retical potassium hydroxide dissolved in the least possible amount of water. The water was distilled out of the solution in an insulated boiling flask. The flame was then turned off and 80% of the theoretical amount of monochloro-2,7-dimethyloctane (based on the potassium hydroxide used) was dropped into the potassium cresolate at such a rate that the temperature (thermometer well in liquid) did not rise above 180°. The decylene distilled off as formed. The product was washed, dried and fractionated. Approximately six kilograms of decylene, boiling from 155–166° and representing a yield of 91.6% of the theoretical were thus obtained.

After a second fractionation, 90% of the principal fraction boiled between 159.6 and 162.8° (A. S. T. M. D 216); f. p. −79.5°; d_4^{20} 0.7418; n_D^{20} 1.4250.

A number of modifications of the described technique were tried. Each of these variations materially reduced the yield of the olefin.

Preparation of Decadiene

Direct treatment with potassium cresolate gave a poor yield in the case of dichloro-2,7-dimethyloctane (b. range 121–125° at 12 mm.; density at 20°, 1.0091; chlorine, by analysis 34.09%, theoretical 33.60%). On the other hand, long-continued boiling with a very large excess of alcoholic potash removed only one molecule of hydrochloric acid but gave a satisfactory yield of the chloro olefin. If the two methods were combined, a good yield of the diolefin was obtained. A chloro-2,7-dimethyloctene was obtained by refluxing the dichlorodimethyloctene with one and one-half moles of alcoholic potash (25% solution) for three hours. The chloro olefin was then treated with potassium cresylate by the method described above. It had a tendency to distil over unchanged and repeated treatment was necessary. The middle 90% of the carefully purified and fractionated product boiled over the range 161.0–166.0° at 764.4 mm.; f. p. −92.6°; d_4^{20} 0.7627; n_D^{20} 1.4410.

Both hydrocarbons were free from chlorine. The number of isomers present or the position of the double bonds was not established for either hydrocarbon. The decylene is apparently largely the 2,7-dimethyloctene (2), b. p. 159–162°, of Kishner.[3]

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(3) Kishner, *Chem. Zentr.*, II, 725 (1900).

UNITED GAS IMPROVEMENT CO.
PHILADELPHIA, PENNA.
RECEIVED APRIL 10, 1934

COMMUNICATIONS TO THE EDITOR

ISOBARIC ISOTOPES

Sir:

The recent publications of most scientists on the subject of isotopes imply that a given atom does not have an isobaric isotope.[1] However, it has been known for more than a decade that Uranium X_2 and Uranium Z[2] are not only isotopes but also isobars.

This example seems to indicate that, within the nucleus, the protons and negatrons or other units not only do not lose their identity completely but actually give rise to nuclear isomerism. If this hypothesis is correct, we should expect that isobaric isotopes should be as numerous as isomerism in the case of compounds. As yet, we have no means of showing the existence of such isotopes in the case of the non-radioactive elements but it is conceivable that the different isobaric isotopes may show differences in artificial disintegration or in artificial radioactivity recently discovered by the Joliots and confirmed by Lord Rutherford.

In all probability, these isomeric nuclei may have different energies of formation from protons and negatrons or other units and, if we accept the current hypothesis of the interconvertibility of mass and energy, may have slightly different atomic weights.

The symbols recently suggested by Harkins [*Science*, **79**, 138 (1934)] for distinguishing isotopes would be identical, and hence useless, for isobaric isotopes. A perfect system of symbols for distinguishing isotopes has, therefore, not yet been devised.

CHICAGO, ILLINOIS HERBERT J. BRENNEN
RECEIVED MAY 31, 1934

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(1) The word "isobar" is used in the generalized sense, namely, for "atoms, the atomic weights of which may differ by small fractions of a unit."

(2) See, for example, Rutherford, Chadwick and Ellis, "Radiations from Radioactive Substances," New York, 1930, p. 24.

THE PEROXIDE EFFECT IN THE ADDITION OF REAGENTS TO UNSATURATED COMPOUNDS

Sir:

In a recent issue of THIS JOURNAL, Sherrill, Mayer and Walter [THIS JOURNAL, **56**, 926 (1934)] claim that the important factor governing addition of hydrogen bromide to pentene-1 is the solvent and not the peroxide content of the reaction mixture. In view of their report we have repeated the work on pentene-1, which was done in this Laboratory about a year ago (and as yet unpublished), and the tables below prove most conclusively that the 2-bromopentane is the "normal" product of the reaction while the 1-bromopentane is the peroxide-catalyzed, "abnormal" product of the reaction.

Table I is a summary of many experiments, and it is most significant that as long as added peroxides are absent, the 2-bromopentane is the only product of the reaction. Table II needs little interpretation. The striking fact about the addition recorded in that table is the completeness of the reversal of the addition in the presence of peroxides (as indicated by the sharpness of the boiling point of the addition product). Solvents, as may be noted, play very little part in governing the direction of addition.

TABLE I

ADDITION OF HYDROGEN BROMIDE TO PENTENE-1[a]

Conditions	B. p., °C.	n_D^{20}	Remarks
Simple addition	118–119	1.4414	The yields in all cases were 84% or better.
Thiocresol	118–119	1.4416	
Acetic acid	118–119	1.4415	
Thiocresol and light	117–119	1.4415	
Thiocresol and acetic acid	118–119	1.4414	
Acetic acid and light	117–118	1.4412	
Thiocresol, acetic acid and light	117–119	1.4416	
Thiocresol, light at 5 – 10°	117–119	1.4415	
Thiocresol, long evacuation	118–119	1.4413	
Thiocresol, separate drying	117–118	1.4418	
Thiocresol	118–119	1.4413	Pentene washed in the vapor phase to remove all possible traces of peroxides.
Diphenylamine	118–119	1.4412	
Hydroquinone	118–119	1.4418	
Thiocresol	118–119	1.4412	
Thiocresol at −80°	118–119	1.4413	

[a] The authors are indebted to Dr. Thomas M. Beck for most of the determinations recorded in this Table.

TABLE II

ADDITION OF HYDROGEN BROMIDE TO PENTENE-1

No.	Pentene, mole	HBr, mole	Agent added		Solvent and conditions	Time, hrs.	Yield, %	B. p., °C.	n_D^{20}	1-Bromopentane, %
1	0.15	0.21	Ascaridole	0.006	None, air	15.75	96	127.8–129.1	1.4442	97–100
2	.17	.19	Ascaridole	.008	Pentane, air	15	81	128.2–129.0	1.4443	100
3	.16	.20	Ascaridole	.011	HAc, air	12	51	118.2–119.5	1.4410	0
4	.17	.22	Ascaridole	.009	Propionic acid, vacuo	20	89	118.0–129.0	1.4423	40
5	.17	.24	Diphenylamine	.002	Pentane, vacuo	16.5	79	118.0–118.2	1.4410	0
6	.14	.21	Diphenylamine	.003	Propionic acid, vacuo	14	80	118.0–118.2	1.4410	0

It is noteworthy, and in agreement with our previous work, that in the presence of organic acids such as acetic and propionic acids, the peroxide effect should be less pronounced, and in conformity with that we find that acetic acid, even in the presence of peroxides, gives quantitative yields of the 2-bromopentane. The observation that, in passing hydrogen bromide into the cooled mixture of acetic acid and pentene, there is a separation of layers probably accounts for this product.

To overcome this difficulty we have modified in Run 4 our vacuum technique addition so as to bubble the hydrogen bromide slowly through a mixture of propionic acid, pentene and ascaridole. A yield of 40% of the 1-bromopentane was then obtained. We feel quite confident that the procedure can be further improved to yield quantitative yields of the 1-bromopentane even in the presence of glacial acetic acid as long as peroxides are added to the reaction mixture.

The technique of addition in all cases was the same as described in our previous papers [Kharasch and Mayo, THIS JOURNAL, **55**, 2468 (1933)]. The bromopentanes obtained were identified, not only by their boiling points and indices of refractions, but by the preparation of the mercury compounds. The mercury compound of the 1-bromopentane melted sharply, without crystallization, at 121°, while the mercury compound from the 2-bromopentane was obtained as a low melting solid. It was therefore identified as the 3,5-dinitrobenzoate. Absolutely consistent determinations of the composition of the mixture were obtained by the use of all of these methods.

JONES CHEMICAL LABORATORY
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS
M. S. KHARASCH
J. A. HINCKLEY, JR.
M. M. GLADSTONE

RECEIVED MAY 31, 1934

PREPARATION OF CRYSTALLINE β-*d*-[α-GALAHEPTOSE][1]

Sir:

Fischer [*Ann.*, **288**, 139 (1895)] prepared the two galaheptoses from galactose and crystallized β-galaheptose, but was unable to obtain α-galaheptose in crystalline condition. We have now succeeded in crystallizing this sugar.

The first crystalline material was obtained from an aqueous sirup resulting from the reduction of crystalline α-galaheptonic lactone in acid solution by sodium amalgam. Following removal of the sodium salt of α-galaheptonic acid by repeated treatments with methyl alcohol, the sirup crystallized after standing in a loosely covered beaker at laboratory temperature for several weeks. With these crystals it was possible to nucleate other sirups and obtain crystallization readily.

β-*d*-(α-Galaheptose) monohydrate crystallizes in clusters of colorless glistening prisms, stable at room temperature upon drying *in vacuo* over calcium chloride or sulfuric acid. When slowly heated in a capillary tube it melts at 77–78° (corr.) to a colorless sirup. Its solution in water shows $(\alpha)^{20}_{\mathrm{D}}$ $-22.5°$ for the monohydrate after three minutes and an equilibrium value of $-14.1°$ in 180 minutes, at 20°. These data establish the fact that the sugar is the less dextrorotatory form of a sugar in the *d*-series, and according to the usual nomenclature [Hudson, THIS JOURNAL, **31**, 66 (1909)] it is to be designated as the β-form. Studies of the *d*-galaheptoses, which closely resemble *l*-mannose and *l*-glucose in configuration, are in progress.

(1) Publication authorized by the Surgeon General, U. S. Public Health Service.

NATIONAL INSTITUTE OF HEALTH
WASHINGTON, D. C.
RAYMOND M. HANN
ALICE T. MERRILL
C. S. HUDSON

RECEIVED JUNE 4, 1934

PHOTOCHEMICAL DECOMPOSITION OF KETENE

Sir:

In a recent paper Ross and Kistiakowsky [THIS JOURNAL, **56**, 1112 (1934)] have confirmed our experimental results on the photochemical decomposition of ketene [*J. Chem. Soc.*, 1533 (1933)]. They have in addition measured the quantum efficiency and find average values of about 1.0 at 3130 Å. and 0.3 at 3650 Å. While agreeing with our primary change

$$CH_2{=}CO \longrightarrow CH_2 + CO$$

they suggest that the secondary change

$$CH_2 + CH_2 \longrightarrow C_2H_4$$

is in better agreement with the unit quantum yield at 3130 Å. than is that postulated by us

$$CH_2 + CH_2CO \longrightarrow C_2H_4 + CO + 9\text{ k. cal.}$$

This reaction cannot, however, be eliminated on such evidence alone. It is not necessarily true that the higher of the two values of the quantum efficiency is its maximum value. Further, it is now apparent that for polyatomic molecules the quantum yield of the primary reaction may be less than unity throughout a considerable portion of a region of continuous absorption. This is true of acetone ($\gamma = 0.2$ for λ 3130 and 0.4 for λ 2650) as has been shown by Damon and Daniels [THIS JOURNAL, **55**, 2363 (1933)] and recently confirmed by us. If the radiationless transition which follows absorption of light be viewed as an Auger effect confined to the carbon atom of the chromophoric (carbonyl) group, we may suppose that it does not in all cases lead to dissolution of the C=C link but that instead it may lead to the degradation of the electronic energy of excitation to molecular vibration, and its dissipation as heat. The relative probabilities of these alternatives would not be expected to remain constant throughout the absorption band but as the wave length of the absorbed radiation decreased the fraction of molecules decomposing would increase.

The spectroscopic observations of ketene made by Lardy [*J. chim. phys.*, **21**, 353 (1924)] and ourselves (Ref. 2) are completely in agreement with these ideas. The absorption spectrum consists of completely diffuse bands throughout its *entire* range. The substance shows no fluorescence. The low quantum yield of 0.3 at λ 3650 increases to 1.1 at λ 3130 (Ref. 1) in full agreement with this theory. As with acetone the value of the quantum yield may be expected to increase toward the theoretical maximum value as the magnitude of the absorbed quantum exceeds by greater amounts the energy necessary to decompose the molecule. This would lead to a maximum over-all quantum yield of 2 if our mechanism is correct, or of 1 if that of Ross and Kistiakowsky is right. The fact that the values of Ross and Kistiakowsky are less than unity at 3650 and somewhat exceed it at 3130 lends probability to the correctness of our theory.

If this view is not taken it is difficult to reconcile the low value of the quantum efficiency at λ 3650 Å. with the diffuse character of the absorption in that region. It is improbable that the fraction of excited molecules which do not decompose could lose their energy by collision for this would involve a life of the excited state of the order of 10^{-8} second, which is about 10^5 times greater than that necessary to produce so diffuse a spectrum.

LABORATORY OF PHYSICAL CHEMISTRY
UNIVERSITY OF CAMBRIDGE
CAMBRIDGE, ENGLAND
RONALD G. W. NORRISH
H. GORDON CRONE
OLIVE D. SALTMARSH

RECEIVED JUNE 7, 1934

THE ADDITION OF HYDROGEN BROMIDE TO PENTENE-1 AND HEPTENE-1

Sir:

In reply to the communication by Kharasch, Hinckley and Gladstone in which they question the validity of our conclusions concerning the importance of the solvent as an influencing factor in hydrogen bromide addition to pentene-1 and heptene-1, we would emphasize the particular conditions under which our addition reactions were carried out. The highly purified hydrocarbons gave no test for peroxide before the addition of hydrogen bromide nor did they give the colored reaction mixtures which we have always obtained in hydrogen bromide addition to hydrocarbons known to contain peroxide. The addition reactions in organic solvents, where we obtained the so-called "abnormal" products, 1-bromopentane and 1-bromoheptane, took place in the absence of air, whereas in water solution the reaction mixtures were shaken for many days in contact with air. The probability of a peroxide effect in the latter solvent is therefore much greater than in the organic solvents but our results gave conclusive evidence of the formation of only the "normal" product 2-bromopentane and 2-bromoheptane in water solution. Careful analysis of the experimental data would seem to justify our conclusion that any peroxide effect was eliminated in these reactions.

Furthermore, our reactions were carried out at atmospheric pressure while those of Kharasch and co-workers must have taken place under increased pressure. This factor complicates any comparison of results since the effect of pressure may be of importance in determining the products of the reaction. In drawing conclusions from our experiments there was no intentional disregard of the importance of the peroxide effect in hydrogen halide addition to unsaturated compounds which has been demonstrated by Kharasch and co-workers. Our results, however, seem to give conclusive evidence that in the absence of peroxide the solvent is an influencing factor.

CHEMICAL LABORATORY
MOUNT HOLYOKE COLLEGE
SOUTH HADLEY, MASSACHUSETTS
MARY L. SHERRILL

RECEIVED JUNE 11, 1934

PREPARATION OF PURE METALLIC HYDROXIDES

Sir:

A recent article by J. H. Long, J. C. W. Frazer and Emil Ott [THIS JOURNAL, **56**, 1101 (1934)] refers to a dissertation by O. G. Bennett [Johns Hopkins University, 1930] which describes the purification of metallic hydroxides by washing the oxides (or hydroxides) by decantation until peptization occurs and then electrodialyzing to remove the alkali salts adsorbed by the oxide hydrate at the moment of precipitation and which cannot be removed from the (usually gelatinous) oxide by mere washing. This ultra-purification is necessary if one is to obtain cobalt or nickel trioxides or manganese dioxides in a state sufficiently pure so as to be capable of catalyzing the reaction of carbon monoxide with oxygen at room temperature.

According to Bennett's dissertation, which was kindly made available by Dr. J. C. W. Frazer, the process of electrodialysis is long and tedious, sometimes requiring weeks. If the oxide could be precipitated in the absence of alkali or metal compound other than manganese or nickel salts, respectively, it would not be necessary to remove adsorbed salts by electrodialysis. It has been found in this Laboratory that passing ozone through neutral solutions of manganous acetate or chloride precipitated a manganese oxide which, after a short washing with concentrated nitric acid and drying by evacuation at 100°, was a very active catalyst for the oxidation of carbon monoxide. The electrolysis of manganous nitrate (with the cathode surrounded by a porous cup containing ammonium nitrate solution) gave a manganese dioxide of equal activity and in greater quantities. (Similarly, ozonizing basic lead acetate solution precipitated an oxide which, after washing with nitric acid and drying *in vacuo* at 100°, was active at 80°, whereas Bennett's PbO_2 did not catalyze the reaction except above 180°.)

It is hoped that this communication will be of aid to workers interested in preparing manganese dioxide (or other higher oxides) free of adsorbed alkali salts and capable of catalyzing gas-oxidation reactions. At no time did these oxides or the salts from which they were obtained come in contact with alkali other than that derived from glass, porcelain, etc., or with any foreign material other than nitric acid and volatile ammonium salts. Further work is now in progress.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN

V. W. MELOCHE
SAMUEL WEINER

RECEIVED JUNE 13, 1934

ASYMMETRIC REARRANGEMENT

Sir:

For some time there has been under way in this Laboratory an investigation of the effect called by Kuhn [*Ber.*, **65**, 49 (1932)] asymmetric rearrangement of the first type (asymmetrische Umlagerung erster Art). Our experiments (as yet unpublished) indicate that Kuhn's hypothesis is not generally valid, and that if it has any field of applicability, that field has not yet been clearly defined. The present communication is prompted by the recent paper of Lesslie and Turner [*J. Chem. Soc.*, 347 (1934); we have searched carefully for the mutarotation described by Lesslie and Turner, but have not been able to find any such phenomenon] in support of Kuhn's idea.

Kuhn bases his hypothesis chiefly on the "anomalous" optical rotation of quinine 4,4'-dinitrodiphenate in chloroform solution; Lesslie and Turner's supporting evidence is derived from the similar behavior of quinine diphenate in the same solvent. The divergences from the normal rotation are explained by what might be called a "dissymmetrizing" effect exerted by the optically active base on the acid. According to this view, the solution of the free acid is an equimolecular mixture of the *d* and *l* forms in labile equilibrium. The dissymmetric base disturbs this equilibrium, and the observed rotation is the resultant of the rotations of the base and the optically activated acid. As soon as the dissymmetrizing base is removed, the equilibrium between the two forms of the acid shifts back very rapidly to form the equimolecular mixture. Physical separation of the stereomeric acids is thus impossible.

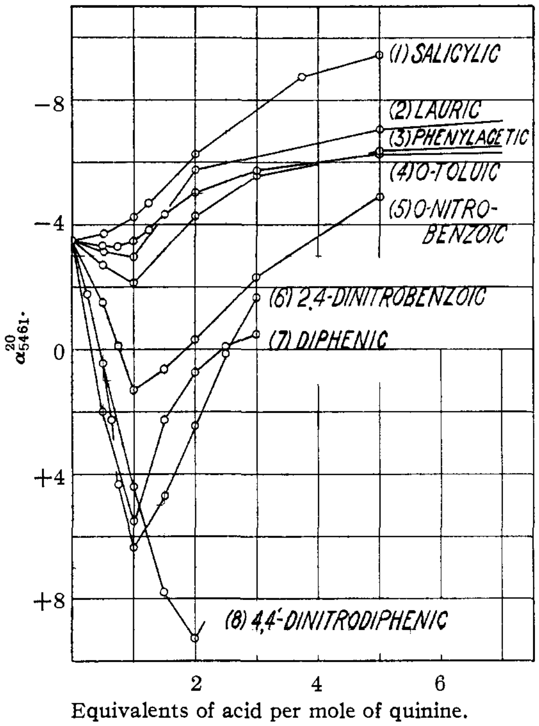

Fig. 1.—Rotations of salts of quinine in chloroform: Curves 1, 2, 3, 4, 5 and 6 were obtained with 0.04 molar solutions, curves 7 and 8 with 0.01 molar solutions of quinine, in a 2-dm. tube. The discrepancy thus introduced is, however, negligible, *e. g.*, for a 0.04 molar solution of quinine containing one equivalent of 4,4'-dinitrodiphenic acid α^{20}_{5461} 4.43°; calculated to the above concentration from a 0.01 molar solution of quinine and one equivalent of acid α^{20}_{5461} 4.40°. Curve 1: Similar curves were obtained with anthranilic, *o*-chlorobenzoic and *o*-iodobenzoic acids. Curves 2 and 3: Similar curves were obtained with acetic, crotonic, chloroacetic, palmitic, phenylpropionic and trichloroacetic acids. Curve 5: Similar curves were obtained with anisic, cinnamic, *m*- and *p*-nitrobenzoic, *p*-toluic and 3,5-dinitrobenzoic acids. Curves 6 and 7: A similar curve was obtained with 2,4,6-trinitrobenzoic acid.

This theory of Kuhn implies an important departure from classic chemical practice. The principle that isomer numbers can be determined from anomalies in the optical rotations of solutions may well have far reaching consequences. It therefore seemed desirable to us, before accepting so radical an idea, to investigate thoroughly the rotations of salts of various optically active bases in chloroform and other solvents. Such an investigation is now approaching completion. All of our data (which we hope soon to publish) support the views previously stated.

For the sake of brevity, we give here only the data on certain organic salts of quinine in chloroform solution. In so far as solubility conditions permit, a uniform concentration of quinine has been maintained, and (where possible) the amount of acid has been varied from $^1/_{10}$ to 20 moles per mole of base. Some of the curves are reproduced in diagram 1.

Our conclusions from the data there given are as follows: (1) The curves are of such diversified character that we do not feel justified in calling any one of them normal or anomalous. (2) The curves for the diphenate and the 4,4'-dinitrodiphenate so closely resemble those of certain other salts (*e. g.*, the 2,4-dinitrobenzoate) that there are no grounds for assuming that quinine dissymmetrizes one of these acids but not the others. That all these acids exist in pairs of mirror image forms is highly improbable.

JONES CHEMICAL LABORATORY
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M. S. KHARASCH
J. K. SENIOR
D. W. STANGER
J. A. CHENICEK

RECEIVED JUNE 18, 1934

ANOTHER INTERPRETATION OF EXPERIMENTS WHICH ARE SUPPOSED TO INDICATE THE EXISTENCE OF OXYACIDS OF FLUORINE

Sir:

Dennis and Rochow [THIS JOURNAL, **54**, 832 (1932); *ibid.*, **55**, 2431 (1933)] found that the action of fluorine produced, in an alkaline solution, an oxidizing agent, a small part of which could not, under certain circumstances, have been a peroxide or ozonate. They concluded, therefore, that the salt of an oxyacid of fluorine had been formed. However, there is another plausible interpretation of their observations. Of their results, the most indicative was that the passage of fluorine through cold 50% potassium hydroxide left in the solution an oxidizing agent, a part of which was not destroyed either by standing at room temperature for seventy hours or by evaporation of the liquid and subsequent fusion of the alkali in a beaker. Surely a peroxide or ozonate could not have resisted such severe treatment.

Attempts of the author to repeat this experiment have usually met with failure. The substance of considerable oxidizing strength has been decomposed by standing at room temperature for several hours or by boiling the solution for a minute. The destruction has been so complete that an acidified sample of the solution did not give a blue color with starch and potassium iodide for several minutes.

Fusion of potassium hydroxide in a Pyrex beaker has been found to produce a soluble substance capable of liberating iodine from a solution of potassium iodide containing sulfuric acid. This makes it difficult to test for an oxidizing agent which was present in the alkali before fusion.

At times it has been possible to reproduce the observations of Dennis and Rochow, but in each case of this sort the solution was found to contain a small amount of chloride ion. It therefore seems quite possible that the stable oxidizing agent was an oxy salt of chlorine which could result from a trace of chloride in either the potassium hydroxide, the potassium acid fluoride used for the preparation of fluorine or the sodium fluoride employed to remove hydrogen fluoride from the fluorine. Since this type of experiment should be a rather sensitive test for chlorine, it is surprising that any negative results have been obtained.

By means of the customary tests with titanium sulfate and with chromic acid, it has been shown that the oxidizing agent, which is so unstable in a strongly alkaline solution, is actually a peroxide. This confirms the work of Moissan, Fichter and Bladergroen [H. Moissan, "Le Fluor," 1900, p. 228; Fichter and Bladergroen, *Helv. Chim. Acta*, **10**, 549 (1927)].

CONTRIBUTION NO. 40
RESEARCH LABORATORY OF
INORGANIC CHEMISTRY
MASSACHUSETTS INSTITUTE
OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS
GEO. H. CADY

RECEIVED JUNE 18, 1934

BINDING AND INTERCHANGE OF WATER MOLECULES IN A SALT HYDRATE

Sir:

The statement of Fresenius ["Quant. Anal.," 1897, p. 799] that cupric sulfate pentahydrate, when heated near 140° in a current of dry air, yields a residue of monohydrate of constant weight is substantially correct for analytical practice, in spite of the fact that the equilibrium dissociation pressure of monohydrate with anhydrous salt is computed as 62 mm. at this temperature [Menzies and Hitchcock, *J. Phys. Chem.*, **35**, 1660 (1931)]. The success of the analytical procedure may be said to rest upon the long duration of the so-called induction period of the monohydrate, during which loss of water fails to begin owing to lack of a starting point, in absence of the new, anhydrous phase.

At 125° a sample of the monohydrate prepared by dehydration of pentahydrate showed, under Fresenius' conditions, an induction period of seventy hours (although monohydrate prepared from the anhydrous salt by rehydration showed no induction period because of its richness in "reaction centers") [Furman and Menzies, unpublished work].

At 75° the apparent stability of monohydrate prepared by dehydration is greater still, and its single water molecule appears to remain undisturbed in the absence of deliberate provocation directed at lessening the effective activation energy for dehydration.

For the three consecutive stages of dehydration of pentahydrate to anhydrous salt, the comparative energies to yield one mole of (unabsorbed) water vapor near 50° are about 13.2, 13.5 and 17.5 large calories [Menzies and Collins, unpublished work; Menzies and Hitchcock, *loc. cit.*].

In these circumstances it appeared to be of interest to prepare $CuSO_4 \cdot H_2O$ by dehydration from pentahydrate, to rehydrate this through the vapor phase by means of vapor of D_2O (heavy water), and then to dehydrate the salt once more in order to find whether the original H_2O had remained *in situ*. Should a solution phase form during the process of hydration, interchange between heavy and light water molecules would appear inevitable, and we endeavored, therefore, to avoid this.

At 35° the pressure of ordinary water vapor in equilibrium with the penta- and trihydrates is 16.2 mm.; with the tri- and mono-hydrates, 10.9 mm.; and with the monohydrate and the anhydrous salt <0.1 and 1.2 mm., respectively at 35 and 75°; and at 35° with the saturated solution of pentahydrate, 40.4 mm. [Collins, Hitchcock, Menzies, *loc. cit.*].

We prepared $CuSO_4 \cdot H_2O$ by dehydrating the pentahydrate at 75° for a few hours in presence of H_2O vapor in equilibrium with H_2O ice at 0° (4.6 mm. pressure) and obtained analytical results little vitiated by adsorbed water. We placed this monohydrate in an evacuated system at 35° and applied vapor of D_2O at a pressure somewhat over 20 mm. The apparent degree of over-all hydration reached a value exceeding four molecules of water overnight. In one experiment, lasting a few hours, we dehydrated this product at 75° in presence of D_2O vapor in equilibrium with D_2O ice at 0°. The weight of the residual monohydrate, constant over many more hours, showed that complete interchange of heavy and light water had taken place, and that the original H_2O had been expelled. In a second experiment, we dehydrated at 35°, which is a much slower process. Here also we found that interchange had taken place.

Further experiments and various interpretations suggest themselves which may find place elsewhere.

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, N. J.
ALAN W. C. MENZIES
FRANCIS T. MILES

RECEIVED JUNE 19, 1934

CRYSTALLINE B_2O_3

Sir:

Of all the glass-forming oxides B_2O_3 is probably the most typical [Zachariasen, THIS JOURNAL, **54**, 3841 (1932)]. Numerous attempts have been made to devitrify boric oxide glass, without success. The usual process of heating H_3BO_3 to drive off the water leaves an extremely viscous liquid which does not crystallize.

Recently we have been able to produce crystalline B_2O_3 by vacuum dehydration of H_3BO_3 at temperatures below 225°. Using a water suction pump, with the sample of boric acid at 180°, we first obtained $2B_2O_3 \cdot H_2O$. On connecting a good oil pump to the sample heated at 200°, we removed the last half molecule of water and obtained material giving three or four sharp lines on an x-ray pattern. The product was sintered for 400 hours at 225° in order to permit crystal growth, after which the x-ray pattern showed about a dozen sharp lines and was free of the diffuse band which characterizes the glass phase. The melting point has been determined by two different methods to be $294 \pm 1°$. The index of refraction is 1.458 ± 0.002. The crystals are apparently isotropic. The specific gravity at 25° is 1.805, while that of the B_2O_3 glass is 1.844, making it expand on freezing, like H_2O. The anhydrous crystalline B_2O_3 is highly desiccant.

Details of measurement and crystal structure data will be given in another publication.

DEPARTMENT OF CERAMICS
PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PA.
NELSON W. TAYLOR
SANDFORD S. COLE

RECEIVED JUNE 22, 1934

THE RELEASE OF SUPERCOOLING IN CRYOSCOPIC DETERMINATIONS

Sir:

The freezing point method of determining molecular weights is one of our most useful procedures and the freezing point lowering of solution is of great theoretical importance. The precise determination of a freezing point may be obtained by supercooling the liquid or solution under suitable conditions and releasing the supercooling to allow the system to come to equilibrium. The exact freezing point is determined in this way. The release of the supercooling without too great supercooling has always been a difficult matter but we have found that a little glass bead may be cooled on a cake of dry ice (solid carbon dioxide) and then introduced into the system and so releasing the slightest amount of supercooling.

Ordinary glass beads 3 mm. in diameter with 0.5 mm. bore may be wet with solvent or liquid and placed on the cake of dry ice for a few minutes and then with forceps may be transferred rapidly to the supercooled liquid. At ordinary laboratory temperatures the little core of ice will not melt in thirty seconds or more, so there is ample time. The suitably cooled bead, quite free of ice, will also release supercooling as it may be introduced into the system while at a very low temperature. If the bead is placed in the closed end of a thin-walled tube it may be cooled on dry ice and rapidly rolled into the supercooled system. We have readily released liquids or solutions supercooled only 0.04° and with experience a supercooling of as little as 0.01° is feasible. This should be of importance in determining the true freezing point of dilute solutions.

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DAVID E. KENYON
GEORGE A. HULETT

RECEIVED JUNE 23, 1934

THE SEPARATION OF THE OXYGEN ISOTOPES

Sir:

Although Washburn, Smith and Frandsen [*Bur. Standards J. Res.*, **11**, 453 (1933)] state that the electrolysis of sodium sulfate and sulfuric acid solutions produces oxygen with a greater proportion of O^{16} than is present in the water electrolyzed, Lewis and Macdonald [*J. Chem. Physics*, **1**, 341 (1933)] reported that no concentration of O^{18} was found when deuterium was concentrated by the electrolysis of sodium hydroxide solutions with nickel electrodes. Their method of analysis may not have been sensitive enough, however, to have detected small shifts in the isotopic composition of the water. We have electrolyzed 5% sodium hydroxide solutions with nickel electrodes and compared the density of water produced by burning this oxygen in purified tank hydrogen with that of water produced by burning air in the same hydrogen. The water from the electrolytic oxygen proved to be 7.7 p. p. m. lighter than Cambridge tap water and that from the air burned in the same hydrogen 1.1 p. p. m. heavier. Our results thus agree with those of Washburn, Smith and Frandsen in indicating a small but definite separation of the oxygen isotopes.

THE CHEMICAL LABORATORIES OF
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CAMBRIDGE, MASS.
CHARLES H. GREENE
ROGER J. VOSKUYL

RECEIVED JUNE 25, 1934

THE RELATIVE PROPORTIONS OF DEUTERIUM IN SOME NATURAL HYDROGEN COMPOUNDS

Sir:

The interesting observations of Lewis [THIS JOURNAL, **55**, 3503 (1933)] upon the antigerminative property of deuterium oxide led us to investigate the isotopic composition of the hydrogen utilized by plants in the synthesis of organic compounds with an expectation of finding a preference for protium in the biological synthesis. We find, however, in common with others who have reported upon parallel investigations [E. W. Washburn and E. R. Smith, *Science*, **79**, 188 (1934); M. Dole, THIS JOURNAL, **56**, 999 (1934)] since we began our work, that in some natural sources deuterium is more abundant than in ordinary water.

In our experiments "Mazola" corn oil was burned in dried air and the products of combustion passed over hot copper oxide before condensing the water. Natural gas from northern Pennsylvania was burned in air of such low humidity that any admixture of the water formed with ordinary water was negligible. After careful purification by standard methods, the samples of water were treated with a small amount of barium hydroxide and twice distilled in vacuum.

The final distillation in vacuum in which the water was evaporated without ebullition and passed through a meter of tubing to the measuring cell was found to effect considerable separation of the isotopic species present. The vacuum distillations were therefore carefully controlled and the densities measured were corrected to correspond to the rejection of equal light and heavy fractions. The corrections were all less than four parts in ten million. The vacuum distillation train was constructed with traps which could be closed by freezing plugs of ice in them so that the water which was measured came in contact with nothing but Pyrex glass. In the distillations at atmospheric pressure care was taken to reject small, nearly equal, light and heavy fractions.

Densities were measured by determining the pressure required for floating equilibrium of a thick-walled Pyrex float at 3.98°. The float was calibrated by means of a small glass rider. Pressure was applied through water-filled capillaries to avoid the solution of air in the sample being measured. In twelve experiments to determine the equilibrium pressure in a standard sample prepared from Cambridge tap water the average deviation from the mean was equivalent to an error of one part in ten million in the density. Our method resembles that used by Gilfillan in determining the isotopic composition of sea water [E. S. Gilfillan, THIS JOURNAL, **56**, 406 (1934)]. In essential agreement with his results we found surface sea water collected a mile off shore at Gloucester, Mass., to have a density greater than Cambridge tap water by 1.8 p. p. m.

The water from the corn oil proved to have a density greater than ordinary water by 4.9 ± 0.1 p. p. m. (two experiments) and that from natural gas, a density greater by 5.7 ± 0.3 p. p. m. (four experiments).

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RECEIVED JUNE 25, 1934

NEW BOOKS

Annual Survey of American Chemistry. Vol. VIII, 1933. Edited by CLARENCE J. WEST, Director, Research Information Service, National Research Council. Published for National Research Council by The Chemical Catalog Company, Inc., 330 West 42d Street, New York, N. Y., 1934. 403 pp. 13.5 × 21.5 cm. Price, $4.50.

The method adopted in reviewing the recent literature is the same as that used in the last volumes of the Annual Survey. The authors are well known in their several fields and have described the new work as fully as is possible in the limited space available. The policy adopted last year of covering only a part of the published work makes it desirable to list the fields reported on in the present volume. They are as follows: Theories of Solutions, Kinetics of Homogeneous Gas Reactions, Subatomic Phenomena, Thermodynamics and Thermochemistry, Colloids, Contact Catalysis, Structure Determination by X-Ray and Electron Diffraction, Electrochemistry, Analytical Chemistry, Compressed Gases, Aliphatic Compounds, Carbocyclic Compounds, Heterocyclic Compounds, Pharmaceuticals, Biochemistry, Ferrous Metals in 1932 and 1933, Insecticides and Fungicides, Chemistry of the Silicates, Ceramics, Petroleum Chemistry and Technology, Cellulose and Paper, Leather, Paints, Rubber, Gaseous Fuels During 1932 and 1933. The book continues to be of great value to one who desires to obtain in a short time a general view of the advances made in Chemistry in America. It is also of value to the specialist as a source of references.

JAMES F. NORRIS

Manuel de Chimie Analytique Qualitative Minérale. (Manual of Inorganic Qualitative Analysis.) By P. WENGER, D.Sc., Professor of Analytical Chemistry, and G. GUTZEIT, Lecturer, University of Geneva. Librairie Georg et Cie., Genève, 5, Corraterie, Switzerland, 1933. 496 pp. 13 × 19.5 cm. Price, argent Suisse frs. 16.

This manual is similar in arrangement to most of the American texts but is much more extensive. The first part is devoted to a brief discussion of the fundamental principles of general chemistry. The second part gives the most important characteristic reactions, with the equations, of the common cations and anions, and also those for the rare metals. The third part of the book is devoted to the systematic analysis of materials, including the different types of preliminary tests. Tables, showing the procedure for the detection of the common cations and anions, are also included. The last part is devoted