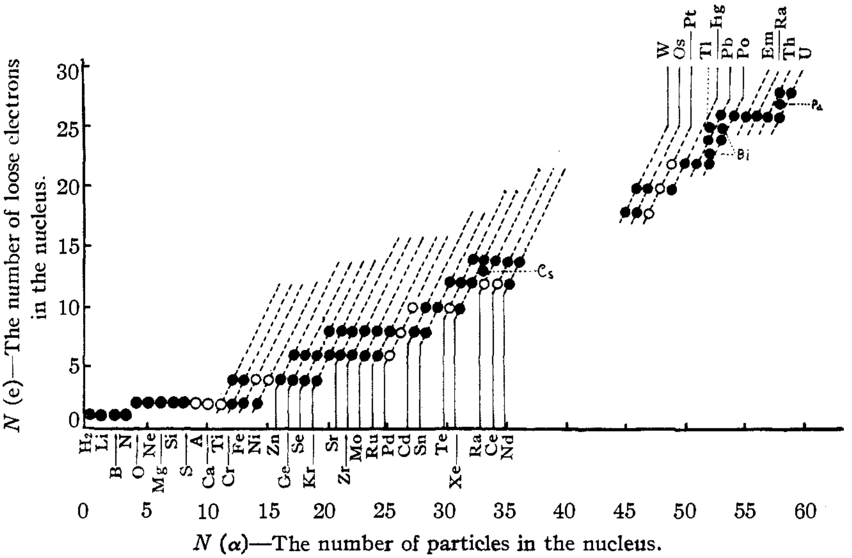

Fig. 3.—Arrangement of the nuclei of 4 $N + 2$ type.

The known nuclei are indicated by circular dots. From the regularity of the various figures the existence of the nuclei shown by circles is apparent.

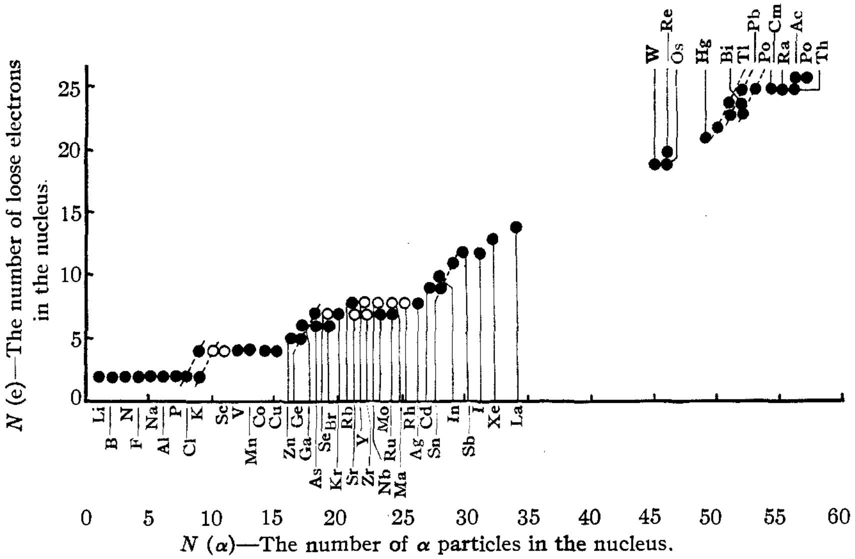

Fig. 4—Arrangement of the nuclei of 4 $N + 3$ type.

In this way the following additional isotopes of elements can safely be predicted to occur: A 38; Ca 42; K 43; Ti 44, 46 and 52; Sc 47; Cr 48 or 56; Fe 56, 60, 57 and 58; Ni 56 or 64, 61 and 62; As 77; Se 79 and 81; Sr 84, 87 and 89; Kr 85; Zr 88, 91 and 93; Y 91; Nb 95; Ma 99; Rh 103; Pd 100, 102, 104, 106, 108 and 110; Cd 108 and 120; Te 116, 120, 122 and 124; Ba 128, 132, 134 and 140; Ce 132, 136, 138, 141 and 144; Nd 136, 140 and 148; La 137; W 188; Pt 190 or 198, 192, 194 and 196; Pb 204 and Hg 208.

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S. B. L. MATHUR

RECEIVED JUNE 12, 1933 PUBLISHED JULY 6, 1933

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## TETRAARYLARSONIUM HALIDES

*Sir:*

Alkyltriarylarsonium compounds have been prepared in considerable number but it seems that the tetraarylarsonium type has not been described hitherto.

It has been found that tetraarylarsonium halides can be obtained readily by interaction of an arylmagnesium halide with a triarylarsine oxide and subsequent treatment of the reaction mixture with a halogen acid: for example, addition of hydrochloric acid to the product formed from phenylmagnesium bromide and triphenylarsine oxide yields tetraphenylarsonium chloride (m. p. 272–274°); by the use of hydrobromic or hydriodic acid the corresponding bromide (m. p. 273–275°) and iodide (m. p. 292–293°) are obtained.

These halides are beautifully crystalline compounds and the halogen is not removed by brief treatment with alcoholic sodium hydroxide or molecular silver.

An extensive investigation of these compounds is in progress.

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RECEIVED JUNE 19, 1933 PUBLISHED JULY 6, 1933

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## HIGHER VALENCE STATES OF SILVER

*Sir:*

Recently considerable attention has been given to the higher valence states of silver, but no reports have appeared on bivalent silver in the form of anhydrous fluoride, although as early as 1891 Moissan stated that silver is attacked by fluorine at 100°, and at red heat the two elements combine with incandescence.

There has been prepared in this Laboratory by the action of fluorine on silver foil at 300°, a black material which differs in every respect from ordinary silver fluoride, and which all evidence indicates to be the difluoride, $AgF_2$. The compound is not very stable, decomposing quickly in moist air, if heated, and becoming covered with a coating of yellow AgF. Decomposition occurs similarly, but more slowly, at room temperature and even efforts to remove all water vapor will not prevent completely this slow change. The material is a powerful oxidizing agent. Qualitatively it will react with dilute acids to liberate ozone, and with aqueous solutions in general to liberate ozone or oxygen. It releases iodine from iodides, converts ferrous salts to ferric salts, chromium salts to chromates, manganese dioxide to permanganates in both acid and basic media and oxidizes alcohol to acetaldehyde.

Analyses of the material indicate that it is a mixture of fluorides of monovalent and bivalent silver, while the iodine liberated from a very cold, concentrated potassium iodide solution shows that at least three-fourths of the silver is in the higher valence state.

By the action of cold concentrated potassium hydroxide on the above fluorides, there is produced a stable material that can be washed free of alkali and dried. Determinations of its silver content and its oxidizing ability support the assumption that it is a mixture of $Ag^{II}O$ and $Ag^{I}OH$, with 70 to 80% of the silver as $Ag^{II}$. However, the oxidizing ability might be explained by presence of the peroxide Ag-O-O-Ag.

There is some evidence that an active complex can be formed from the bivalent silver fluoride by molten $KHF_2$.

Further work will be undertaken on all three phases of this problem.

In addition, Hettich [private communication] in this Laboratory, has obtained some evidence that silver in higher valence form can be obtained by electrolysis.

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RECEIVED JUNE 20, 1933 PUBLISHED JULY 6, 1933

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## SOME PROPERTIES OF PURE $H^2H^2O$

*Sir:*

We have recently pointed out [Lewis and Macdonald, *J. Phys. Chem.*, **1**, 341 (1933)] that our process of concentrating the isotope of hydrogen could easily be continued to the point of eliminating practically all of the $H^1$. Before trying this experiment we had hoped to accumulate a considerable amount of heavy water, but the demand for this material has been so great that we have been obliged to proceed with the amount obtained in one series of electrolyses, which yielded 0.3 cc. of water in which, by our calculations, over 99% of the hydrogen should be $H^2$. The specific gravity, however, proved to be 1.1059 as against 1.111 calculated for pure $H^2H^2O$, assuming the same molecular volume as for ordinary water. To test this assumption the water was electrolyzed further until only 0.12 cc. remained. The density was found to be 1.1053. With such small volumes accurate determinations of densities are difficult and we may conclude that we have electrolyzed to constant density and take 1.1056 as a provisional value for the specific gravity of pure $H^2H^2O$ at 25°. Our calculations show that in our final sample no more than 0.01% of the hydrogen can be $H^1$.

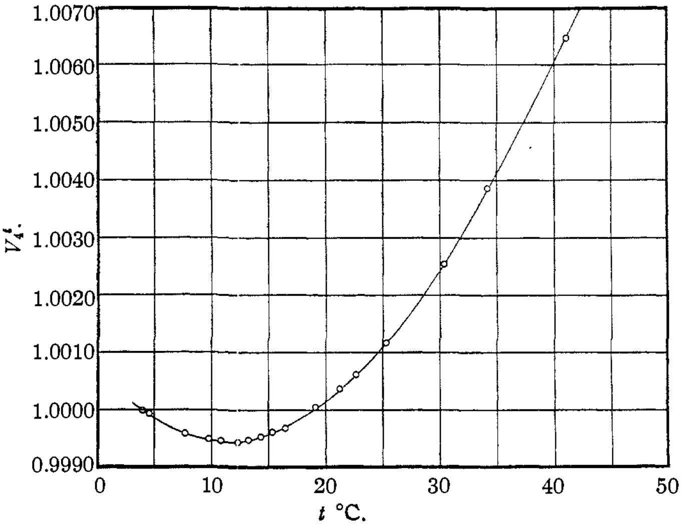

Fig. 1.

With this small amount of pure $H^2H^2O$ we have been able to make the following measurements. The freezing point is +3.8°, the normal boiling point 101.42°. The vapor pressure was compared with that of ordinary water in a differential tensimeter with the results given in Table I, where

TABLE I

| $t$ | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 | 110 |
|---|---|---|---|---|---|---|---|---|---|---|
| $p_1 - p_2$ | 2.3 | 3.9 | 6.1 | 9.1 | 13.1 | 18.0 | 23.9 | 30.7 | 38.4 | 47.0 |
| $p_2/p_1$ | 0.87 | 0.88 | 0.89 | 0.90 | 0.913 | 0.923 | 0.933 | 0.942 | 0.949 | 0.956 |

$p_1$ is the vapor pressure of common water (mm. Hg), $p_2$ that of $H^2H^2O$, and $t$ is the centigrade temperature, the measurements being accurate to about 0.1 mm.

When log $p_2/p_1$ is plotted against $1/T$ a straight line is obtained as far as 90°, and the heat of vaporization proves to be greater than that of ordinary water by 259 calories per mole, this value being accurate to 3 or 4 units.

In a tiny but accurate dilatometer the change of volume with temperature was studied. The volume divided by the volume at 4° is given at several even temperatures in Table II, while the individual measurements (corrected for the expansion of Pyrex glass according to Buffington and Latimer [This Journal, **48,** 2305 (1926)]) are shown in the figure. Like common water there is a temperature of maximum density which for $H^2H^2O$ is about 11.6°.

Table II

| $t$ | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 |
|---|---|---|---|---|---|---|---|---|
| $V_4^t$ | 0.99987 | 0.99948 | 0.99958 | 1.00016 | 1.00111 | 1.00243 | 1.00415 | 1.00605 |

In the various respects in which water is said to be an abnormal liquid $H^2H^2O$ seems to be more abnormal, but the differences between the two become smaller with rising temperature.

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Ronald T. Macdonald

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# NEW BOOKS

**Qualitative Chemical Analysis.** Certain Principles and Methods Used in Identifying Inorganic Substances together with a Systematic Survey of the Chemistry of these Materials. Based upon the Text by A. B. Prescott and O. C. Johnson. By Roy K. McAlpine and Byron A. Soule, University of Michigan. D. Van Nostrand Company, Inc., 250 Fourth Ave., New York, 1933. xii + 696 pp. 15.5 × 23.5 cm. Price, $4.50.

"The remarkable vitality of the older book," to quote the authors, is well illustrated by the ruinous condition of the copy accessible to the classes of the undersigned. In the present revision, the sections dealing with properties, reactions and detection of elements and compounds have been modernized, and amplified so as to include practically all the atomic types as well as many of the less common anions. Inert gases, only, are omitted. Systematic and detailed directions are now given for separation and detection of twenty-three common cations and about the same number of anions. Although it would not at first be clear how to extend this scheme so as to analyze any imaginable mixture, the student could at once detect the rarer cations or anions occurring alone or in the presence of a very few others. Thereafter his resourcefulness would increase with his grasp of the data supplied. To this extent the discipline of the older book, which often left the analyst to invent his own procedure, is preserved.

A hundred and forty pages now recount principles and theories underlying qualitative analysis. Recent interpretations are duly mentioned, but the classical point of view predominates. This section is clear and helpful. More emphasis might well be laid, in so extended a discussion, upon dispersion and coagulation.