

TABLE I
 ANALYSES OF HYDROGEN AND DEUTERIUM ANALOGS

In order to obtain satisfactory analyses on the acids and anhydrides, only copper oxide was used in the combustion tube, which was twice as long as that ordinarily employed. The combustions were run very slowly.

			Subst., mg.	CO ₂ , mg.	H ₂ O, mg.	% C	% Hydrogen isotopes	% Calcd. as H ₂ O
							($\frac{2.82}{18.82}$)	($\frac{2.02}{18.02}$)
Dimethyl succinate- α - d_2 , α' - d_2	(found)	(I)	4.447	7.84	2.81	48.09	9.47	(7.09)
		(II)	3.922	6.93	2.50	48.19	9.55	(7.15)
	(calcd.)	48.00	9.39	..
Dimethyl succinate	(found)	(I)	4.594	8.29	2.89	49.22	(9.37)	7.04
		(II)	3.692	6.70	2.32	49.48	(9.36)	7.03
	(calcd.)	49.31	..	6.85
							($\frac{3.36}{19.36}$)	
Succinic- α - d_2 , α' - d_2 acid	(found)	(I)	4.200	6.12	2.06	39.74	8.53	(5.45)
		(II)	4.248	6.13	2.03	39.35	8.31	(5.36)
	(calcd.)	39.34	8.24	..
Succinic acid	(found)	(I)	3.728	5.58	1.75	40.82	(8.17)	5.25
	(calcd.)	40.68	..	5.08
								% Calcd. as D ₂ O
							($\frac{4.03}{20.03}$)	
Succinic- α - d_2 , α' - d_2 anhydride	(found)	(I)	4.158	7.05	1.64	46.24	7.92	(4.42)
		(II)	4.120	7.00	1.60	46.33	7.80	(4.36)
	(calcd.)	46.15	7.72	..
Succinic anhydride	(found)	(I)	3.842	6.78	1.41	48.13	(7.37)	4.10
		(II)	3.600	6.35	1.36	48.11	(7.59)	4.22
	(calcd.)	48.00	..	4.00

has been taken as 1.008 and of deuterium as 2.013.⁴

A comparison of the density of a deuterium-containing compound with that of its light hydrogen analog should allow conclusions to be drawn with greater certainty, as in this case the actual figures obtained are free from assumptions regarding the composition of the compounds involved. The succinic acids both decompose appreciably at their melting points into the anhydride and water and so are unsuitable for density determinations, but the dimethyl esters and the anhydrides are amenable to such measurements (Table II) by the methods described in the experimental part.

TABLE II

Compound	d_4^t	Temp., t, °C.
Dimethyl succinate- α - d_2 , α' - d_2	1.1450	20
Dimethyl succinate	1.1185	20
Succinic- α - d_2 , α' - d_2 anhydride	1.2799	131
Succinic anhydride	1.2340	131

The difference in the densities of the hydrogen and deuterium analogs is striking and shows with a fair degree of certainty that deuterium atoms in

(4) Bainbridge, *Phys. Rev.*, **42**, 1 (1932).

methylene- d_2 groups do not readily interchange with hydrogen atoms in other molecules or in other parts of the same molecule. There were three separate times during the transition from ester to anhydride at which interchange might have taken place, namely, shaking with platinum in the presence of ethyl acetate, hydrolysis in the presence of water and nitric acid and interchange with carboxylic hydrogen at the acid stage. Lewis and Schultz⁵ have indicated that the last of these does not take place in the case of acetic acid- d , but other investigations might have led to the belief that interchange was possible during the first and second operations.

On the assumption that the molecular volume of hydrogen and deuterium in organic compounds is essentially the same, it should be possible to evolve a general equation for calculating the density of any deuterium compound provided the density of the hydrogen analog is known. Such an equation follows.

$$d_D = d_H \left[1 + \frac{N_D(1.006)}{M} \right]$$

where d_H is the density of the hydrogen analog, N_D is the number of deuterium atoms in the mole-

(5) Lewis and Schultz, *This Journal*, **56**, 498 (1934).

cule and M the molecular weight of the hydrogen compound.⁶ Density data on deuterium compounds are very scarce; in fact, those for deuterium oxide,⁷ benzene- d_6 ⁸ and deuteriochloroform have been the only ones available for comparison up until this time.

In the following table experimental values and calculated values are given for the five pairs of compounds thus far studied.

Only in the cases of the benzene- d_6 and the deuteriochloroform do the calculated values agree probably within experimental error with the found values. These substances were shown by Raman spectra analyses to be free from hydrogen. One of two conclusions may be deduced from the other results—(1) that the deuterium compounds were not pure or (2) that the replacement of hydrogens in these molecules by deuterium atoms may increase the molecular volume of the com-

TABLE III
CALCULATED AND FOUND DENSITIES OF DEUTERIUM COMPOUNDS

Compound	d_f	Temp., $t, ^\circ\text{C.}$	Calcd.
Benzene ⁹	0.8736	25
Benzene- d_6 ⁸	0.9417	25	0.9411
Chloroform	1.4888	20
Deuteriochloroform ¹⁰	1.5004	20	1.5013
Water	0.9982	20
Deuterium oxide ⁷	1.1059	20	1.1097
Dimethyl succinate	1.1185	20
Dimethyl succinate- α - d_2 , α' - d_2	1.1450	20	1.1493
Succinic anhydride	1.2340	131
Succinic- α - d_2 , α' - d_2 anhydride	1.2799	131	1.2836

pounds. Further experiments must be completed before a decision can be reached. If it could be ascertained that with pure substances the density of a deuterium compound could be predicted, a valuable means would be available for analysis of many unknown deuterium compounds of which the density could be determined and of

(6) This equation is derived in the following manner:

$$V_D = V_H \quad (1)$$

$$d_H = M/V \quad (2)$$

$$d_D = \frac{M + N_D \left(\frac{\text{at. wt. D}}{\text{at. wt. H}} - 1 \right)}{V} \quad (3)$$

$$\frac{d_D}{d_H} = \frac{M + N_D(1.006)}{M} \quad (4)$$

$$d_D = d_H \left[1 + \frac{N_D(1.006)}{M} \right] \quad (5)$$

(7) Taylor and Selwood, *THIS JOURNAL*, **56**, 998 (1934).

(8) Bowman, Benedict and Taylor, *ibid.*, **57**, 960 (1935); see also Brienmeyer, *Helv. Chim. Acta*, **18**, 1464 (1935).

(9) Kallan, *Z. physik. Chem.*, **88**, 67 (1914).

(10) Breuer, *THIS JOURNAL*, **87**, 2236 (1935).

which the density of the hydrogen analog was known.

Of the few crystalline organic molecules containing deuterium that have been examined, it seems to be general that the melting point is lower than that of the light hydrogen analog.¹¹ The following (Table IV) melting points were found for the succinic acid derivatives now being discussed.

TABLE IV
MELTING POINTS OF SUCCINIC ACID AND ITS DERIVATIVES

Compound	d_f compound	Melting Points, $^\circ\text{C.}$ Hydrogen compound
Ester	17.0	18.2
Acid ^{11a}	180.0–180.5	184.5–185.0
Anhydride	119.3–119.6	119.3–119.6

Each melting point quoted is the mean of several observations and the values for corresponding deuterium and hydrogen compounds were taken in the same bath at the same time. No difference could be observed in the melting points of the anhydrides and three mixtures containing varying amounts of the two analogs melted at the same temperature. In the case of the acids, a mixture containing approximately 50% of each melted at 181–184 $^\circ$.

As the two dimethyl succinates are liquids at room temperature, opportunity was taken to measure their refractive indices.

Compound	n_D^{20}	B. P., (743 mm.), $^\circ\text{C.}$
Dimethyl succinate- α - d_2 , α' - d_2	1.4202	195.3
Dimethyl succinate	1.4198	196.0

This relatively small difference in the refractive index values is reflected in the boiling points of the two esters.

Experimental

Methyl Acetylenedicarboxylate.—This diester was prepared by the method of Moreau and Bongrand,¹² b. p. 73 $^\circ$ (4 mm.).

Dimethyl Succinate- α - d_2 , α' - d_2 .—The product from three reductions with practically 100% deuterium, as described below, was filtered from catalyst and the ethyl acetate solvent distilled off under slightly reduced pressure by heating to 50–60 $^\circ$. The remaining yellowish oil could be crystallized by cooling in ice water, but the whole was distilled under reduced pressure before further purification. The boiling point (99.5 $^\circ$ at 25 mm.) was quite constant, and the distillate was a colorless liquid which crystallized

(11) Wilson, *J. Chem. Soc.*, 492 (1935).

(11a) The melting point of succinic acid or the deuterium analog varies considerably, dependent on the conditions used. For the above values, the melting point tubes were immersed in a cold bath and brought, first rapidly and then very slowly, to the melting point temperature.

(12) Moreau and Bongrand, *Ann. chim.*, [9] **14**, 12 (1920).

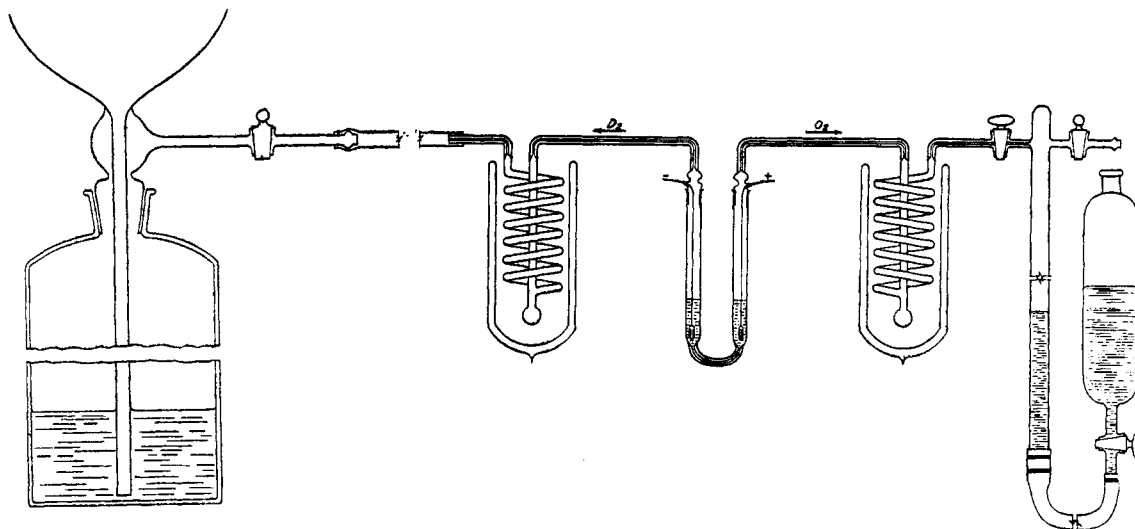


Fig. 1.

easily and completely in ice water, but the newly melted substance contained a few crystals which remained at temperatures above the melting point of dimethyl succinate. By repeatedly crystallizing and then filtering the newly melted ester, diminishing crops of these crystals were obtained, the total amount being 0.15 g. This substance was evidently a dimethyl fumarate as after recrystallization it melted at 102–103° and instantly decolorized alkaline potassium permanganate. The amount obtained was, however, too small to purify and prove with certainty whether it was $C_2H_2(COOCH_3)_2$ or $C_2D_2(COOCH_3)_2$. The liquid ester was again distilled at atmospheric pressure, the first half of the distillate, which it was hoped would contain the impurity, being collected separately. The latter half boiled constantly, but alkaline permanganate showed it still contained traces of unsaturated substance. As an extra check on the course of the purification the density was measured. The liquid was once more distilled at atmospheric pressure, approximately the first third of the distillate being collected separately. The latter fraction was free from unsaturated compound; its boiling point and density, however, were the same as before within the limits of experimental accuracy.

Dimethyl Succinate.—The constants of the purified ester checked with those recorded in the literature.

Succinic- α - d_2 , α' - d_2 Acid.—Dimethyl succinate- α - d_2 , α' - d_2 (10 g.) was saponified by boiling for four hours with 100 cc. of water and three drops of concentrated nitric acid.¹³ The nitric acid was neutralized by adding the calculated quantity of sodium carbonate and the solution evaporated to dryness *in vacuo* at 40–50° to give 8 g. of crude acid. Three crystallizations from ether-alcohol (5:1) yielded an acid whose melting point was not changed on further crystallization, and which did not decolorize alkaline permanganate.

Succinic Acid.—A pure specimen of succinic acid was prepared in the same way as the above by the saponification of dimethyl succinate. Its melting point checked with the value most commonly recorded in the literature.

Succinic- α - d_2 , α' - d_2 Anhydride.—The purified tetradeuterio acid (2.95 g.) was heated with phosphorus oxychloride (1.92 g.) and the anhydride distilled according to the method of "Organic Syntheses."¹⁴ Two grams of crude anhydride was obtained. Two crystallizations from freshly distilled acetic anhydride followed by washing with ice-cold, absolute ether, yielded a product of constant melting point. The density of this and of the following compound was measured at 131° as described below.

Succinic Anhydride.—This anhydride was prepared in the same way as the tetradeuterio compound. Its density is not quoted in the literature, but its melting point checked with recorded values.

Ethyl Acetate.—About 1 liter of commercial ethyl acetate was shaken with anhydrous calcium chloride and the mixture was allowed to stand for several days. The calcium chloride was then filtered off and the ethyl acetate distilled, the first 100 cc. being discarded, as was also a larger quantity remaining in the flask. The middle fraction was again distilled from a modified Claisen flask and the fraction boiling at 76.8–76.9° (uncorr.) collected.

Platinum Catalyst.—This was prepared in the usual way.¹⁵

Deuterium by Electrolysis of 99.9% Deuterium Oxide.—When this investigation was started, heavy water was available only in small quantities and the cell sketched in Fig. 1 was devised for the electrolysis of 2 cc. or less down to approximately 0.3 cc. Later it was used just as successfully with 8 to 10 cc. of electrolyte. The electrodes were of platinum foil (apparent surface area about 1 sq. cm.) and were initially polished but, after being in use for some time, the cathode acquired a light but tenacious coating of platinum black. The deuterium, after passing through a condensing spiral immersed in ice water, was collected in a glass gas-holder over pure decalin. The oxygen corresponding to the deuterium was also passed through a condensing spiral and collected over mercury in a buret at known temperature and pressure. From

(14) "Organic Syntheses," Vol. XII, 1932, p. 67.

(15) "Organic Syntheses," Coll. Vol., 1932, p. 452.

(13) Phelps and Hubbard, *Am. J. Sci.*, [4] 23, 211 (1907).

this known volume of oxygen, the volume of deuterium at S. T. P. could be calculated. Usually about 1600 cc. (S. T. P.) of deuterium was collected for one reduction. During the electrolysis the pressure in the anode compartment of the cell increased at a greater rate than in the cathode compartment, and it was necessary to regulate the levels of the electrolyte in the cell arms from time to time by means of an adjustable head of mercury connected to the oxygen buret.

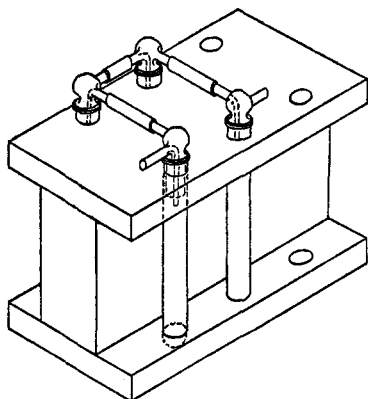


Fig. 2.

In the first instance the electrolyte was made by dissolving potassium hydroxide in 99.5% deuterium oxide to give a 5% solution. The electrolysis was then run until 1500 cc. of hydrogen isotope mixture had been evolved. This gas was merely oxidized to deuterium oxide and was not used in the reductions described in this paper, but the gas evolved thereafter was used and assumed to be pure deuterium. Direct current was taken from a 110-volt source, a lampbank resistance being placed in series with the cell. It was found that 1-3 lamps of 120 watts were sufficient to maintain a convenient evolution of gas without unduly heating the cell which was immersed in an ice-water bath and kept thereby at 5° (Fig. 1).

In connection with this set-up and its operation there are some observations of interest. It has already been mentioned that, after being in use for some time, the initially bright platinum cathode became tarnished with platinum black. In some experiments, not now reported, on the concentration of 14.75% deuterium oxide, it was indicated by density measurements before and after the electrolysis that the bright electrodes caused a more rapid concentration of deuterium oxide than was the case after the cathode had become dull. This is in accord with the observation by Topley and Eyring¹⁶ that bright platinum electrodes are more efficient than those coated with platinum black in the electrolytic separation of the hydrogen isotopes. A second point is that there was some evidence of the evolution of ozone at the anode. Thus rubber connections between the line from the cell and the oxygen buret were found, during the course of a month, to be attacked in the manner characteristic of ozone, although the glass ends were pressed closely together within the connection. Also, the surface of the mercury in the oxygen buret became tarnished. A test with potassium iodide-starch paper, however, failed to reveal the presence

of ozone. It is known that small quantities of ozone are liberated at the anode during the electrolysis of aqueous acid solutions, but no reference to ozone from alkaline solutions could be found in the literature.

Reductions.—The reductions with deuterium were carried out in the apparatus described in "Organic Syntheses"¹⁷ modified to accommodate small quantities of materials. Instead of the usual pressure bottle, 13-cm. Pyrex test-tubes fitted with two side-arms at right angles to one another and ground-in glass caps were used as reaction chambers (Fig. 2). These were mounted rigidly in a wooden frame during the shaking and separated from the gas holders by condensing spirals packed in dry ice. The number of reaction chambers used depended on the quantities of the reactants. In a typical run where 1500 cc. (S. T. P.) of deuterium were available, four such tubes were employed, each being charged with 1.17 g. of dimethylacetylene dicarboxylate, 0.03 g. of platinum catalyst and 4 cc. of ethyl acetate. These quantities ensure an excess of deuterium. During the reduction, the pressure within the system was at no time greater than 20 mm. above atmospheric pressure, and the highest temperature reached was about 40°. It was found that occasional streaming of the whole volume of deuterium through the reaction chambers accelerated the absorption of gas. This was done by attaching a gas holder at each end of the series of reduction tubes and driving the gas back and forth by air pressure. Absorption of gas usually ceased after about four hours of shaking, by which time on an average 98% of the theoretical amount had been absorbed. Longer shaking did not lead to appreciable diminution in the volume of the residual gas.

In the preliminary reduction experiments of dimethyl acetylene dicarboxylate mentioned in the introduction, the theoretical volume of a 2% deuterium mixture was absorbed in one hundred and sixty-five minutes, whereas a 60% deuterium mixture required two hundred and ten minutes and 100% deuterium required one hundred and seventy minutes.

In Table V the results are given of several experiments in which sufficient dimethyl acetylene dicarboxylate was used to absorb about one-quarter of the original hydrogen isotopes when reduction was complete. When absorption no longer took place, the residual gas was passed slowly through a condensing spiral immersed in solid carbon dioxide and then over copper oxide heated to 500°. In this way combustion of excess hydrogen and deuterium to deuterium oxide and to water was complete. The water was carefully distilled, its density determined and hence its deuterium oxide content. Table V summarizes the results of these experiments.

TABLE V

Original water in cell, g.	D ₂ O in original cell water, %	Weight of water electrolyzed, g.	D ₂ O in residual cell water, %	D ₂ O in gas Before reduction, %	D ₂ O in gas After reduction, %
3.9922	14.75	1.4090	21.25	2.84	1.75
4.0128	14.75	1.3780	21.25	2.32	1.75
4.2231	60.93	1.4700	80.45	24.36	19.45
4.2165	60.93	1.4840	80.80	24.32	19.45
4.2774	82.70	1.5580	95.75	59.95	54.15
4.5518	82.70	1.5132	94.20	59.60	51.00

(16) Topley and Eyring, *Nature*, 292 (1934).

(17) "Organic Syntheses," Coll. Vol. 1932, p. 53.

Examination of this table indicates the relatively rapid concentration of deuterium oxide obtained with the type of apparatus employed. This is due, probably, to the careful control of the temperature of the electrolysis at 5° and possibly to the slow evolution of the gases (300–400 cc. in eight hours).

The last two columns might lead to the deduction that there had been a preferential absorption of deuterium or that deuterium had been lost by interchange with hydrogen in some part of the system. The greater speed of the hydrogen reductions would appear to disprove the first of these possibilities. The differences, however, between the values in the next to the last column and the last column are not significant due to sources of experimental error. First, the original concentration of deuterium oxide and thus the concentration of the deuterium–hydrogen mixture, is subject to error due to the potassium hydroxide added for electrolysis. Another error may arise from the fact that the catalyst is $\text{PtO}_2 \cdot \text{H}_2\text{O}$ and thus a certain amount of water is always present. Moreover, an amount of gas is lost in the reduction of the oxide to platinum black. It may be stated also that in spite of all precautions the manipulative error is relatively large in the production of the gas, the passage of the gas through the reduction apparatus and the subsequent burning of the gas to deuterium oxide and water to obtain the percentage of deuterium present.

As the time which the mixture of isotopes may be passed through the reaction mixture may be varied without changing the percentages of the isotopes in the residual mixture, it is reasonable to assume that if the hydrogen–deuterium interchange does take place, it does so only to a very slight extent.

Density Determinations.—For the measurement of the density of compounds liquid at room temperature, pycnometers and counterpoises, holding from 0.5–1.5 cc., were made in pairs from Pyrex glass as described by Hartley and Barrett.¹⁸ Constant temperature was attained by immersing the pycnometers in a thermostat of which the maximum variation was $\pm 0.02^\circ$. The formula developed by these authors was also employed in the calculation of the densities.

Dean, Hill, Smith and Jacobs¹⁹ have described a form of pycnometer which they used for rough density determinations of viscous petroleum oils. The apparatus shown in Fig. 3 is an adaptation of this type of pycnometer suitable for the determination of densities of compounds that are solid at ordinary temperatures and melt without decomposition. It consists of a capillary pipet ground at each end to fit glass caps, and also a small receptacle as shown in which the solid substance is melted. A constant temperature jacket made of glass completes the parts of this equipment. The pycnometer is first weighed empty and then filled with water at two different temperatures. To obtain the pycnometer full of water at a given temperature, it is first filled by suction at room temperature, and then placed in a constant temperature jacket in a horizontal position, where it is held by plugs of cotton on each side of the bulb. At this stage, the

jacket is conveniently maintained at a constant temperature by passing water from a thermostatic source through it fairly rapidly. A preliminary test with a thermometer will show the time required for the central tubular space to reach constant temperature. In the case of the present apparatus, this time was about five minutes at temperatures from 15–30°. The pycnometer is allowed to remain in the jacket for twenty minutes, during which time water is either added by holding a drop on the end of a glass rod to the capillary, or wiped away with filter paper as it flows out, depending on the difference between room temperature and the temperature of the measurement. The ends are then covered with the caps, the pycnometer taken out of the jacket, placed on a suitable chair in the balance case and, after fifteen to twenty minutes, weighed. The same procedure is repeated to obtain the weight of the pycnometer full of water at a different temperature.

The pycnometer has now to be filled with the compound, of which the density is required, at a known temperature above its melting point. To carry out this part of the determination, the jacket is placed in a vertical position and, when the melting point of the compound is above 100°, is heated by circulating through it a rapid stream of vapor from a reservoir of liquid boiling at a temperature above the melting point. In the present instance the compound whose density was required melted at 119.5°, and it was found convenient to heat the jacket with the vapor from pure boiling chlorobenzene (b. p. 132°). A preliminary test with a thermometer shows the time required for the central tubular space to acquire constant temperature in the range required, and also that temperature. In the present instance this was about ten minutes and the constant temperature was 131°. Beneath the jacket is placed a small electrical heating element controlled by a rheostat, and insulated from the jacket by a heavy asbestos board. This element is used to melt the compound in the small receptacle, which is fitted into a hole in the asbestos board. The pycnometer is placed in the jacket so that the capillary tip dips into the molten compound and the neck of the receptacle fits around the stem. This position is shown in Fig. 3. The pycnometer is held in place and air currents in the central space prevented by means of small cork rings placed above and below the bulb. After ten minutes the pycnometer is sufficiently heated and the molten substance is very slowly drawn into it by suction or preferably forced in by carefully controlled dry air pressure. Too rapid filling causes bubbles to form in the pycnometer. The rubber tube through which the suction was applied is then pinched or the air pressure is stopped and the pycnometer allowed to remain in the constant temperature jacket for twenty minutes. It will be found that a solid cap of the substance forms on the upper end of the capillary, and while the pycnometer is in the jacket it fills itself at the temperature of the central jacket space by taking up from or emptying out more liquid into the receptacle. The receptacle is now removed, the heating in the jacket cut off, and the contents of the pycnometer rapidly solidified by blowing air against it. The pycnometer is taken out of the jacket, any solid substance carefully removed from the outside by washing with a volatile solvent, the caps

(18) Hartley and Barrett, *J. Chem. Soc.*, 99, 1072 (1911).

(19) Dean, Hill, Smith and Jacobs, *Bull. 207, Bureau of Mines*, p. 42.

put on, and the whole allowed to remain in the balance case for twenty minutes before weighing.

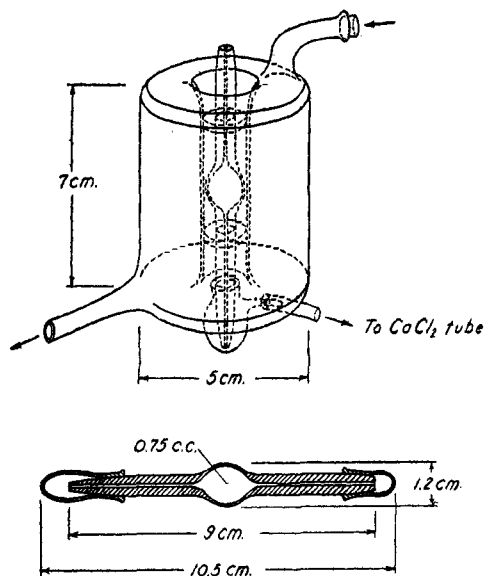


Fig. 3.

The density is then calculated as follows:²⁰ If the pycnometer contains v_1 cc. (w_1 g.) of water at temperature t_1 and v_2 cc. (w_2 g.) at temperature t_2 and v_3 cc. (w_3 g.) of liquid, of which the density, d , is required, at temperature t_3 and if the coefficient of linear expansion of the glass of which the pycnometer is made is α , then

(20) Cf., Reilly and Rae, "Physico-Chemical Methods," 1933, p. 337.

$$\begin{aligned} v_2 - v_1 &= 3\alpha v_1 (t_2 - t_1) \\ \text{and } v_3 - v_1 &= 3\alpha v_1 (t_3 - t_1) \\ \therefore v_3 - v_1 &= (v_2 - v_1) \frac{(t_3 - t_1)}{(t_2 - t_1)} \\ &= k(t_3 - t_1) \text{ where } k = \frac{(v_2 - v_1)}{(t_2 - t_1)} \\ \therefore d_4^{t_3} &= \frac{w_3}{v_3} = \frac{w_3}{v_1 + k(t_3 - t_1)} \end{aligned}$$

Summary

1. A convenient apparatus is described for the production of deuterium and reduction of organic compounds with this gas.

2. Dimethyl acetylene dicarboxylate was reduced with deuterium to dimethyl succinate- α - d_2 , α' - d_2 and from it by hydrolysis succinic- α - d_2 , α' - d_2 acid was obtained. This latter was converted by means of phosphorus oxychloride to succinic- α - d_2 , α' - d_2 anhydride.

3. The analyses, boiling points, melting points, densities and indices of refraction were determined and compared with those of the hydrogen analogs.

4. An apparatus for determining the density of solids which melt without decomposition is described.

5. It has been demonstrated that, under the conditions used, the replacement of deuterium by hydrogen, if it takes place at all, is a very slow reaction.

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[CONTRIBUTION FROM SUN OIL COMPANY RESEARCH LABORATORY]

The Freezing Point and Boiling Point of Propane¹

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1. Introduction

Although the freezing points of the pure normal hydrocarbons with an odd number of carbon atoms are, in all cases, considerably lower than those of the even-numbered compounds of the same series, the generally accepted value, -189.9° , given for the freezing point of propane seems unduly low. It is not only lower than that of its lower even-numbered homolog, ethane (f. p. -172.0°), but also is lower than that of methane (f. p. -184°). For this reason it was suspected that perhaps the value found in the literature for the freezing point of propane was

not correct and that a higher value might be obtained by intensive purification of the propane, and improved technique in the determination of its freezing point.

Furthermore, the value -189.9° , reported by Maas and Wright² was determined by carefully raising and lowering the temperature of a bath in which was suspended a sealed glass bulb that contained less than 2 ml. of propane. These authors state that difficulty was experienced with supercooling, but that this effect was minimized by freezing the sample more than one time, successively. However, in a procedure such as that given above, it was not the temperature of the

(1) Presented before the Division of Petroleum Chemistry at the 91st meeting of the American Chemical Society, Kansas City, Missouri, April 13-17, 1936.

(2) Maas and Wright, *THIS JOURNAL*, **43**, 1098-1111 (1921).