acid, ketene dimer and traces of ketene. The statement regarding ketene dimer should be withdrawn for it has not been possible to obtain this substance from acetylphthalimide in subsequent experimentation. The volatile products found were acetic acid, acetic anhydride, acetone and a small quantity of ketene.

This aligns acetylphthalimide with propionyl-, *n*-butyryl- and caproylphthalimides (all $C_6H_4(CO)_2N—COCH_2R$), all of which give rise on pyrolysis to phthalimide, the acid RCH_2COOH or its anhydride, and the ketone $(RCH_2)_2CO$. In contrast, isobutyryl- and diphenylacetylphthalimides (both $C_6H_4(CO)_2N—COCHR_2$) pyrolyze satisfactorily to ketenes, $R_2C=C=O$.

For a time it was considered that the non-production of ketene dimer from acetylphthalimide (dried as before by the toluene distillation method) was due to moisture. The same results were produced, however, on acetylphthalimide which was dried in a desiccator over phosphorus pentoxide for ten months.

Ethyl acetate was found to be an excellent solvent from which to crystallize acetylphthalimide. After such a purification it was dried thoroughly as mentioned above and 50 g. of it subjected to pyrolysis. In the 6 g. of distillate which was collected during two hours there was found 1.0 g. of acetone (b. p. 56–60°, soluble in water and identified by converting to dibenzylideneacetone of m. p. 111–112°), 1.1 g. of acetic anhydride (analyzed by the method of Whitford[2] with oxalic acid and pyridine), and 3.4 g. of acetic acid. The total acidity (acetic acid + anhydride) was 4.5 g. The distillate reacted with aniline to produce acetanilide, m. p. 112–113°. If acetoacetanilide was present also its quantity was too small for identification. Evidence for ketene was found by condensing the liquid products at 0° and passing the vapors into aniline. The yield of acetanilide was 0.4–0.5 g.

The above experiment was representative of several which were performed. Variations included the manner of drying, the size of the run (up to 108 g.) and the manner of heating (free flame or salt-bath so that the temperature within the flask ascended gradually from 220 to 325°). The results were essentially the same in all.

Summary.—The volatile products from the pyrolysis of acetylphthalimide are acetic acid, acetic anhydride, acetone and a small quantity of ketene. No significant amount of ketene dimer was produced.

[2] Whitford, This Journal, 47, 2939 (1925).

CHEMICAL LABORATORY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS
RECEIVED FEBRUARY 28, 1935

COMMUNICATIONS TO THE EDITOR

COPPER SULFIDE–WATER CONTACT ANGLES

Sir:

Evidence has been obtained in this Laboratory which indicates that the presence of an adsorbed air film is the most probable cause of the contact angle of water with copper sulfide. Wark [Wark and Cox, *Am. Inst. Min. Met. Eng.*, Tech. Pub., No. 461 (1932)] has shown that a copper sulfide surface that has been ground under water exhibits no contact angle with water. If such a polished surface is exposed to air the contact angle with water assumes a definite value.

If a copper sulfide, covellite, surface is ground under water, such a surface has a zero contact angle with water; exposed to air this surface gives a definite contact angle with water. However, when such a specimen is put into a vessel in contact with water and the water is completely removed by evaporation at reduced pressure, the specimen being finally subjected to gentle warming while the container is evacuated, it is found that the surface again exhibits a zero contact angle with water. Further, when the water is again removed from the copper sulfide and air let into the vessel, the contact angle with water is again developed. Preliminary experiments with copper xanthate indicate a similar characteristic behavior.

Further work along these lines with liquids known to give contact angles with certain similar solids is planned.

DEPARTMENT OF CHEMISTRY
MICHIGAN COLLEGE OF
MINING AND TECHNOLOGY
HOUGHTON, MICHIGAN
C. C. DE WITT

RECEIVED APRIL 11, 1933

SURFACE PRESSURES AND POTENTIALS OF MONOMOLECULAR FILMS OF LONG MOLECULES: POLYMERS OF ω-HYDROXYDECANOIC ACID

Sir:

Remarkable relations are exhibited by films of linear polymers of the formula $HO[(CH_2)_9COO]_x H$ with molecular weights as high as 25,200 and values of x to 148 as obtained from Drs. W. H. Carothers, E. O. Kraemer and F. J. Van Natta [Kraemer and Van Natta, *J. Phys. Chem.*, **36**, 3175 (1932); Carothers and Van Natta, THIS JOURNAL, **55**, 4714 (1933)].

The most prominent characteristics are listed with specific values which refer to condensed films under a pressure of 3 dynes per cm. unless otherwise stated.

1. Thickness of films from 4.0 to 5.0 Å.
2. Distance between centers of adjacent chains 4.0 to 4.8 Å.
3. Apparent vertical cross section of molecule 19.4 to 19.9 sq. Å., or nearly the same as the horizontal cross section (20.5) of molecules, such as stearic acid, oriented vertically.
4. The area (a) per molecule in condensed films is nearly proportional to the molecular weight at any given film pressure (f).

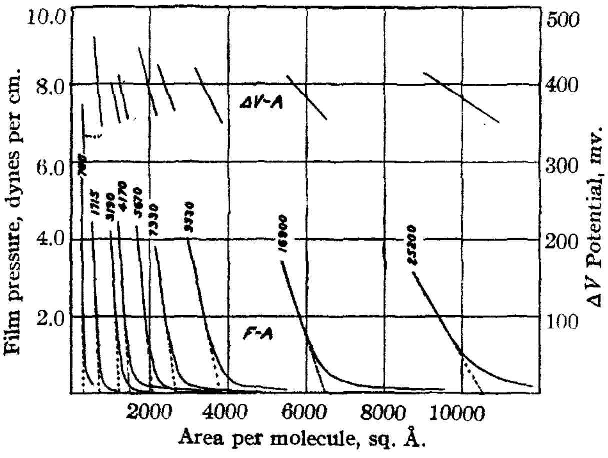

Fig. 1.—Film pressures and surface potentials for linear polymers of ω-hydroxydecanoic acid.

5. The compressibility is very large, since the value of $[(a_0 - a_1)/a_0]/(f_1 - f_0)$ lies between 0.040 and 0.053, and is almost independent of molecular size. Similar values for vertically oriented molecules are in general only one-tenth to one-sixtieth as large.

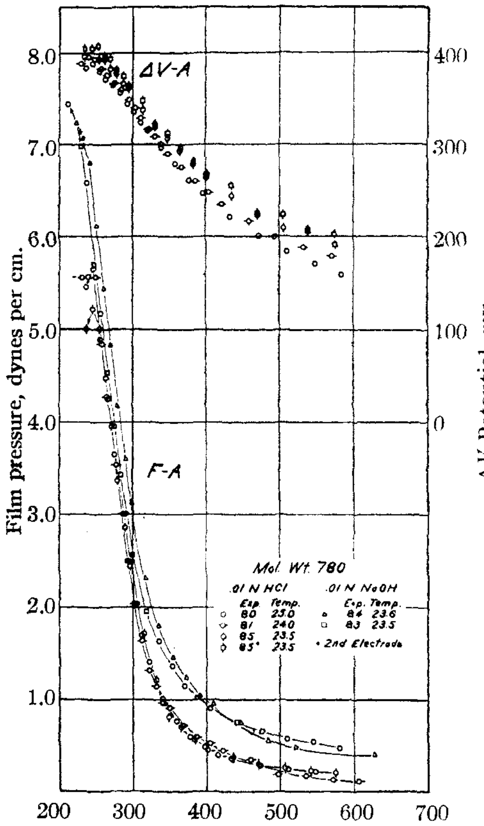

Fig. 2.—Values for polymer of molecular weight 780.

6. The pressure of collapse on 0.01 *M* hydrochloric acid increases from 3.2 to 5.7 dynes as the molecule becomes shorter, and after collapse the pressure decreases rapidly for a time. On 0.01 *M* sodium hydroxide the pressure of collapse is higher.
7. At pressures below 1.3 to 2 dynes the films are "expanded," with considerably higher molecular areas if spread on a base than if on an acid aqueous solution.
8. The surface potential (ΔV) of any one of the condensed films increases about 13% less rapidly than the surface density of the film. Thus the surface potential seems to increase with and nearly as the number of polar groups per unit area. However, the mutual effect of the dipoles is such as to decrease the potential.
9. At low pressures the expanded films become nonhomogeneous, since the surface potential varies with the location on the surface. This island effect is much more prominent for polymers of high than for those of low molecular weight.
10. The molecular area of the compound of molecular weight 25,200 is 10,400 sq. Å. for zero pressure, or 8800 sq. Å. at 3 dynes per cm. pressure. This is the largest area thus far found for any molecule.

TABLE I

FILMS OF POLYMERS OF ω-HYDROXYDECANOIC ACID ON WATER

Mean values at temperatures from 21.5 to 26.0°. Concentration of hydrogen chloride in the water 0.01 *M*
Columns 2 and 3 are taken mostly from the paper of Carothers and Van Natta

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Mol. wt.	Density d^{25}_4	Length of molecule in Å.	Vol. of molecule in cu. Å.	Area per molecule at a film pressure			Maximum force f_m	t = thickness of film at a film pressure			d = width of molecular space at			$f \times d$ molecular cross sect. at 3 dynes in sq. Å.	Compressibility of $f=0$
				$f=0$	$f=3$	$f=$ max.		$f=0$	$f=3.0$	$f=$ max.	$f=0$	$f=3.0$	$f=$ max.		
780	1.0957	60	1170	330	290	246	5.7	3.6	4.0	4.8	5.5	4.8	4.1	19.5	0.040
1715	1.0935	133	2590	700	604	556	4.5	3.7	4.3	4.7	5.3	4.5	4.2	19.4	.046
3190	1.0877	248	4840	1260	1080	970	4.2	3.9	4.5	5.0	5.1	4.4	3.9	19.6	.048
4170	1.0814	324	6360	1490	1300	1130	4.5	4.3	4.9	5.6	4.6	4.0	3.5	19.6	.043
5670	1.0751	440	8700	2050	1800	1688	4.4	4.2	4.8	5.2	4.7	4.1	3.8	19.7	.041
7330	1.0715	570	11330	2670	2277	2180	3.8	4.2	5.0	5.2	4.7	4.0	3.8	19.9	.049
9330	1.0668	730	14450	3800	3200	3000	4.0	3.8	4.5	4.8	5.2	4.4	4.1	19.8	.053
16900	1.0627	1320	26200	6440	5510	5270	3.4	4.1	4.8	5.0	4.9	4.2	4.0	19.9	.048
25200	1.0621	1970	39100	10430	8800	8700	3.2	3.8	4.4	4.5	5.3	4.5	4.4	19.9	.052

These relations, particularly 1, 2, 3, 4, 5 and 10, show conclusively that the molecules of these polymers lie flat on the surface. The molecules are anchored in this position by the polar groups at the ends and at every tenth carbon atom. Thus the molecule acts as a type of centipede, with as many as 149 regions of attachment.

The general relations are exhibited by Table I and Figs. 1, 2 and 3.

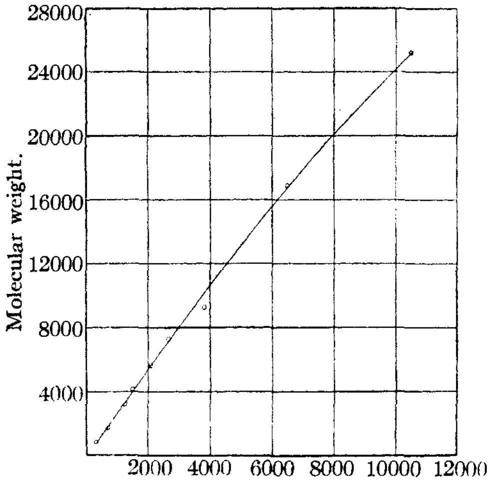

Fig. 3.—Surface area as a nearly linear function of the molecular weight.

The work given here was begun in this Laboratory by Dr. E. H. Fischer.

GEORGE HERBERT JONES CHEMICAL LABORATORY
UNIVERSITY OF CHICAGO
CHICAGO, ILL.

WILLIAM D. HARKINS
HERMAN E. RIES, JR.
EVERETT F. CARMAN

RECEIVED MARCH 4, 1935

d-GULO-METHYLOSE (6-DESOXY-*d*-GULOSE) AND ITS RELATION TO A REPORTED INVERSION PRODUCT OF *l*-RHAMNOSE

Sir:

We wish to report the synthesis of a new methyl pentose, *d*-gulo-methylose (6-desoxy-*d*-gulose) by use of the cyanhydrin reaction on *d*-xylo-methylose (5-desoxy-*d*-xylose) [Levene and Compton, *Science*, **81**, 156 (1935)], followed by reduction of the lactone with Na–Hg amalgam in the usual manner. The physical constants of this substance along with several derivatives are recorded below.

Substance	M. p., °C.	$[\alpha]_D$	Solvent
(1) *d*-Gulo-methylose	Glassy solid	−35.7° (constant)	water
a (substance of Muskat	amorphous solid *ca.* 65	+14° → −14°	water)
(2) *p*-Bromophenylhydrazone of (1)	135	−16.1° → +9.2°	ethanol
a (substance of Muskat [1a]	162	− 6.1 → +13°	ethanol)
(3) *p*-Bromophenylosazone of (1)	195–196	±0.00° → 15.3°	pyridine–ethanol 3:2
(4) *d*-Gulo-methylonic lactone	180–181	−68.0°	water
(5) *p*-Bromophenylhydrazide of (4)	132–133	+8.83°	water
(6) *d*-Gulo-methylonic acid	—	−5.00°	water
(7) Sodium salt of (6)	—	+11.03°	water

The synthesis was undertaken for the purpose of testing the claim of Dr. I. E. Muskat [THIS JOURNAL, **56**, 2653 (1934) (this article, although published as a contribution from the Laboratories of the Rockefeller Institute for Medical Research, was never seen prior to publication by the senior author of this Communication)] that a Walden inversion occurred during the alkaline hydrolysis of 5-*p*-toluenesulfonyl-2,3-acetone methylrhamnofuranoside. A comparison of the properties of the free sugar and its derivatives prepared by Muskat with those of the newer substances reported above shows clearly that the product obtained by this author is not *d*-gulo-methylose.

It may be added that Dr. A. L. Raymond of this Laboratory has failed to observe a Walden inversion in the cases of 3-*p*-toluenesulfonyl diacetone glucose and 3-*p*-toluenesulfonyl-5-methyl monoacetone xylose.

THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH
NEW YORK, N. Y.
P. A. LEVENE
JACK COMPTON

RECEIVED MARCH 11, 1935

6-DESOXY-*d*-GULOSE*

Sir:

In the preceding note P. A. Levene and Jack Compton [THIS JOURNAL, **57**, 777 (1935)] present some data on a supposed 6-desoxy-*d*-gulose which they have prepared. The properties of this substance seem to differ from an inverted compound previously obtained by this author.

While at the Rockefeller Institute as a National Research Council fellow, I studied, independently, the mechanism of Walden inversion of sugars. As a result of theoretical considerations it was decided to investigate the alkaline hydrolysis of two *p*-toluenesulfonyl esters of rhamnose. It was definitely established that an inversion occurred during the hydrolysis of both sugars. No effort was made to determine the structure of the inverted product, for neither of the sugars nor derivatives isolated in this work had been previously prepared. Insufficient material was available to determine the structures by other than empirical and, therefore, unreliable means. The inverted sugar obtained from the rhamnofuranoside was *assumed* to be 6-desoxy-*d*-gulose since it was not clear how any other product could be formed under the particular conditions of the experiment. I may mention here that in the original paper as sent to the Journal this fact was clearly stated, but due to the necessity of limiting its size, it was inadvertently omitted in the final paper. Consequently, it is true that the author did not definitely establish the identity of the inverted product as 6-desoxy-*d*-gulose.

An examination of the evidence presented by Levene and Compton for the structure of their product reveals the following facts. Their starting material, 5-desoxy-*d*-xylose, is a sirup. This was treated with hydrogen cyanide, hydrolyzed to a lactone, and then reduced to the aldose sugar. It may be well to point out that two different sugars, each having two forms (furanose and pyranose) may result from such reactions. In other words, any or all of *four* different compounds may have composed the final product. Levene and Compton must have overlooked this simple fact, since they present no evidence that the sugar they have obtained is a 6-desoxy-*d*-gulose. Of course the rotations of the lactone and of its bromophenylhydrazide may be taken as indications of such a structure, but insufficient work has been done on these particular sugars to use such empirical rules as anything but supporting data. Consequently, Levene and Compton do not know the structure of their sugar and their criticism is therefore invalid. From the data they present it may be that they have an entirely different sugar or simply an impure form of 6-desoxy-*d*-gulose.

Levene and Compton state that "A. L. Raymond of this Laboratory has failed to observe a Walden inversion in the cases of 3-*p*-toluenesulfonyl diacetone glucose and 3-*p*-toluenesulfonyl-5-methyl-monoacetone xylose." The author wishes to call their attention to page 2653 of his article in which it is stated "It is not suggested that a Walden inversion will necessarily occur in all reactions of type (II)," and on page 2654, "Whether an inversion will or will not occur, and if it will, to what extent, will depend on the steric effects in the sugar molecule and the experimental conditions." It may be that no inversion has occurred in these two sugars or, as Levene and Compton so aptly put it, "Raymond has *failed* to observe it."

MELLON INSTITUTE
PITTSBURGH, PA.
IRVING E. MUSKAT

RECEIVED MARCH 21, 1935

THE ALLEGED ISOTOPIC INTERCHANGE BETWEEN WATER AND ACETYLENE

Sir:

It has recently been reported [L. H. Reyerson and S. Yuster, THIS JOURNAL, **56**, 1426 (1934)] that an isotopic interchange takes place between water and acetylene in alkaline solution. Experiments in this Laboratory have failed to give any in-

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* This letter was received prior to the addition of items six and seven to the table in the preceding communication—EDITOR.

dication of such an interchange, even under conditions more drastic than those previously employed.

Each experiment was carried out with 10–15 cc. of water containing about 1.5 mole per cent. of deuterium. The density was determined pycnometrically with an accuracy of 0.002%, so that interchange of hydrogen to an extent of 2% could have been detected with certainty. The acetylene was prepared from calcium carbide and purified by passing through solutions of sodium hydroxide and chromic acid; it was passed continuously through the solutions being investigated at about 500 cc. per hour. In the experiments at 76° the evaporation loss was reduced to less than 5% by a reflux condenser. After removing the acetylene by a current of air or carbon dioxide the solutions were distilled at least twice *in vacuo* at 40–50°, and the density determined. The density was in each case unchanged by repeated distillation, provided that the whole of the water was distilled over. The following experiments were carried out:

N NaOH	Acetylene passed 11 hours at 0°
Pure water	Acetylene passed 5 hours at 76°
N NaCl	Acetylene passed 5 hours at 76°
0.01 *N* $Ba(OH)_2$	Acetylene passed 3.5 hours at 76°
0.1 *N* $Ba(OH)_2$	Acetylene passed 5 hours at 76°
0.5 *N* $Ba(OH)_2$	Acetylene passed 9.5 hours at 76°

In no case was any change in isotopic composition observed. (The hydrogen contained in the hydroxides was taken into account in calculating the original composition.)

These results are completely at variance with those of Reyerson and Yuster, who obtained about 50% interchange on treating *N* sodium hydroxide with acetylene for eight hours at 0°. It is difficult to suggest an explanation for this discrepancy.

PHYSICAL CHEMISTRY LABORATORY R. P. BELL
BALLIOL COLLEGE AND TRINITY COLLEGE
OXFORD, ENGLAND

RECEIVED MARCH 8, 1935

THE ISOTOPIC INTERCHANGE BETWEEN ACETYLENE AND HEAVY WATER

Sir:

Dr. R. P. Bell was kind enough to send me a copy of the communication to the Journal concerning his failure to obtain the isotopic interchange between acetylene and heavy water which we previously had reported. In answer to the question raised by Dr. Bell, I wish to report that under the conditions of our experiments there is no question but that the isotopic exchange takes place. Since our previous publication several equilibrium studies of this reaction have been completed in this Laboratory. They have been carried out at 0, 25 and 100° in closed systems using various pressures of acetylene which was prepared by the action of carefully distilled water on very pure calcium carbide, the acetylene being further purified. The concentrations of deuterium in the water used varied from about 9 to 18%. Except for a small temperature coefficient the equilibrium constants checked excellently. This work is being written up for a lengthier publication on the subject. In addition to the above evidence Mr. A. O. Nier working in Professor J. T. Tate's laboratory in physics has completed an analysis of the products of one of our equilibrium studies by means of the mass spectrograph. He reports that about 10% of the gas submitted for analysis consisted of C_2HD. This checks very well the value calculated from the density change in the water as determined in this Laboratory.

Dr. Bell states in his communication that his experiments were carried out under more drastic conditions than those reported by us. This does not seem to be borne out by the facts. The concentration used in our solutions was from six to eight times as great, and the rate of passage of the acetylene through the solution was approximately seven times as great as that reported by Dr. Bell. Since all but one of his reported experiments were carried out at 76° it must be he considered this to be more drastic treatment. However, in order for the exchange to occur the acetylene must dissolve in the solution and then ionize. The solubility of acetylene is much less at 76° than at zero so that the chance for exchange is thereby reduced. A simple calculation from our equilibrium constant values obtained for the reaction

$$C_2H_2 + HDO \rightleftharpoons C_2HD + H_2O \text{ at } 0°\text{C.}$$

shows that the amount of exchange with 1.5% deuterium should be very small, even under equilibrium conditions, conditions which are obviously not reached by bubbling the gas through the solution for the length of time reported. It seems therefore that Dr. Bell did not lose sufficient deuterium from the water to detect it by the technique he employed. Dr. Yuster in a private communication to the author suggested a further possibility for Dr. Bell's failure to observe the exchange. All of our studies have been carried out in Pyrex glass systems so that there is undoubtedly some borate present in the alkaline solutions. If Dr. Bell's studies were carried out in soft glass then it is possible that the borate acts as a catalyst in the rapid establishment of exchange equilibrium while the soluble substances from soft glass do not act as efficiently.

UNIVERSITY OF MINNESOTA L. H. REYERSON
MINNEAPOLIS, MINN.
RECEIVED MARCH 23, 1935

CONCENTRATION OF TRITIUM (H^3)

Sir:

About a year ago detection of the hydrogen isotope of mass 3 in substantially protium-free deuterium was reported by Lozier, Smith and Bleakney [*Phys. Rev.*, **45**, 655 (1934)]. At that time the tritium concentration was estimated as 5 in 10^6 after the initial volume of ordinary water had been reduced by electrolysis to 1 part in 225,000. Electrolysis has been continued during the past year until the volume has now been reduced to 1 part in 150,000,000. That is, approximately 75 metric tons of ordinary water have been electrolyzed down to 0.5 cc. During this time the tritium concentration as determined by the mass spectrograph has increased to about 1 in 10^4. We are now in a position to obtain the ratio of specific discharge rates of deuterium and tritium, and to estimate the abundance of tritium in nature.

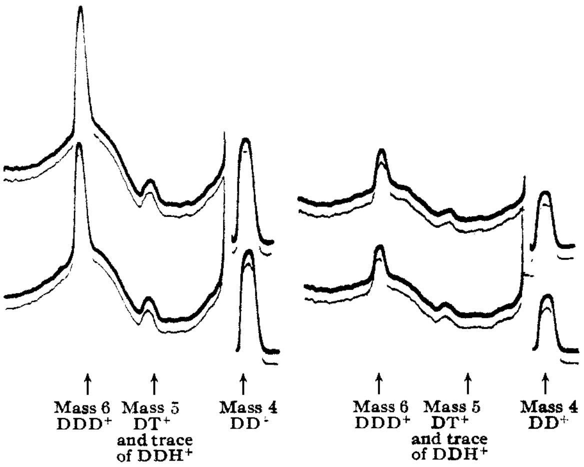

Fig. 1.

The discharge ratio (α_T^D) for deuterium and tritium may be obtained by graphical integration of the total tritium evolved during substantially complete electrolysis of a given sample of protium-free deuterium oxide. The value so obtained is 2.0, in good agreement with the theoretical prediction of Eyring [*Scientific Monthly*, **39**, 415 (1935)]. We have the relation $\alpha_T^H = \alpha_T^D \cdot \alpha_D^H$, and as α_D^H averages about 6 in the Princeton heavy water plant, α_T^H = about 12. In estimating the abundance of tritium in nature it must be borne in mind that during the earlier part of electrolysis, tritium is concentrated chiefly with respect to protium, but during the latter part entirely with respect to deuterium. For the purpose of making a rough computation we assume that α changes from 12 to 2 when the H:D ratio is 1–1. The abundance of tritium in ordinary water is then 7 in 10^{10}.

Figure 1 shows the intensities, recorded automatically, of the ions of masses 6, 5 and 4, the latter on a much reduced scale owing to its great abundance in the mixture. The intensities in the left half of the diagram are at a greater pressure than those on the right. From the pressure influence thus examined over a series of pressures we find that the intensity due to the ion of mass 6 varies as the square of the pressure. It is therefore triatomic and must be DDD^+. The ion of mass 5 varies in intensity nearly directly with the pressure and must therefore be mainly diatomic and hence DT^+. It is from the plot of the intensity–pressure ratio against pressure that, as has been previously described, the atomic content of tritium is deduced. Our results show that by further electrolysis of the deuterium oxide preparations now produced in commercial quantities both in this country and Europe, residues rich in tritium can readily be assembled without significant loss of deuterium since the electrolytic gas so produced can be recombined to yield deuterium oxide from which the tritium has been partially removed.

FRICK CHEMICAL LAB. P. W. SELWOOD
PALMER PHYSICAL LAB. H. S. TAYLOR
PRINCETON UNIV. W. W. LOZIER
PRINCETON, N. J. WALKER BLEAKNEY
RECEIVED MARCH 22, 1935

DEVELOPMENT OF AN AIR-DRIVEN ULTRACENTRIFUGE

Sir:

Up to last summer, Svedberg alone had produced convectionless centrifuges whose contents could be submitted to optical observation while in motion. In 1931, we undertook at Stanford the task of developing the air-driven spinning top of Henriot and Huguenard [*Compt. rend.*, **180,** 1389 (1925); *J. Phys. Radium*, **8,** 433 (1927)] as a Svedberg ultracentrifuge, of equal power and possibilities but at an expense so low as to make it fairly generally available. Out of many designs, two may be mentioned here. With the latter we are able to obtain sedimentation velocity measurements similar to that illustrated in the accompanying photograph, which shows all four characteristic features of such measurements.

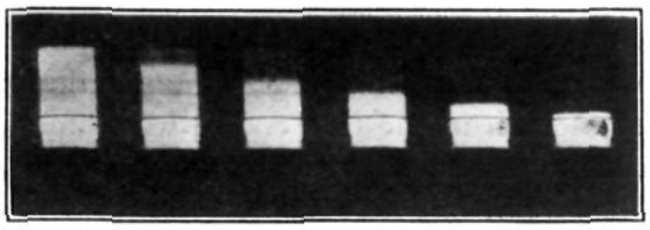

Fig. 1.

An essential part of both designs is that a stationary periscope reaches through a hole in the hollow conical base of the steel rotor and serves to pass light of any desired wave length in the visible or ultraviolet through the cell to a camera. The rotor revolves around the periscope, driven by air supplied at constant pressure and adjusted temperature. The speed of rotation is very accurately measured by beating the note produced by the top either directly or with the assistance of a photoelectric cell against a standard variable oscillator. Speeds are limited solely by the strength of the strongest materials available.

The former cell consists of two disks of crystalline quartz 30 mm. in diameter made water-tight by an expanding rubber seal between them stretched over a baffle plate of hard rubber in which sectorial openings contain the liquid. A fortunate accident enabled us to observe the sedimentation velocity of a boundary in aqueous solution of mercuric chloride: $S = 0.891 \times 10^{-13}$ cm./sec./dyne; theory $= 0.890 \times 10^{-13}$.

The latter cell is of a Svedberg type, about one quarter of the size of his, but with a more homogeneous centrifugal field (14% compared with 20%). It fits into a hole in the steel rotor. The photograph refers to the respiratory protein of the blood of the earthworm at 2020 r. p. s. at 22.5°: $S = 72 \times 10^{-13}$.

In the photograph, the uppermost light portion is oil resting on the solution (5% blood of *lumbricus terrestris* in 1% potassium chloride). There is but one boundary and the solution beneath is homogeneous, indicating only one size of protein particle. The boundary becomes blurred with time through diffusion and the solution below becomes more dilute through radial expansion and increasing velocity. The immobile streaks were due to a smear of cement.

An elegant alternative solution is that of Beams and Pickles recently communicated to *Science*. They have sedimented diluted human blood (not hemoglobin itself).

We envisage four different fields for the air-driven ultracentrifuge. First, that of Svedberg above, applicable to all molecules. Second, immobilized systems in the hollow spinning top perfected by Henriot and Huguenard (see letter recently submitted to *Nature* on the many kinds of measurement so afforded). Third, sedimentation of the Bechhold type in the hollow top. This is presumably the kind of sedimentation we have observed with hemoglobin, methylene blue, etc., during the past few years. Fourth, convectionless sedimentation in a mechanically immobilized liquid of any kind (including for example virus, phage or sucrose).

DEPARTMENT OF CHEMISTRY JAMES W. MCBAIN
STANFORD UNIVERSITY CARROLL M. O'SULLIVAN, S.J.
STANFORD UNIV., CALIF.

RECEIVED MARCH 23, 1935

RADIO-CESIUM ACTIVATED BY NEUTRONS

Sir:

All cases of radioactivity induced by neutron bombardment which have been investigated have been shown to be β-activity. However, it seemed possible that radio-cesium might be an exception to the rule and emit a positron since the emission of an electron would result in the formation of Ba^{134} which apparently does not exist in nature, while the emission of a positron would form a known isotope of xenon, Xe^{134}. The cesium case is also simplified by the fact that it has only one isotope, 133, and that the observed activity, of 100 minute half-life, is hydrogen sensitive, *i. e.*, is due to the capture of a slow neutron. We have therefore determined the sign of the particle and have found that in this case too it is an electron. The measurements were made with a screen-wall Geiger-Müller counter by bending the particles around a lead shield 5 mm. thick with a field of 5000 gauss. The observed effect decayed with a half-life of 80–100 minutes, and we also find the activation greatly increased by a hydrogenic environment.

Since the Ba^{134} resulting from the decomposition is not found by mass spectrum analysis, it may be presumed to be unstable. However, we have added a small amount of barium to cesium nitrate activated by neutrons and upon precipitating the barium chemically, have found that the barium shows no activity of half-lives between ten minutes and three days. Chemical separations also show the absence of radio-iodine or radio-xenon.

We are indebted to Dr. L. R. Taussig and the University of California Hospital for 150 millicuries of radon used in the experiments.

DEPARTMENT OF CHEMISTRY W. M. LATIMER
UNIVERSITY OF CALIFORNIA D. E. HULL
BERKELEY, CALIFORNIA W. F. LIBBY

RECEIVED MARCH 25, 1935

THE REACTION OF FLUORINE WITH NITRIC ACID AND WITH SOLID POTASSIUM NITRATE TO FORM NO_3F

Sir:

Cady [THIS JOURNAL, **56**, 2635 (1934)] has recently discovered that when fluorine is bubbled through 3 N nitric acid, the remarkable compound NO_3F is formed. Through Dr. Cady's kindness his apparatus was made available to us and we have repeated the preparation. The resulting material has all the properties described by him. It boils at about −42°, it liberates iodine from iodides and, in the gaseous form, it explodes when heated to some 200 or 300°.

We have found that NO_3F reacts very slowly with VO^{++} to give vanadic acid, and that no appreciable reaction takes place with Mn^{++} in 6 N H_2SO_4, as judged by color changes. When, however, the gas is brought in contact with solutions of silver nitrate, a black precipitate (Ag_2O_3) forms at once. Mixtures of Mn^{++} and Ag^+ in 6 N H_2SO_4 reacted with the NO_3F to give permanganate. The reaction with silver ion is convenient for testing purposes if ozone and OF_2 are known to be absent.

We have also found that fluorine reacts readily and efficiently with solid potassium nitrate to form a substance that appears to be NO_3F. The gas explodes on heating, it reacts with iodide ion and silver ion in the manner described above, and the boiling point agrees, qualitatively, with that given by Cady for NO_3F. Twenty cc. of the substance in the liquid state (at −79°) was prepared. By allowing it to boil at atmospheric pressure for a time it was freed from any of the more volatile impurities. The vapor, at atmospheric pressure, was then passed through dilute nitric acid to remove any hydrolyzable impurities. It was then distilled from a trap cooled to −78° into a trap immersed in liquid air. The resulting material had, when molten, and unlike the material prepared from nitric acid, a very slightly yellowish color. Due to some other substances, or to a slow decomposition, an apparently constant pressure of from 5 to 10 mm. developed above the material cooled with liquid air, even after repeated pumping. The solid material, while under vacuum in the trap cooled with liquid air, eventually exploded very violently (danger!), and for no obvious reason.

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RECEIVED MARCH 25, 1935

1,2-BENZPYRENE

Sir:

In preparing a quantity of 1,2-benzpyrene required in a study which is being carried out in collaboration with the Office of Cancer Investigations, U. S. Public Health Service, the synthesis of Cook and Hewett [*J. Chem. Soc.*, 398 (1933)] has been modified to advantage in certain details, the over-all yield from pyrene being 36%.

The condensation of pyrene (0.6 mole) with succinic anhydride (0.72 mole) in nitrobenzene solution (600 cc.) with aluminum chloride (190 g.) was carried out as described [THIS JOURNAL, **54**, 4351 (1932)] for the similar condensation of acenaphthene. Sodium β-1-pyrenoylpropionate was collected after one crystallization and washed free of tars with alcohol and ether. The material was directly pure and suitable for reduction; yield 90–94%. The method of reduction of Cook and Hewett was not improved in yield (71–75%, pure), but the process was simplified. After acidifying the solution of γ-1-pyrenylbutyric acid, the suspension was heated at the boiling point for one hour to dehydrate the hydroxy acid and give a granular product. This was extracted with hot sodium bicarbonate solution, then with cold soda solution, and the combined filtrates were acidified and digested. The crude acid (m. p. 181–183°) was crystallized once from xylene (m. p. 187–188°).

For the ring closure, 50 g. of the pure acid was suspended in 0.5 liter of dry ether with 75 cc. of thionyl chloride, and pyridine (3 drops) was added. In one to two hours (25°) the acid had dissolved and the solution, filtered if necessary, was concentrated at the pump with gentle warming. The acid chloride, which soon solidified, was freed of reagent by adding and evaporating portions of ether, breaking the lumps and evacuating. A solution of the gray solid in 0.5 liter of carbon disulfide was cooled in ice and treated with 25 cc. of stannic chloride in 25 cc. of solvent, when the solution slowly deposited a purplish-red complex. After three hours at 0°, the mixture was refluxed for three hours, decomposed with ice and acid and steam distilled. The yellow solid was extracted with glacial acetic acid from some dark tar and precipitated with water. The ketotetrahydrobenzpyrene was bright yellow, m. p. 169–171°, and suitable for further use; yield, 37.5–39.5 g. (80–84%).

The ketone was reduced in yields of only 40–55% with hydrazine and sodium ethylate, through the semicarbazone, or by the Clemmensen method using alcohol, acetic acid or (best) dioxane. The best method was by hydrogenation in alcohol at 200° and 3000 lb. pressure with copper chromite catalyst, the yield of distilled material (m. p. 98–101°) suitable for dehydrogenation being 84%. 1′,2′,3′,4′-Tetrahydro-1,2-benzpyrene crystallizes from alcohol as faintly yellow plates, m. p. 113° (calcd.: C, 93.71; H, 6.30. Found: C, 93.66; H, 6.49); picrate, red needles, m. p. 166° (calcd.: N, 8.66. Found: N, 8.44).

The crude tetrahydride (8 g.) was dehydrogenated with selenium (14 g.), added in 3 portions, at 330° for thirty-six hours. The product was extracted with benzene, distilled (6.8 g., m. p. 168–170°), and crystallized from glacial acetic acid, giving 5.5 g. of 1,2-benzpyrene, m. p. 176–176.5° and, from the mother liquor, 0.7 g. of material, m. p. 172–173°; yield, 79%. Mixtures of 1,2-benzpyrene and its tetrahydride are not easily separated by crystallization, but such material can be purified with little loss by further treatment with selenium. Our purest material melted at 176.5–177° and the plates from glacial acetic acid rapidly changed to micro needles on standing with cold acetic acid or alcohol. It is possible that the very active 1,2-benzpyrene preparation of Maisin and Liégeois [*Compt. rend. soc. biol.*, **115**, 733 (1934)] contained the tetrahydro compound as an impurity [compare Winterstein and Vetter, *Z. physiol. Chem.*, **230**, 169 (1934)], and the latter substance is being tested. A rapid method of preparing small amounts of 1,2-benzpyrene (m. p. 174–175°) consisted in the pyrolysis of a mixture of the cyclic ketone (2 g.) with zinc dust (50 g.), covered with zinc dust (50 g.).

Two other hydrocarbons which are being tested were prepared by the reaction of ketotetrahydrobenzpyrene in benzene solution with methylmagnesium iodide. This gave directly 4′-methyl-1′,2′-dihydro-1,2-benzpyrene. The crude material (m. p. 151–153°, 73% yield) was crystallized from dilute acetic acid; pale yellow plates, m. p. 155–156° (calcd.: C, 93.99; H, 6.01. Found: C, 93.82; H, 6.23). Treatment with selenium at 330° gave 4′-methyl-1,2-benzpyrene: large yellow plates, m. p. 217.5–218°, red-yellow fluorescence in concentrated sulfuric acid (calcd.: C, 94.70; H, 5.30. Found: C, 94.68; H, 5.52). The picrate forms dark purplish-brown needles, m. p. 203–204°, from benzene (calcd.: N, 8.49. Found: N, 8.94).

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RECEIVED MARCH 26, 1935