

D. Sc. 1915

THE TEMPERATURE OF IGNITION

of

GASEOUS MIXTURES:

Reported by J.W. McDavid.



THE TEMPERATURE OF IGNITION OF GASEOUS MIXTURES:

Numerous methods for the determination of the ignition temperature of gaseous mixtures are to be found in the literature and these have already been classed into three groups by Dixon and Coward^x in their paper on this subject.

The experimental conditions governing this division are as follows:-

- I. A bulb containing the gaseous mixture was plunged into a bath which was maintained at a constant temperature.
- II. A mixture of the gases was passed through a tube in a bath which was gradually being heated up.
- III. The gaseous mixture was compressed adiabatically and from the pressure required to ignite the gaseous mixture the temperature of the mixture at the ignition point was calculated.

In each of the above methods the gaseous mixture is retained in the state necessary for ignition for some considerable time, and it is quite possible therefore that before the ignition temperature is reached a state of slow combustion ensues which generates sufficient heat to raise the remainder of the gaseous mixture to its ignition point.

With regard to the third method, which was that used by Falk^y, Dixon and Coward point out that the temperature of ignition of a gaseous mixture under abnormal pressure may be totally different to that of the same mixture under normal pressure.

In the method adopted by Dixon and Coward, the two gases were allowed to flow through two concentric tubes, which were heated in an electric furnace and allowed to mix at the top of the shorter (inner) tube. A thermocouple was placed near to the nozzle of the inner tube. In these experiments, in addition to the time factor, the fact/

^x J.C.S. 1909, ^t.514.

^y J.A.C.S. 1906, 28, 1517, 1907, 29, 1536.

fact that the gases are flowing must also be taken into consideration, and the results obtained by these authors show that the rate of flow and the size of the nozzle of the inner tube affect the results. For example, when the rate of flow of hydrogen was very slow, viz. 2.4 c.c. per minute and the rate of flow of oxygen was 50 c.c. per minute, the temperature of ignition was 792°C ., while when the rate of flow of hydrogen was 19 c.c. per minute, oxygen still flowing at 50 c.c. per minute, the ignition temperature was found to be 599°C . These authors, however, give in their paper a definition as to what they have taken as the temperature of ignition.

It seems, however, that it is advisable to eliminate, as far as possible, the time factor, in determining the ignition temperature, and it is also preferable to have a stationary volume of gas.

In Table I the results obtained by various workers for several gaseous mixtures are given.

TABLE I/

TABLE I:

Gases	Observer	Reference	Temp. of Ignition found °C.
Hydrogen and Oxygen	Meyer, Krause Askenasy	Annalen 1891, 264, 85 1892, 269, 49, 2421 Zeit.phys.chem.1893,11,28	518 - 606
"	Bodenstein	Zeit.phys.Chem.1899,29,565	653-710
"	Meyer and Freyer	Ber. 1892, 25, 662	700
"	Gautier and Helier	Comp.Rend.1896, 122, 566	840
"	Helier	Ann.Chim. Phys. 1897	845
"	Falk	J.Am.Chem.Soc.1906,28,1517 1907,29,1536	514-540
"	Dixon and Coward	J.C.S. 1909, 95, 514	580-590
Methane and Oxygen	Meyer and Freyer	Zeit.phys.Chem. 1893,11,28	606-650
"	Meyer and Munch	Ber. 1893, 26, 2421	656-678
"	Dixon and Coward	loc.cit	556-700
Ethylene and Oxygen	Meyer and Freyer	loc.cit	530-606
"	Meyer and Munch	" "	577-590
"	Dixon and Coward	" "	500-519
Carbon Monoxide and Oxygen	Meyer and Freyer	" "	650-730
"	Meyer and Munch	" "	Combined quietly
"	Dixon and Coward	" "	637-658

The method adopted by the present author eliminates, as far as is practically possible, the time factor. The temperature of ignition in these experiments is taken to be that temperature to which the gaseous mixture must be heated by the application of a hot body, so as to cause instantaneous ignition.

The temperature of ignition has in the present work only been determined for ^{gas} air. Dixon and Coward have, however shown that there is very little difference in the temperatures found when air or oxygen respectively are employed.

The essence of the method employed in the following experiments consists in the ignition of a small volume of the gaseous mixture contained in a soap bubble, by means of an electrically heated wire, or other red-hot body, the temperature at which ignition just takes place being noted.

A mixture of the gas to be experimented on was mixed with air and made up to the required concentration in a 10 litre gas holder. To the outlet tube of the holder was attached a piece of capillary tubing terminating in a bulb tube, shaped like the head of an ordinary tobacco pipe. This tube when not in use was dipped into a solution of sodium oleate and glycerine in water.

The apparatus employed for igniting the gas consisted of a platinum wire measuring about 0.01 inch in diameter, which was wound evenly round a small thin walled silica tube. A thermo couple made of platinum and platinum-rhodium which had previously been carefully standardised against a standard ^{pyrometer} ~~hydrometer~~ was passed through the inside of the silica tube so that the thermo junction was in the centre of the tube. The terminals of the thermo couple were connected up to a millivoltmeter from which the temperature could be read off. The experiments were carried out in a darkened room as in some cases the flame of the ignited gas was almost invisible in day-light.

The procedure was as follows:— When all connections had been made the heating current, which could be varied by means of a rheostat, was switched on. When the temperature as indicated by the milli-voltmeter was constant, the tap of the gas holder was/

was opened and the mixture, flowing through the pipe stem and soap solution produced a bubble. The tap was closed and the bubble still on the end of the pipe was placed in contact with the hot coil. Ignition/^{which}was instantaneous was usually accompanied by a slight explosion, but in some cases this was so faint as to be detected only with difficulty. The temperature was varied over 60-80° until a sufficient number of readings had been obtained.

The gases employed in the first instance were prepared as follows:—

Hydrogen from pure zinc and sulphuric acid.

Methane by the action of a zinc copper couple on methyl iodide. The gas was passed through a tube containing more of the zinc copper couple in order to free it from methyl iodide vapour.

Ethylene by passing alcohol vapour over heated Al_2O_3 . The gas obtained contained 9% methane.

Coal Gas Samples were taken from time to time from the local gas supply.

Petrol Commercial petrol was fractionated and the fraction boiling between 0 and 80° was taken.

The results found are given in Tables I, II and III.

TABLE II/

TABLE II:

Coal Gas 9 1/2% Mixture.		Methane 9 1/2% Mixture.	
Temperature	Result	Temperature	Result.
760°	No ignition	840°	No ignition
780°	Ignition	860°	-do-
780°	No ignition	865°	-do-
780°	-do-	870°	-do-
790°	-do-	880°	-do-
790°	-do-	880°	-do-
795°	Ignition	880°	-do-
795°	-do-	880°	-do-
800°	No ignition	880°	-do-
800°	Ignition	880°	Ignition
800°	-do-	880°	-do-
800°	-do-	880°	-do-
810°	-do-	890°	-do-
820°	-do-	920°	-do-

Temperature of Ignition = 800°C. Temperature of Ignition = 880°C.

TABLE III:

Coal Gas 13 1/2% Mixture.		Hydrogen 13 1/2% Mixture.		Methane 13 1/2% Mixture.	
Temperature	Result.	Temperature	Result.	Temperature	Result.
800°	No Ignition	670°	No Ignition	860°	No Ignition
800°	-do-	680°	-do-	870°	-do-
805°	-do-	680°	-do-	875°	-do-
805°	-do-	690°	-do-	875°	Ignition
805°	Ignition	690°	-do-	880°	No ignition
810°	No ignition	690°	-do-	885°	Ignition
810°	-do-	690°	Ignition	885°	-do-
810°	-do-	690°	-do-	890°	-do-
810°	Ignition	700°	No ignition	900°	-do-
810°	-do-	700°	Ignition	910°	-do-
815°	-do-	700°	-do-		
820°	Ignition	710°	No ignition		
820°	Ignition	710°	Ignition		
		710°	-do-		
		720°	-do-		

Temp. of Ignition = 810°C. Temp. of Ignition = 695°C. Temp. of Ignition = 885°C.

TABLE IV/

TABLE IV:

Mixture of 9.1% C ₂ H ₄ 0.9% CH ₄ and 90% air.			Mixture of 2.0 c.c. Petrol (0°-80°C) vapourised and made up with air to 10 litres.		
Temperature	No. of Readings.	Result.	Temperature.	No. of Readings.	Result.
845°	1	Ignition	900°	3	Ignition
840°	2	"	890°	3	"
830°	7	"	880°	6	"
825°	8	"	880°	7	No Ignition
825°	1	No Ignition	875°	2	Ignition
820°	4	Ignition	875°	5	No Ignition
820°	12	No Ignition	870°	5	"
815°	3	"	865°	2	"
810°	3	"			
Temperature of Ignition = 825°C.			Temperature of Ignition = 885°C.		

A second series of experiments was carried out in which the heating coil was replaced by a semi-cylindrical piece of iron about 1¹/₂" long by 3/4" in diameter, covered round the circumference with thick asbestos cloth (No. 1 iron block). Running down the centre of the flat surface and about 1/32" under the surface was a small hole to carry the thermo couple. The block was hung by two platinum wires from a stand. The block was then heated up until about 50° above the required temperature when the blow-pipe was removed and bubbles of gas brought into contact with the red-hot surface while the latter was cooling. When the temperature became too low for ignition to take place the block was simply heated up again and the procedure carried out as before until a sufficient number of readings had been obtained. An improvement was made in No. 2 block by boring a small hole in the centre of the flat face perpendicular to the face. By this means the thermo couple became exposed to the air and since it lay close to the surface it ought to give a comparatively true figure for the temperature of the igniting surface. Tables V, VI, VII and VIII give comparative results found by the above three methods.

TABLE V/

TABLE V:

13 1/2% Mixture of Coal Gas with Air.					
Electric Coil Method.			Iron Block (No.1 Block) Method.		
Temp. °C.	No. of Readings.	Result.	Temp. °C.	No. of Readings.	Result.
770	3	No ignition	720	1	No Ignition
775	2	"	730	2	"
780	4	"	740	3	"
780	2	Ignition	750	2	"
785	1	No Ignition	760	1	Ignition
785	1	Ignition	765	1	"
790	1	No Ignition	770	1	"
790	3	Ignition	790	2	"
795	1	"	800	2	"
800	1	"	810	1	"
810	1	"			
Temperature of Ignition = 785°C.			Temperature of Ignition = 760°C.		

TABLE VI:

Mixture of Hydrogen with Air 15%.								
Electric Coil.			No.1 Iron Block.			No 2 Iron Block.		
Temp. °C.	No. of Readings	Result.	Temp. °C.	No. of Readings	Result.	Temp. °C.	No. of Readings	Result.
690	2	Ignition	720	6	Ignition	705	2	Ignition
685	2	"	710	9	"	700	4	"
680	3	"	705	3	"	695	3	"
675	2	"	705	3	No Ignition	690	4	"
675	3	No Ignition	700	7	"	685	3	"
670	4	"	695	3	"	680	2	"
665	1	"	690	3	"	680	6	No Ignition
660	1	"				675	2	"
						670	6	"
						665	1	"
Temp. of Ignition = 680°C.			Temp. of Ignition = 705°C.			Temp. of Ignition = 685°C.		

TABLE VII/

TABLE VII:

Mixture of two Volumes Hydrogen with five Volumes Air. Two series carried out with No. 2 Iron Block.					
1st Series.			2nd Series.		
Temp. °C.	No. of Readings.	Result.	Temp. °C.	No. of Readings.	Result.
730	3	Ignition	730	2	Ignition
720	3	"	725	1	"
715	1	"	720	3	"
710	2	"	715	1	"
705	1	"	710	5	"
700	1	"	700	2	"
700	1	No Ignition	695	3	No Ignition
695	3	"	690	4	" ⁵
690	1	"	685	1	"
685	1	"	680	2	"
680	1	"	670	1	"
Temperature of Ignition = 700°C.			Temperature of Ignition = 700°C.		

TABLE VIII:

13 ¹ / ₂ % Mixture of Coal Gas with Air.								
Electric Coil.			No. 1 Iron Block.			No. 2 Iron Block.		
Temp. °C.	No. of Readings.	Result.	Temp. °C.	No. of Readings.	Result.	Temp. °C.	No. of Readings.	Result.
785	6	Ignition	810	6	Ignition	800	3	Ignition
782	3	"	805	1	"	795	1	"
780	3	"	800	1	"	790	3	"
775	3	"	795	3	"	785	2	"
775	1	No ignition	795	2	No Ignition	780	2	"
772	2	Ignition	790	1	Ignition	775	2	"
772	5	No Ignition	790	3	No Ignition	770	3	"
770	3	"	785	1	"	770	1	No Ignition
768	3	"	780	4	"	765	3	Ignition
765	1	Ignition	775	3	"	765	3	No Ignition
765	3	No Ignition				760	3	"
760	1	"				755	1	"
						750	2	"
Temp. of Ignition = 775°C.			Temp. of Ignition = 795°C.			Temp. of Ignition = 765°C.		

From the results given in Tables II ^{Co} VIII it will be observed that the method

gives a very sharp ignition point, and since the time taken to determine the temperature/

temperature of ignition of any mixture was only about fifteen minutes it is evident that for purposes of comparison at least the method is very suitable. As however, the rate of cooling in the iron block method was very rapid the method was not very satisfactory for the purpose of obtaining absolute values. Accordingly, it was discarded in favour of the method first described. Even in this method there are several factors which may affect the absolute value of the results while in no way affecting their comparative value. These factors are the cooling effect of the bubble, the presence of moisture in the gases, the catalytic action of the platinum wire and the size of the silica tube.

That the cooling effect of the bubble is negligible was clearly proved by the fact that the size of the bubble had no effect on the temperature of ignition.

With regard to the presence of moisture Dixon and Coward (loc.cit) have shown that the presence of moisture did not affect the ignition temperature in the case of hydrogen and oxygen, and in several other cases the difference was very small.

The chief defect in this method lay in the fact that the temperature registered by the thermo couple was probably slightly lower than that of the coil since the former was separated from the coil by the thickness of the silica and a volume of air. It is of course obvious that the thermo junction ought to be near to the centre of the tube and that the coil must be as evenly wound as possible so that there may be no unequal heating. In order to study the effect of the size of the silica tube on the temperature recorded by the thermo couple, and, if possible to obtain absolute values for the temperature of ignition of various gases a large number of determinations were carried out. For this purpose the gases employed were obtained in as pure a state as possible, and on analysis gave the following results:—

Hydrogen $H_2 = 99.6\%$
 $CO_2 = 0.4\%$

Carbon Monoxide $CO = 94.0\%$
 Air = 6%

Ethylene/

Ethylene = 93.8%
Air = 6.2%

Methane CH₄ = 95.36%
(Natural Gas) CO = 0.50%
C₂H₄ = 0.31%
H₂ = 1.43%
N₂ = 2.40%

In making up the gaseous mixtures allowance was always made for the quantity of air present in the gas.

Table IX gives the dimensions of the various silica tubes employed in the determinations. These were drawn out as evenly as possible from ordinary silica tubing.

The experiments were carried out in the same manner as before except that the ends of the silica tubes were in all cases stopped up with asbestos fibre so as to diminish loss of heat within the tube by convection. Platinum and eureka resistance wire were employed for making the ignition coils. The results found for hydrogen are given in Table IX

TABLE IX

Showing effect of the size of the silica tube on the Temperature of Ignition of Hydrogen:

No. of Tube.	Thickness of Wall of Tube (In.)	Internal Diameter (in)	Length cm.	Temperature of Ignition of 20% Hydrogen in Air using:-	
				Eureka Wire	Platinum Wire.
1	0.022	0.063	6	682°C.	712°C.
2	0.014	0.059	6	688° C	712°C.
3	0.012	0.048	6	690)°C	"
4	0.017	0.031	6	695) 710) 712)°C.	"
5	0.012	0.030	3	735°C	"
6	0.014	0.030	6	726°C	(735°C)
7	0.014	0.038	5.5	"	(735°C)
8	0.011	0.031	6	735°C.	725
9	0.009	0.026	4	735°C.	
10	0.010	0.026	4	735°C.	758°C.

It will be observed in the first place that for the same tube the figures found

by/

by using platinum are higher than those obtained when using Eureka wire, indicating a catalysing effect in the case of the latter. It is however, probable that both substances exert a catalytic influence on the temperature of ignition.

The internal diameter of the tube and the thickness of the silica wall seem to have considerable influence, up to a certain point, on the results. In the case of Eureka wire, however, tubes Nos. 5, 8, 9 and 10 all give the same result, even though they vary in length, width and thickness of wall. It appears therefore, as if a limiting value had been reached, indicating that the temperature registered by the thermo couple was identical with that of the coil. If this be so then the temperature of ignition of a hydrogen air mixture by means of Eureka wire is 735°C , while in the case of platinum it is 758°C . It was found impossible to employ a smaller tube than No. 9 since the diameter of the thermo couple at the junction was 0.022 in. and owing to slight irregularities in the tubes the thermo couple could not be inserted. It would be interesting to compare the results found by the above method with determinations made using Joly's Meldometer. In this instrument which is chiefly used for determining melting points of small particles of metals, a platinum strip is heated electrically and the linear expansion of the platinum is measured and from this the temperature is obtained to 1° in 1000° . If the Meldometer were used for measuring the temperature of ignition, it is obvious that since the igniting surface would be identical with that giving the temperature, results could be obtained for platinum with absolute certainty and from this value the apparatus used in the method described above could be calibrated. This work is being arranged for.

Table X summarises the results found for the temperatures of ignition for various gases mixed with air. The analysis of these gases has already been given (see p 104)

TABLE/ X

TABLE X

Gas.	% in Air.	No of Spiral (Eureka Wire)	Temperature of Ignition
Carbon Monoxide.	20%	5	880°C.
Ethylene	10%	5 8	875°C. 865°C.
Coal Gas.	20%	10	820°C.
Hydrogen	20%	1	688°C.
"	10%	1	685°C
Methane	13%	1	No Ignition up to 1000°C.
(1000 c.c. CH ₄) (1000 c.c. H ₂)	20%	10	796°C
1500 c.c. CH ₄ 500 c.c. H ₂	20%	10	835°C
(1200 c.c. CH ₄) (60 c.c. H ₂)	12%	10	No Ignition up to 970°C.
(1200 c.c. CH ₄) (90 c.c. H ₂)	12%	10	" " " " "

Since the spirals Nos. 5, 8 and 10 gave the same value with hydrogen, the following may be taken as the temperatures of the various gases tested, when ignited by a hot Eureka wire.

Gas.	Temperature of Ignition using Eureka Wire igniting coil. °C.
Hydrogen	735
Carbon Monoxide	880
Ethylene	865-875
Coal Gas	820
Petrol (0-80°)	930
Methane	No Ignition below 1000°C.

In Tables II + III the ignition temperature of methane in air was found to be 880-885°C., but the gas was not analysed before testing and probably contained a considerable/

considerable quantity of hydrogen. The result given above viz. that methane did not ignite below 1000°C . is very interesting in view of the statement given in "Brunswig's "Explosives" (English Edition)p.55, in which it is stated that in the case of methane and air there is delayed ignition at 600 to 700°C ., but that instantaneous ignition does not take place below 1000°C .

The temperature given for a petrol-air mixture in the above table was calculated from the result given in Table IV. This result was obtained with Spiral No.2 with which hydrogen had a value of 688°C .

The comparative results obtained for a 10% and a 20% hydrogen-air mixture are the same showing that within the explosion limits the concentration has no effect. This is also shown in the results given in Tables II and III.

The method used in the above experiments is very rapid and convenient, and only a comparatively small quantity of gas is required for the determination. 10 litres of the gaseous mixture containing from 10% to 20% of the inflammable gas is sufficient for determining the temperature of ignition.

The results obtained agree very closely and in a series of experiments the ignition temperature can usually be determined to within 5°C .

Research Laboratories,
Messrs. Nobel's Explosives Co., Ltd.,
Ardeer Factory.

25/6/15.

The Preparation of
DIHYDROCARBOSTYRIL ACETIC ACID.

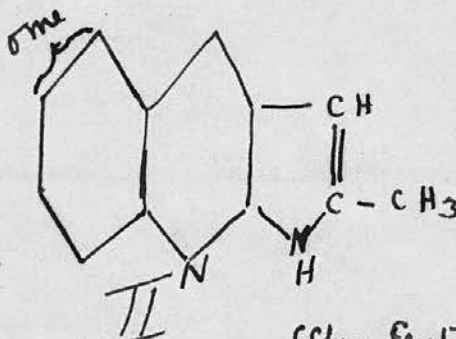
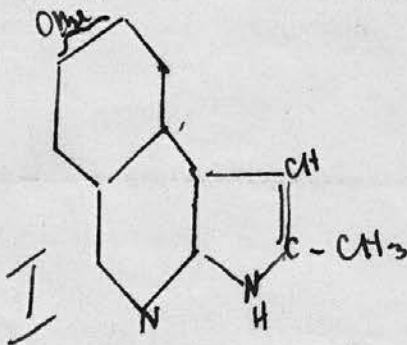
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J.W. McDavid.

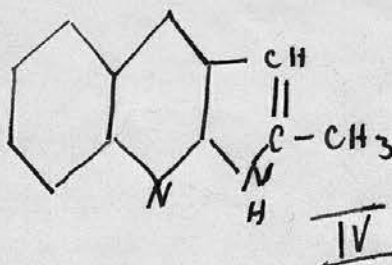
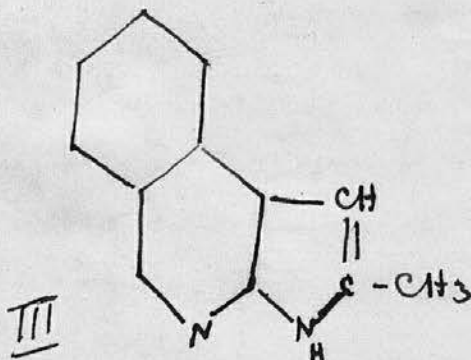
THE PREPARATION OF DIHYDROCARBOSTYRIL ACETIC ACID:

While the researches on the constitution of harmine and harmaline were being carried out by Perkin and Robinson { J.C.S. 1912, P 154, T. 1775 } it was thought advisable to prepare as many as possible of the derivatives of harman and its isomers.

At the time when this research was commenced, the constitution of harmine was not clearly established being either I or II



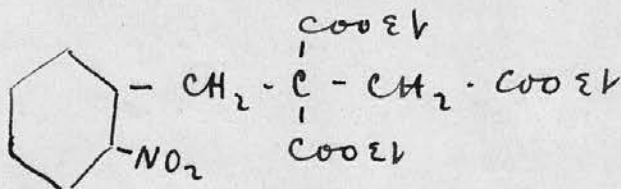
Consequently, harman which was prepared by O. Fischer { Chem. Zentr 1901 } by splitting off the methoxy group had the constitution represented either by III or IV.



The substance represented by IV has since been prepared (Perkin and Robinson P 1912, 154). It was found to differ from harman and was, in consequence, named iso-harman. Meanwhile, in the hope of preparing a tetrahydro derivative of substance IV, the following research was commenced.

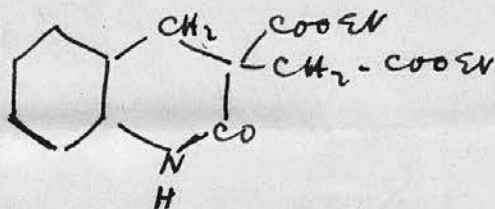
The/

The tri-ethyl ester of ethan tricarboxy acid was condensed with ortho nitro benzyl chloride, whereby o-nitro benzyl carboxy succinic ester, whose constitution is represented by V, was obtained.



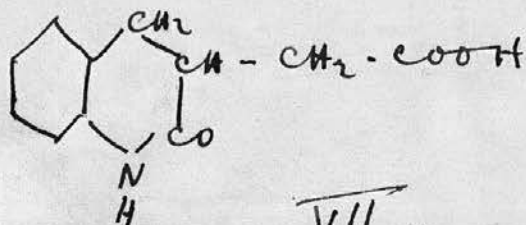
V

Considerable difficulty was experienced in reducing this substance, but, ultimately, this was successfully accomplished by means of ferrous sulphate and ammonia when the second ring was closed, giving the substance represented by VI.



VI

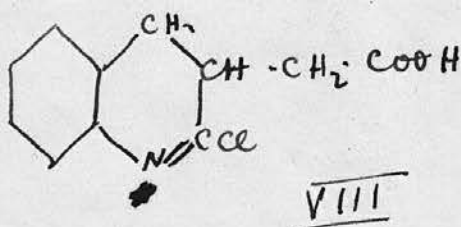
This substance, which was a colourless crystalline solid, is a di-ethyl ester of dihydrocarbostyryl succinic acid. On hydrolysis with concentrated hydrochloric acid, it loses carbon dioxide giving dihydrocarbostyryl acetic acid (VII)



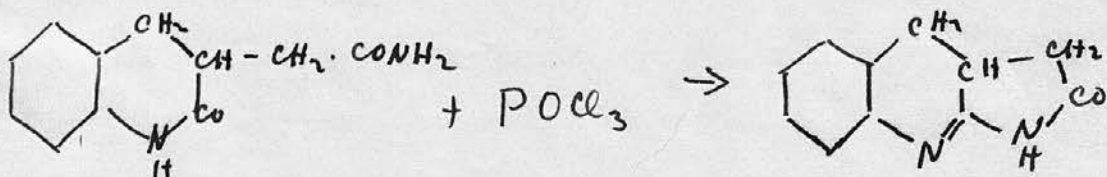
VII

In order to close the last ring, various methods were tried. Acetic anhydride instead of closing the ring gave the acetyl derivative of the acid, the acetyl group combining with the nitrogen. Phosphorus pentachloride was no more successful, most of/

of the substance remaining unchanged, while a small quantity of the chlor acid represented by VIII was isolated.



This chlor acid was boiled with ammonia, treated with methyl alcohol and boiled with ammonia, but no result was obtained. On heating in a sealed tube with a saturated solution of ammonia in alcohol, a small quantity of an acid was isolated which was afterwards found to be identical with the carbostyryl acetic acid prepared by Perkin and Robinson (*loc.cit.*). Meanwhile, Perkin and Robinson had succeeded in closing the last ring in the synthesis of iso-harman by forming the amide of the carbostyryl acetic acid and acting on that with phosphorus oxychloride. The methyl ester and then the amide of hydrocarbostyryl acetic acid were accordingly prepared and it was hoped to close up the ring according to the scheme



Unfortunately, however, this action did not take place; the phosphorus oxychloride certainly acted on the amide, but the substance so obtained seemed to be a compound of phosphorus with the amide, and since by this time the synthesis of iso-harman had been established, further attempts at closing the ring were abandoned.

Experimental:

Tri-ethyl ester of ethan tri-carboxy acid (carboxy-succinic ester):— This substance was made according to the method of Bischoff (Annalen 214, 38). 2.3 gm. sodium were dissolved in 35 gm. absolute alcohol and 16 gm. malonic ester added. After the mixture had been well shaken and cooled, 13 gm. chloracetic ester were run in; the mixture was well shaken and then placed in a flask fitted with a reflux condenser and heated on a water bath for about 4 hours. The alcohol was distilled off, the mixture diluted with water and extracted with ether. The ethereal solution was dried by means of potassium carbonate and, after the ether had been boiled off, the liquid was distilled under 15 m.m. pressure and the portion boiling at 156–158°C. collected. The ester so obtained was a colourless liquid with very little odour.

Tri-ethyl ester of o-nitro benzyl carboxy succinic acid: 2.3 gm. sodium were dissolved in 35 gm. absolute alcohol and 24.6 gm. of the tri-ethyl ester of carboxy succinic acid were added. After the mixture had been well shaken, 17 gm. o-nitro-benzyl chloride were slowly added. The whole was heated for about 4 hours in a steam bath in a flask fitted with a reflux condenser. After boiling off the alcohol, the mixture was diluted with water and extracted with ether. The ethereal solution was dried as before by means of potassium carbonate, and the ether evaporated off. The dark coloured liquid so obtained was distilled under 15 m.m. pressure, when a pale yellow liquid was obtained, the yield being about 24 gm. This substance on analysis gave the following results:—

0.1230 gm. subs. gave 0.2571 gm. CO₂ and 0.0664 gm. H₂O

C = 57.0% H = 6.0%.

C₁₈H₂₃NO₈ requires: C = 56.7%, H = 6.0%.

The ester was a very viscid liquid, and attempts were made to solidify it by agitation and by cooling but without success.

Reduction of o-nitro benzyl carboxy succinic ester: Various methods were tried in order to reduce this substance to the amine compound, when the closing of the ring according to the scheme already indicated would have been a comparatively easy matter. A few grams of the substance were treated with tin and hydrochloric acid, and after the action had proceeded for some time the presence of an amine was indicated by the characteristic colour given after diazotising a few drops and adding an alkaline solution of β naphthol. Great difficulty was, however, experienced in isolating the amine compound, as, on diluting the solution, stannous chloride and an oil were precipitated together and it was impossible to separate them.

Alkaline stannous chloride was next employed, the ester being boiled with the reducing agent until solution was complete. Zinc was added to replace the tin, and the solution after filtration was concentrated. After it had been acidified, it was extracted with ether and the ethereal layer dried. On evaporating off the ether, a very small quantity of a colourless crystalline solid was obtained. The yield was very small and the quantity of substance isolated was insufficient to analyse. It was, however, diazotised and tested with β naphthol when the presence of an amine was indicated. The substance was in all probability ortho-toluidine-carboxy succinic ester. The third method of reduction was by means of ferrous sulphate and ammonia and by this means more successful results were obtained. The method is described below:

Dihydro-carbostyryl succinic ester: 2 kilos crystallised ferrous sulphate were dissolved in water to form a saturated solution. This solution was added to 100 gm. of the nitro ester dissolved in a small quantity of methyl alcohol. A concentrated solution of ammonia was gradually added, the mixture being warmed and well shaken from time to time. Ammonia was added until its odour could just be detected in the mixture after/

after shaking. The contents of the flask were then cooled, filtered and the precipitate dried at 30° . When thoroughly dry, it was extracted with ether in a large Soxhlet apparatus. The ethereal solution, which was usually reddish brown in colour, was evaporated to small bulk when beautiful colourless needle shaped crystals separated out. The yield was 70 gm. or about 87% of the theoretical quantity. The crystals melted at 92°C . and on analysis gave the following results:

- I. 0.1212 gm. substance gave 0.2800 gm. CO_2 and 0.0685 gm. H_2O .
 II. 0.1095 " " " 0.2519 " " " 0.0615 " "
- I. C = 63.00%, H = 6.28%.
 II. C = 62.74%, H = 6.24%.

$\text{C}_{16}\text{H}_{19}\text{NO}_5$ requires C = 62.94%, H = 6.23%.

The substance obtained by the above reduction process was insoluble in water, and in dilute acid or alkali; it did not give a colouration with β naphthol on diazotising, showing that there was no free amino group present, the $-\text{NH}_2$ group and one of the $-\text{COOEt}$ groups having joined up with loss of alcohol.

Hydrocarbostyryl acetic acid: 30 gm. of the ester were heated in a flask on a steam bath with 100 gm. concentrated hydrochloric acid for several hours. The ester which melted on warming, gradually dissolved in the acid, and on the solution being cooled, grayish white crystals separated out. These crystals were washed with water and dried and were found to melt at 201°C . A sample recrystallised from acetone gave the same melting point. The results of analysis were:

- I. 0.1050 gm. substance gave 0.2455 gm. CO_2 and 0.0522 gm. H_2O .
 II. 0.1071 " " " 0.2526 " " " 0.0545 " "
- I. C = 64.03 H = 5.65
 II. C = 64.32 H = 5.52.

$\text{C}_{11}\text{H}_{11}\text{NO}_3$ requires C = 64.39% H = 5.41%.

This/

This substance is soluble in sodium carbonate solution, carbon dioxide being given off. It is very slightly soluble in water.

The methyl ester of dihydrocarbostyryl acetic acid was prepared in the usual manner by heating together 20 gm. of the acid, 50 gm. methyl alcohol and 5 gm. sulphuric acid for 3 hours in a flask fitted with a reflux condenser. On boiling off the bulk of the alcohol and cooling, the ester separated out. It recrystallised readily from methyl alcohol giving yellowish plates which melted at 147°C . On analysis, it gave the following results:-

0.1147 gm. substance gave 0.2231 gm. CO_2 and 0.0629 gm. H_2O .

C = 65.77%, H = 6.09%.

$\text{C}_{12}\text{H}_{13}\text{NO}_3$ requires C = 65.75% H = 5.94%.

The ester was, of course, insoluble in water, and in dilute sodium carbonate, but was readily hydrolysed by means of hydrochloric acid.

Dihydrocarbostyryl acetamide was prepared by heating together in a sealed tube in a boiling water bath for two days 3 gm. of the methyl ester and 20 c.c. concentrated ammonia solution. The contents of the tube were then filtered and the residue crystallised, first from methyl alcohol and then from acetic acid and water. Gray crystalline plates melting at 215°C . were isolated. The results of analysis of this substance were:

I. 0.1090 gm. substance gave 0.2600 gm. CO_2 and 0.0601 gm. H_2O

II. 0.1346 " " " 16.9 c.c. nitrogen at 22.5°C . and 747 mm.

C = 65.05, H = 6.13, N = 13.9%.

$\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_2$ requires C = 64.70%, H = 5.88%, N = 13.7%.

1 gm. of the amide so prepared was dissolved in phosphorus oxychloride and heated at 110°C . for about 10 minutes; on boiling off the excess of phosphorus oxychloride and diluting with water, a very small quantity of solid was precipitated. It was impure and/

and even repeated attempts failed to yield sufficient for analysis. The possibility is that a compound with phosphorus was formed which did not dissociate on adding water. The action of thionyl chloride on the amide was also tried, but no satisfactory results were obtained.

N-aceto hydrocarbostyryl acetic acid: 1 gm. hydrocarbostyryl acetic acid was heated on a steam bath with excess of acetic anhydride for 2 hours. The solution was then evaporated to dryness and the solid so obtained recrystallised from ether. A pale yellow crystalline substance which melted at 110°C . was obtained. It was soluble in sodium carbonate, carbon dioxide being evolved, and on analysis proved to be the acetyl derivative of the acid. The results of analysis were:

0.1054 gm. substance gave 0.2425 gm. CO_2 and 0.0508 gm. H_2O

$\text{C} = 62.75\%$, $\text{H} = 5.35\%$.

$\text{C}_{13}\text{H}_{13}\text{NO}_4$ requires $\text{C} = 63.15\%$, $\text{H} = 5.26\%$.

Monochlor dihydrocarbostyryl acetic acid: To 1 gm. dihydrocarbostyryl acetic acid was added a slight excess (about 2.1 gm.) of phosphorus pentachloride and one drop of water. The mixture was heated at 140°C . for 2 hours, cooled, and diluted with water. A yellow semi-solid substance was precipitated which, on being filtered off from the aqueous solution, was dissolved in ether, and allowed to crystallise. Pale yellow crystals melting at 165°C ., were obtained. A large quantity of tarry matter was formed, owing probably to the high temperature. The experiment was therefore repeated, the temperature being kept at 70° . In this case the yield was better. On analysis the following results were found:

0.0967 gm. substance gave 0.2092 gm. CO_2 and 0.0357 gm. H_2O

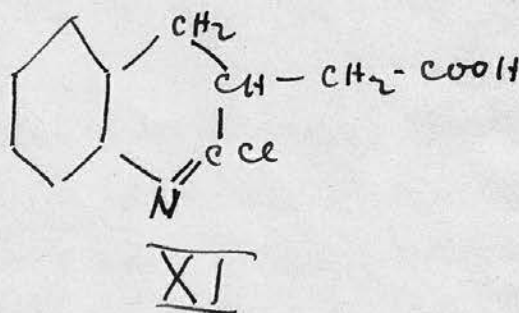
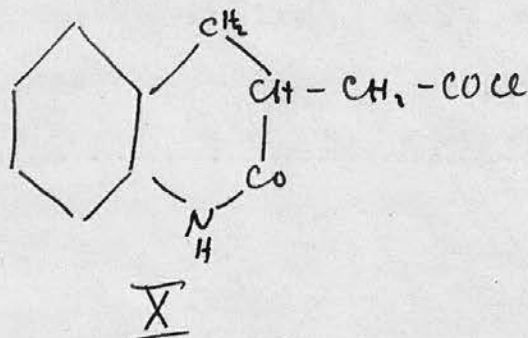
$\text{C} = 59.00\%$ $\text{H} = 4.10\%$.

$\text{C}_{11}\text{H}_{10}\text{NO}_2$ requires $\text{C} = 59.06\%$, $\text{H} = 4.47\%$.

The/

This substance was soluble in sodium carbonate, carbon dioxide being given off. The substance in question could have the constitution represented either by X or by

XI:



The substance was accordingly boiled up with a solution of ammonia but no change took place. Treatment with methyl alcohol and ammonia likewise produced no result, indicating that the substance could not be an acichloride and must therefore be the chlor acid whose formula is represented by XI.

A small quantity of the acid in question was next heated in a sealed tube to 130°. with a saturated solution of ammonia in alcohol for 7 or 8 hours. A yellow solid was obtained which after being dissolved in hydrochloric acid separated out in the form of gray brown crystals melting at 269°C. The crystals were insoluble in water but soluble in sodium carbonate solution with evolution of carbon dioxide. They crystallised well from a boiling solution of acetic acid to which boiling water was added. On analysis the following results were found:

- I. 0.1062 gm. substance gave 0.2543 gm. CO₂ and 0.0450 gm. H₂O.
 II. 0.1257 " " " 0.2995 " " " 0.0557 " "
 III. 0.2157 " " " 13.0 c.c. N₂ at 20°C. and 738 mm. pressure.

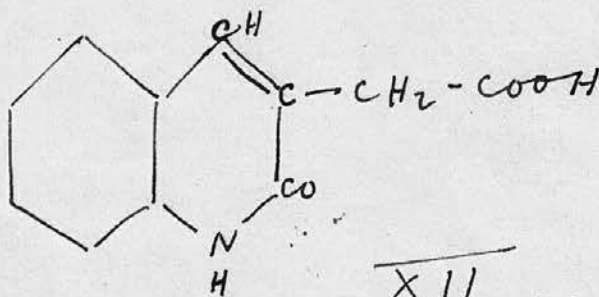
I. C = 65.30%, H = 4.7%, N = 6.7%.

II. C = 64.98%, H = 4.92%.

C₁₁H₉NO₃ requires C = 65.02%, H = 4.43%, N = 6.9%.

From/

From the analysis, melting point and the other properties described above, this substance was shown to be identical with carbostyryl acetic acid (XII) prepared by Perkin and Robinson. The yield was small and the method of preparation is not so convenient as that adopted by Perkin and Robinson.



THE EXHAUSTIVE ALKYLATION OF TETRAHYDRO
BERBERINE.

BY

JAMES WALLACE McDAVID,
WILLIAM HENRY PERKIN, JUN.,

AND

ROBERT ROBINSON.

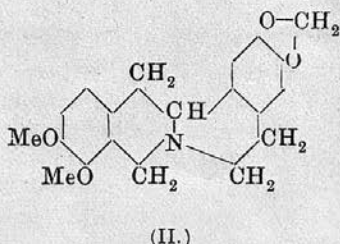
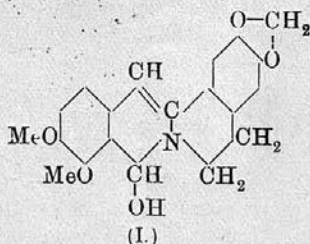
From the Transactions of the Chemical Society, 1912. Vol. 101.

CXXXI.—*The Exhaustive Alkylation of Tetrahydroberberine.*

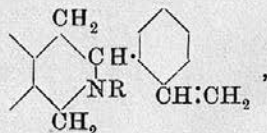
By JAMES WALLACE McDAVID, WILLIAM HENRY PERKIN, jun.,
and ROBERT ROBINSON.

ALTHOUGH analytical and synthetical methods have completely established the constitution of berberine (I) and most of its degradation products, there are still some problems connected with the constitution of this interesting alkaloid which have not been investigated, and since it is so readily available and its reactions always serve to shed valuable light on the structure of the rarer alkaloids, we have continued its investigation in the new direction described in this paper. This communication is an account of the exhaustive alkylation of tetrahydroberberine (II), a substance

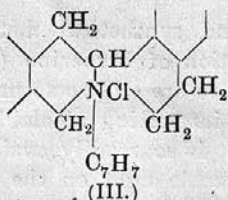
which, as is well known, results from the reduction of berberine (I) with acid reducing agents:



Tetrahydroberberine, containing as it does a system of fixed rings having a nitrogen atom common to two of them, requires a larger number of stages for the elimination of the nitrogen by exhaustive alkylation than any other base which has been investigated in this respect. The preparation of a methyltetrahydroberberine, or which, since it is actually derived from a base isomeric with tetrahydroberberine and containing the group:



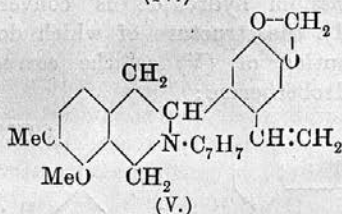
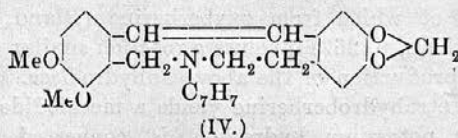
we prefer to call methyltetrahydroberberine, has already been accomplished by Gaze (Beilstein's "Handbuch," III., 801, *Privatmitteilung*). This substance is produced from tetrahydroberberine by combination with methyl iodide and subsequent conversion into the methyl hydroxide, which, on heating in a stream of hydrogen at 100°, loses water and yields methyltetrahydroberberine. We have endeavoured to improve this rather tedious process, but without success, and in consequence we experimented with benzyl chloride in the hope that the corresponding benzyl hydroxide would be less stable than the methyl hydroxide. Tetrahydroberberine benzyl chloride (III), produced by the action of benzyl chloride on tetrahydroberberine, is obtained in two modifications:



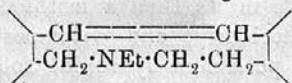
which are doubtless stereoisomeric; the one (a) crystallising with two, and the other (b) with six molecules of water of crystallisation

and melting at 197° and 87° respectively. That these hydrated substances are really different tetrahydroberberine benzyl chlorides is confirmed by the fact that, on complete dehydration over phosphoric oxide, they yield different substances, melting at 203° and 165° respectively. The possibility of stereoisomerism will be readily understood when we consider that, whilst tetrahydroberberine contains an asymmetric carbon atom, the addition of the benzyl chloride brings about asymmetry of the nitrogen atom also, so that *cis-trans*-isomerism becomes possible. One of these isomerides must, however, be exceedingly labile, since both yield one and the same substance containing one molecule of solvent on crystallisation from alcohol. A case which is probably of a similar type, namely, the existence of isomeric ethiodides of *d*- and *l*-canadine (*d*- and *l*-tetrahydroberberine), has already been observed by Gadamer and Voss (*Arch. Pharm.*, 1910, 248, 43).

When either of the tetrahydroberberine benzyl chlorides is decomposed by means of alcoholic potassium hydroxide, an anhydro-base, *N*-benzylisotetrahydroberberine, is produced. This reaction might conceivably proceed in two directions, so as to yield substances of the constitutions (IV) and (V):

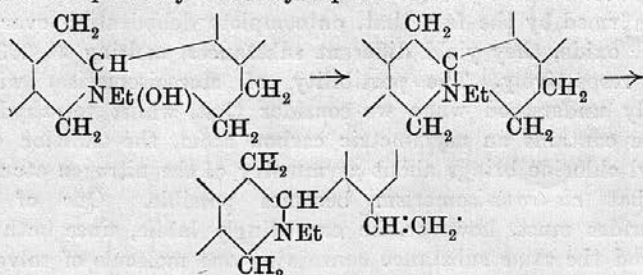


but formula (IV), containing as it does a ten-membered ring, seems improbable, and would not have been discussed were it not for the fact that a similar structure containing the group:

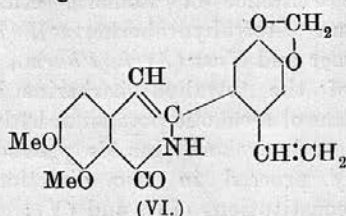


is proposed by Gadamer and Voss (*loc. cit.*) for the anhydro-base derived from tetrahydroberberine (or canadine) ethiodide. The argument employed by these authors in support of their contention is based on the production of an optically inactive anhydro-base from optically active canadine ethyl hydroxide by heat. This certainly indicates that the asymmetric carbon atom is concerned

in the change, and the present authors suggest that the reactions involved are probably correctly represented in the scheme:

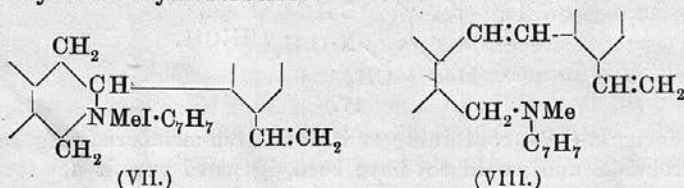


Formula (V) is analogous in structure to *isooxyberberine* (VI):

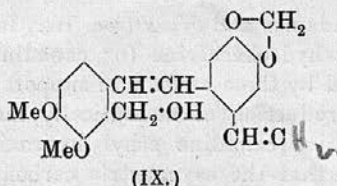


the formation of which from oxyberberine (Bland, Perkin, and Robinson, this vol., p. 262) involves a reaction similar to that which occurs in the production of the above anhydro-base.

N-Benzylisotetrahydroberberine yields a methiodide (VII) which with alcoholic potassium hydroxide is converted into a new anhydro-base (VIII), the structure of which does not necessarily depend on the adoption of (V) as the correct expression for *N*-benzylisotetrahydroberberine:



The new base yields in its turn a methiodide which was converted into the methochloride and decomposed by boiling with concentrated aqueous potassium hydroxide followed by prolonged



distillation in a current of steam. Benzyl dimethylamine was formed, together with a neutral substance, $C_{20}H_{20}O_6$, which evidently has the constitution (IX).

This substance is 3:4-dimethoxy-3':4'-methylenedioxy-2-hydroxy-methyl-6'-vinylstilbene, but for the sake of convenience it may be called *berberilene*.

EXPERIMENTAL.

Tetrahydroberberine.

This substance was prepared by a slight modification of the process described by Hlasiwetz and Gilm (*Annalen, Suppl.*, 1863, 2, 192). Berberine sulphate (25 grams) dissolved in boiling water (500 c.c.) containing sulphuric acid (40 grams) and acetic acid (80 grams) was reduced by means of excess of zinc ribbon during several hours, and until the yellow colour of the solution had almost disappeared. After filtration, the solution was saturated with common salt, when tetrahydroberberine hydrochloride was precipitated as a pale yellow, amorphous solid. This was collected, dissolved in hot water, and decomposed with ammonia. The base was then purified by crystallisation from benzene, when prisms melting at 167° were obtained.

Tetrahydroberberine Methosulphate.—This derivative was prepared because it was thought that it might be more readily decomposed by alkali than the methiodide, which, however, is not the case.

Tetrahydroberberine (1 mol.) was dissolved in benzene and treated with pure methyl sulphate (1 mol.), when heat was developed and in a few seconds the additive compound crystallised. It was collected, washed with benzene, and recrystallised from ethyl alcohol, when colourless prisms melting at 224° were obtained:

0.1092 gave 0.2285 CO_2 and 0.0560 H_2O . C=56.8; H=5.7.

$C_{20}H_{21}O_4N(CH_3)_2SO_4$ requires C=56.8; H=5.8 per cent.

The substance is fairly readily soluble in hot water, from which it separates in large prisms containing solvent of crystallisation. When its solution in hot water was treated with a large excess of concentrated aqueous potassium hydroxide, no decomposition took place, since the salt crystallised unchanged from the solution, and after recrystallisation from alcohol the melting point was 224° :

0.1116 gave 0.2323 CO_2 and 0.0610 H_2O . C=56.8; H=6.1.

On boiling with alcoholic potassium hydroxide the salt was, however, decomposed, and tetrahydroberberine methyl hydroxide melting at $160-164^\circ$ and identical with the substance prepared by Gaze (*loc. cit.*) was obtained. Since this substance requires to

be heated at 100° in hydrogen to effect its decomposition into water and the anhydro-base, the process was abandoned in favour of a more convenient method.

The Tetrahydroberberine Benzyl Chlorides (a and b) (III, p. 1219).

In preparing these substances, tetrahydroberberine (30 grams) and benzyl chloride (12 grams) were heated at 100° for thirty hours. The resulting greyish-yellow solid was washed with ether and crystallised from water, when the salt separated in two distinct modifications; the first crop (*a*), when dried in the air, melted at 197°, and the second more soluble substance (*b*) melted at 87°. When these substances were recrystallised separately from water they did not undergo any change, and there can be little doubt that they are hydrated stereoisomeric tetrahydroberberine benzyl chlorides (compare p. 1220). As the following analyses clearly show, (*a*) has two, and (*b*) six molecules of water of crystallisation:

(*a*) 0.1229 gave 0.2892 CO₂ and 0.0708 H₂O. C=64.2; H=6.4.
 0.1490 „ 0.3545 CO₂ „ 0.0877 H₂O. C=64.9; H=6.5.
 0.3446 lost 0.0246 on exposure in a vacuum over P₂O₅.
 H₂O=7.1.

C₂₇H₂₈O₄NCl, 2H₂O requires C=64.6; H=6.4; H₂O=7.1 per cent.

(*b*) 0.1779 gave 0.3624 CO₂ and 0.1116 H₂O. C=55.9; H=7.0.
 0.1460 „ 0.3024 CO₂ „ 0.0934 H₂O. C=56.3; H=7.1.
 0.1563 „ 4.2 c.c. N₂ at 22° and 746.5 mm. N=3.0.
 0.3296 „ 8.6 c.c. N₂ „ 20° „ 726 mm. N=3.0.
 0.3772 „ 0.0965 AgCl. Cl=6.3.
 0.4365 lost 0.0750 in a vacuum over P₂O₅. H₂O=17.2.

C₂₇H₂₈O₄NCl, 6H₂O requires C=56.1; H=7.0; N=2.5; Cl=6.2;
 H₂O=17.1 per cent.

The anhydrous solid obtained by the dehydration of (*a*) melted at 203°, and on analysis:

0.1121 gave 0.2863 CO₂ and 0.0620 H₂O. C=69.6; H=6.1.
 0.1123 „ 0.2837 CO₂ „ 0.0625 H₂O. C=69.2; H=6.1.
 C₂₇H₂₈O₄NCl requires C=69.6; H=6.0 per cent.

On the other hand, the anhydrous compound derived from (*b*) melted at 165°, and in this case the analytical result was not quite so sharp:

0.1095 gave 0.2753 CO₂ and 0.0599 H₂O. C=68.5; H=6.1.

On crystallisation from alcohol the original crude additive product, or the substances (*a*) or (*b*) yield colourless prisms melting at 200°. These were found to consist of tetrahydroberberine benzyl

chloride with one molecule of ethyl alcohol of crystallisation. On analysis of air-dried specimens:

0.1064 gave 0.2671 CO_2 and 0.0645 H_2O . C=68.3; H=6.7.

0.1086 „ 0.2719 CO_2 „ 0.0665 H_2O . C=68.3; H=6.7.

0.1784 „ 0.0460 AgCl . Cl=6.4.

$\text{C}_{27}\text{H}_{23}\text{O}_4\text{NCl}$, $\text{C}_2\text{H}_5\text{O}$ requires C=68.0; H=6.6; Cl=6.8 per cent.

The presence of alcohol was confirmed by drying the substance at 50° , and distilling with water, when alcohol was recognised in the distillate by means of the iodoform reaction.

It is a very curious phenomenon that the two different substances (a) and (b) should yield the same compound after crystallisation from alcohol, and the high melting point would seem to indicate that the transformation is from (b) into (a).

N-Benzylisotetrahydroberberine (V, p. 1220).

Tetrahydroberberine benzyl chloride was found to be almost unchanged by aqueous potassium hydroxide, but its decomposition was readily effected in alcoholic solution.

Tetrahydroberberine benzyl chloride (20 grams) was dissolved in hot ethyl alcohol (100 grams), and boiled with an excess of solid potassium hydroxide for an hour on the steam-bath. After filtration, most of the alcohol was distilled off, when a brown, resinous solid (15 grams) separated from the residue. This could not be crystallised, but yielded a hydrochloride which separated from ethyl alcohol in colourless needles, and after drying at 120° melted at 214° . On analysis of a specimen dried at 120° :

0.1051 gave 0.2667 CO_2 and 0.0585 H_2O . C=69.2; H=6.2.

0.0847 „ 0.2160 CO_2 „ 0.0473 H_2O . C=69.4; H=6.2.

$\text{C}_{27}\text{H}_{25}\text{O}_4\text{NCl}$ requires C=69.6; H=6.0 per cent.

The Dibromide Hydrochloride.—In order to confirm the constitution assigned to this substance a few grams of the hydrochloride were dissolved in cold chloroform and treated with a 20 per cent. solution of bromine in chloroform, drop by drop, until the bromine was no longer absorbed. On allowing the solution to remain, pale yellow crystals melting at 195° separated, which consisted of the dibromide of N-benzylisotetrahydroberberine hydrochloride:

0.1069 gave 0.2655 CO_2 and 0.0466 H_2O . C=52.3; H=4.6.

$\text{C}_{27}\text{H}_{25}\text{O}_4\text{NClBr}_2$ requires C=51.8; H=4.5 per cent.

Methiodide.—This substance was easily prepared by boiling the base with an excess of pure methyl iodide for two hours, and the colourless solid which gradually separated from the clear solution was collected and crystallised from alcohol. This methiodide occurs in prisms melting at 187° :

0.1141 gave 0.2468 CO₂ and 0.0559 H₂O. C=57.0; H=5.4.

0.1130 „ 0.2462 CO₂ „ 0.0549 H₂O. C=59.4; H=5.4.

C₂₈H₃₀O₄NI requires C=58.9; H=5.3 per cent.

In order to make quite sure that this compound is really the methiodide and not the hydriodide, the latter was prepared, and found to be quite a different substance. For this purpose *N*-benzylisotetrahydroberberine hydrochloride was treated in aqueous solution with potassium iodide; the precipitated salt was recrystallised from ethyl alcohol, when pale yellow crystals of the hydriodide melting at 197° were obtained.

Anhydro-N-benzylisotetrahydroberberine Methyl Hydroxide Methiodide, MeO and the Corresponding Methochloride.

N-Benzylisotetrahydroberberine methiodide, like tetrahydroberberine methiodide, is not decomposed by aqueous alkali. When boiled with alcoholic potassium hydroxide it is, however, converted into a new amorphous base.

The methiodide (115 grams) was dissolved in alcohol (80 grams), and boiled with excess of powdered potassium hydroxide on the steam-bath for about an hour. The bulk of the alcohol was removed by distillation, and the solution cooled, when a yellow, semi-solid substance separated, which was several times washed with warm water and then dried. It became brittle on keeping, but all attempts to crystallise the substance or its salts failed. This base, which probably has the constitution assigned to it in the introduction (p. 1221), was therefore at once converted into its crystalline methiodide by boiling with an excess of methyl iodide during two hours. The colourless substance was recrystallised several times from methyl alcohol, from which it separates in transparent, well defined, rhombohedral plates melting at 191°. This methiodide is almost unaffected even by boiling alcoholic potassium hydroxide, and is only very slowly attacked by silver hydroxide. Since this behaviour is probably due to the sparing solubility of the substance in water, it was converted into the corresponding methochloride. For this purpose a paste of the methiodide and silver chloride with water was added to more water and boiled during two hours. The filtered solution contained no iodine, and, after concentrating and cooling, deposited a quantity of pale yellow plates which were recrystallised from acetone. The dry substance melts at 180°:

0.1096 gave 0.2825 CO₂ and 0.0693 H₂O. C=70.3; H=7.0.

0.1008 „ 0.2599 CO₂ „ 0.0622 H₂O. C=70.4; H=6.8.

C₂₉H₃₂O₄NCl requires C=70.5; H=6.5 per cent.

This methochloride is gradually decomposed by silver hydroxide, but it was found to be more advantageous to employ a concentrated aqueous solution of potassium hydroxide as described in the next section.

3:4-Dimethoxy-3':4'-methylenedioxy-2-hydroxymethyl-6'-vinyl-stilbene (Berberilene) (IX, p. 1221).

The methochloride (15 grams) described in the last section was dissolved in water, and a concentrated aqueous solution of potassium hydroxide added. A dark brown precipitate was soon formed, and the mixture was boiled and then subjected to steam distillation for fifteen hours at least. The aqueous distillate was acidified with hydrochloric acid, and evaporated nearly to dryness. Platinic chloride was then added, and the solution allowed to remain in the cold, when orange-yellow needles separated, and these after recrystallisation from water melted at 195°. (Found, Pt=28.7. (C₇H₇NMe₂)₂H₂PtCl₆ requires Pt=28.7 per cent.)

The base produced is therefore benzyldimethylamine. Under the above conditions, however, the decomposition was still incomplete, since the residue in the flask contained nitrogen. The solid residue was therefore washed with water to free it from potassium hydroxide, dried, and heated for eight hours at 130°. The product was collected and extracted with alcohol, dissolved in a small quantity of methyl ethyl ketone, and gradually precipitated by the addition of hot alcohol to the solution. The pale yellow powder so obtained commenced to decompose at 250°, and melted about 280°. It contained neither nitrogen nor halogen, and its analysis, combined with its method of preparation, is consistent only with the formula suggested:

0.1135 gave 0.2940 CO₂ and 0.0638 H₂O. C=70.6; H=6.2.

C₂₀H₂₀O₅ requires C=70.6; H=6.0 per cent.

Unfortunately, owing to the very small quantity of this substance available we have not yet been able to submit it to further investigation or to prepare derivatives.

THE UNIVERSITY,
MANCHESTER.

REPRINT FROM THE
PROCEEDINGS
OF THE
ROYAL SOCIETY OF EDINBURGH.
SESSION 1909-1910.

VOL. XXX.—PART VI.—(No. 29.)

Equilibrium in the Ternary System: Water,
Potassium carbonate, Potassium ethyl di-
propyl-malonate.

By J. W. M'David, B.Sc.

EDINBURGH:
PUBLISHED BY ROBERT GRANT & SON, 107 PRINCES STREET, AND
WILLIAMS & NORGATE, 14 HENRIETTA STREET, COVENT GARDEN, LONDON.

MDCCCX.

Price Sixpence.

XXIX.—Equilibrium in the Ternary System: Water, Potassium carbonate, Potassium ethyl di-propyl-malonate. By J. W. M'David, B.Sc., Carnegie Research Scholar. *Communicated by* Professor JAMES WALKER.

(MS. received April 13, 1910. Read May 16, 1910.)

DURING the electrolysis of a solution of potassium ethyl di-propyl-malonate it was discovered by Crichton* that when a concentrated aqueous solution of the salt was shaken up with a concentrated aqueous solution of potassium carbonate two distinct layers were formed. The peculiarity of this case lies in the fact that both substances are salts of the same metal, though cases of the non-miscibility of aqueous solutions of two totally different substances are common, as, for example, that of potassium carbonate and alcohol.

The object of the following investigation is to show how the miscibility of the two solutions depends on their concentrations, temperature, etc.

The potassium ethyl salt was prepared from di-propyl-malonic ester by half saponification with a solution of potassium hydroxide in methyl alcohol. The saponification was done in four stages, one-fourth of the amount of alkali necessary for half saponification being used each time. After addition of water the unsaponified ester which separated was removed by means of ether and the aqueous solution evaporated to dryness. The potassium ethyl salt was freed from di-potassium salt by dissolving in hot absolute alcohol in which the latter salt is practically insoluble. The ester salt so obtained was analysed, but was still found to contain a small quantity of di-potassium salt. A fresh sample was made as above described, but the saponification was only carried out to the third stage. The ester salt, purified as before, was found on analysis to be free from di-potassium salt.

0.2164 gm. potassium ethyl salt yielded 0.0744 gm. K_2SO_4 ;
i.e. 100 parts " " " " 34.37 parts "

Theory—

100 parts $KC_{11}H_{19}O_4$ yield 34.27 parts K_2SO_4 .

An attempt was made to determine the solubility of the pure potassium

* *Journal Chem. Soc.*, vol. lxxxix, p. 929 (1906).

ethyl salt. It was, however, found impossible to obtain a saturated solution, the liquid gradually assuming the consistency of a thick syrup in which solid particles were suspended in a fine state of division. A concentrated solution of the ester salt was then made and shaken up with a saturated solution of potassium carbonate. Mixture only took place to a limited extent, two distinct layers separating when the liquid was allowed to stand. Water was added drop by drop from a burette to the liquid, with constant stirring, until the two layers disappeared and one homogeneous solution was left. The disappearance of the two layers was quite sharply defined. The above experiment was then repeated quantitatively. 5.5 gms. potassium ethyl di-propyl-malonate were dissolved in 2 gms. water and 1.05 c.cs. of this solution were put into a graduated tube. 1.05 c.cs. of a saturated solution (about 52 per cent.) of potassium carbonate were added, and thereafter water drop by drop.

The following readings were taken:—

Total Volume of Liquid.	Vol. of K_2CO_3 Solution.	Vol. of KEt. Salt Solution.
2.10	1.05	1.05
3.05	1.55	1.50
3.45	1.65	1.80
3.80	1.45	2.35
3.95	1.15	2.80
4.05	homogeneous.	

From the above table it is seen that, while at first the volumes of both layers increase on addition of water, the potassium carbonate layer soon begins to diminish in volume while the volume of the ester salt solution increases steadily. This seems to indicate that it is the carbonate solution which gradually passes into that of the ester salt, one homogeneous liquid being obtained when the whole of the potassium carbonate solution disappears into the other layer. As will be seen later, on more accurate analysis this was found to be the case.

The mixtures to be investigated were made up by putting weighed quantities of potassium ethyl di-propyl-malonate, potassium carbonate and water into a stoppered tube and thoroughly mixing in a thermostat at 25° C. The mixture was then allowed to settle into two layers at the temperature of the bath.

Methods of analysing the two layers had next to be devised. The first method attempted was to find the total percentage of potassium in each layer, and then the percentage of carbon dioxide in the layers was found by

adding hydrochloric acid to a weighed quantity of solution and collecting the dried carbon dioxide in two weighed soda-lime tubes. From the amount of carbon dioxide obtained the percentage of potassium carbonate could be found, and hence the amount of potassium due to the carbonate could be calculated. This being subtracted from the total potassium gave the amount due to the potassium ethyl salt, and from this amount the

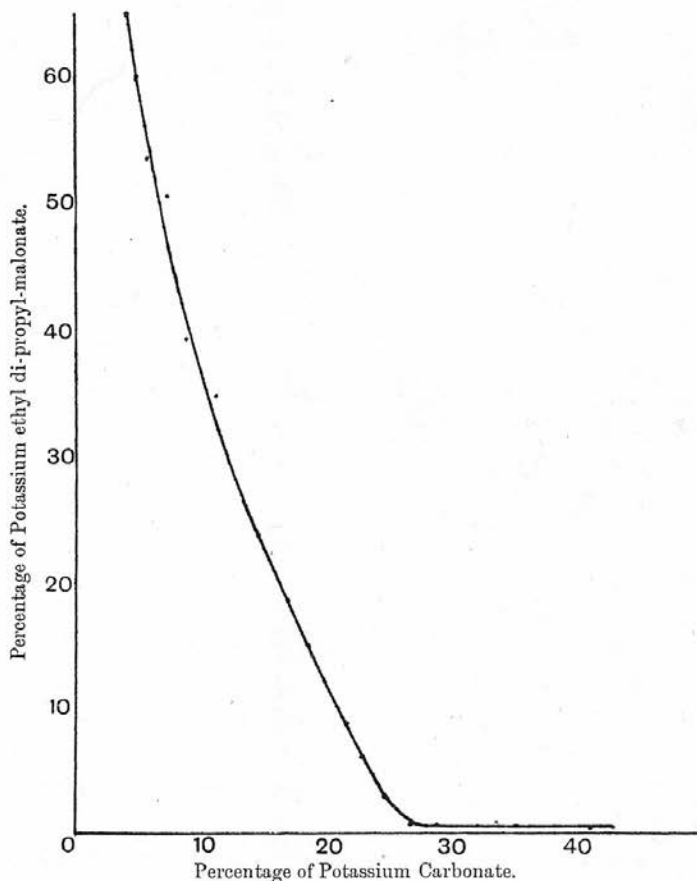


FIG. 1.

percentage of the ester salt could be ascertained. This method, however, failed to give concordant results. Finally the following methods were adopted. To determine the percentage of potassium ethyl salt, a weighed quantity of the solution was acidified with dilute sulphuric acid, when hydrogen ethyl di-propyl-malonate was precipitated. The ester acid was extracted with ether and washed to get rid of sulphuric acid. The ether was then evaporated off, and after addition of a little water the residue was titrated with a standard solution of baryta. To determine the percentage

of potassium carbonate present, the fact that the colour of phenolphthalein disappears when the potassium carbonate is changed to bicarbonate was made use of. A weighed quantity of solution was therefore titrated with an acid of known strength, phenolphthalein being used as indicator, and the percentage of potassium carbonate obtained. In order to check these results, in most cases the total potassium was determined gravimetrically. The results obtained were concordant.

A series of mixtures were made up as follows:—

No. of Mixture.	Weight of KEt. Salt (gms.).	Weight of K_2CO_3 (gms.).	Weight of Water (gms.).
1	3.081	3.081	5.115
2	3.011	3.010	6.025
3	1.953	4.333	9.210
4	3.059	3.048	8.158
5	3.058	3.143	9.654
6	3.017	3.125	10.673
7	3.027	3.203	12.032
8 } 9 }	unknown.		

Nos. 1, 2, 4, 5, 6 and 7 were made up by taking approximately equal weights of the two salts. No. 3 was made up by taking totally different proportions of the salts, while the last two mixtures were obtained by diluting two of the more concentrated with water to nearly the point at which complete mixture took place.

The solutions were analysed, after equilibrium had been attained, by the methods explained above, with the following results:—

No. of Mixture.	Upper Layer.			Lower Layer.		
	Per Cent. KEt. Salt.	Per Cent. K_2CO_3 .	Per cent. H_2O .	Per Cent. KEt. Salt.	Per Cent. K_2CO_3 .	Per cent. H_2O .
1	65.1	4.05	30.85	0.4	42.6	57.0
2	59.8	4.9	35.3	0.4	40.7	58.9
3	53.5	5.6	40.9	0.5	35.0	64.5
4	50.5	7.2	42.3	0.9	33.5	65.6
5	39.2	8.7	52.1	0.7	28.9	70.4
6	34.6	11.0	54.4	0.8	26.8	72.4
7	23.5	14.5	62.0	3.0	24.8	72.2
8	18.6	17.0	64.4	6.05	23.1	70.85
9	15.0	18.6	66.4	8.7	21.7	69.6

As will be seen from the above table, even in the case of concentrated solutions there is a considerable quantity of potassium carbonate in the

upper layer. On the other hand, the amount of potassium ethyl di-propyl-malonate in the potassium carbonate layer is scarcely appreciable in the first six mixtures, and it is only when the solutions are comparatively dilute that there is any appreciable increase in the amount of the ester salt in the lower layer. This confirms the results of the rough experiment previously referred to, viz. that in order to produce equilibrium when a mixture is

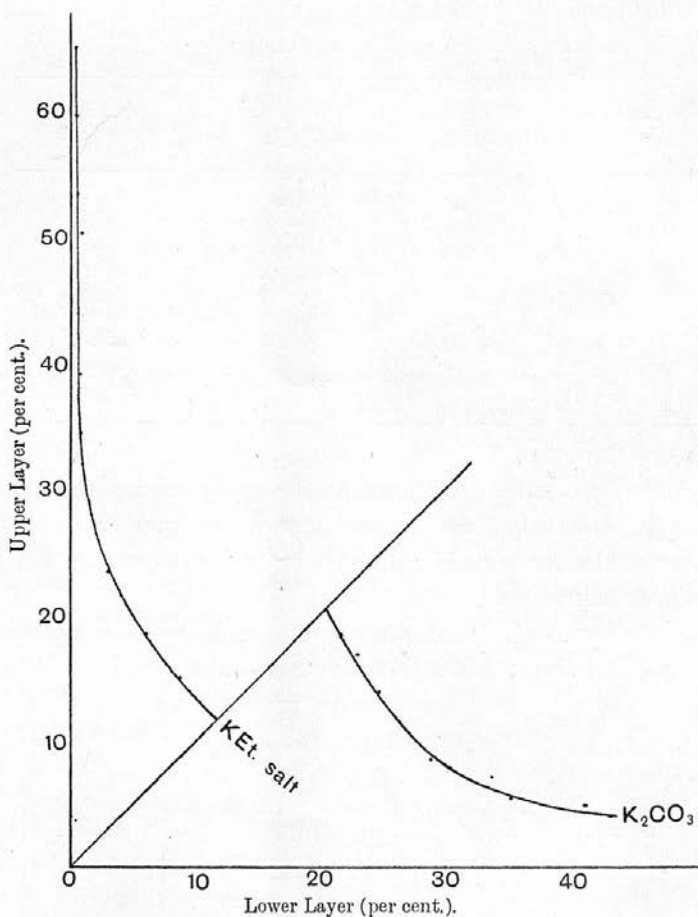


FIG. 2.

diluted, some potassium carbonate passes from the lower to the upper layer. It will also be observed that the percentage of water in the lower layer at first increases and then diminishes as the mixtures become more dilute.

The results shown in the above table may be represented graphically. By plotting the percentage of potassium ethyl di-propyl-malonate against that of potassium carbonate in each layer in the series 1 to 7, two curves (fig. 1) are obtained representing the upper and lower layers respectively.

The points for Nos. 8 and 9 lie on these curves produced. If the two curves are produced still further, they meet and form one continuous curve at the point where the two layers become homogeneous. This occurs when the composition of the two layers is identical. The percentage of each salt in the solution at this point can be determined from the curves in

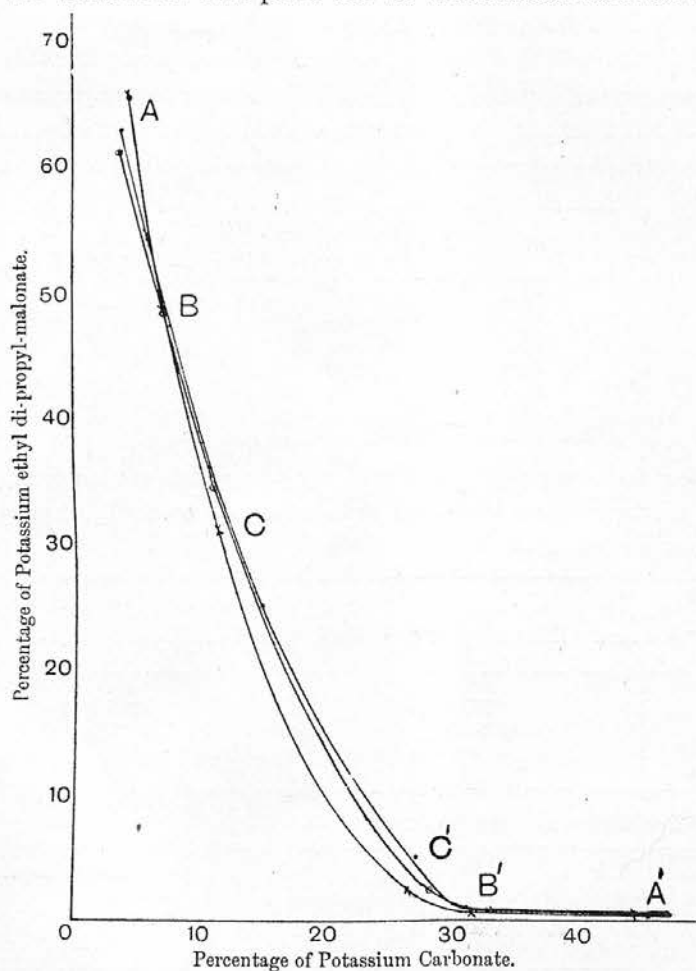


FIG. 3.

fig. 2. The curve to the left shows the connection between the percentage of potassium ethyl salt in the upper and lower layers respectively, while that to the right represents similarly the percentages of potassium carbonate in the two layers. A line drawn through the origin at an angle of 45° to the axes cuts the curves at points which give the percentage of potassium ethyl salt, and of potassium carbonate when the two layers become identical. Thus when the solution becomes homogeneous it contains 11.6 per cent.

potassium ethyl di-propyl-malonate, 20.6 per cent. potassium carbonate, and 67.8 per cent. water.

The above investigations all were carried out at 25° C. To ascertain roughly the effect of temperature, a mixture was made up which just gave a homogeneous solution at the above temperature. This solution was then heated slowly in a water-bath. A slight opalescence occurred at 25.4 C., indicating that the solution was separating into two layers. Another portion of the same mixture was cooled to zero, but there was no apparent change.

Some of No. 2 mixture was put into a graduated tube and heated slowly in a water-bath, the volumes of the two layers being noted as follows:—

Temperature °C.	Vol. of Upper Layer (c.cs.).	Vol. of Lower Layer (c.cs.).
0.2	1.90	2.90
16.1	1.91	2.92
25.3	1.92	2.94
44.0	1.93	2.96
66.0	1.96	2.98
82.0	1.97	2.99

In order to observe more accurately the effect of temperature, the following mixtures were made up and brought into equilibrium at three different temperatures:—

No. of Mixture.	Weight of KEt. salt (gms.).	Weight of K ₂ CO ₃ (gms.).	Weight of Water (gms.).
10	6.063	6.161	10.014
11	6.372	6.265	23.030
12		obtained by dilution.	

The following results were obtained:—

No. of Mixture.	Temperature °C.	Upper Layer.		Lower Layer.	
		Per Cent. KEt. Salt.	Per Cent. K ₂ CO ₃ .	Per Cent. KEt. Salt.	Per Cent. K ₂ CO ₃ .
10	2°	25.0	15.0	5.1	27.3
	25	31.0	11.35	2.6	26.55
	56	34.35	11.25	2.45	28.35
11	2	62.9	3.95	0.55	45.5
	25	65.9	4.35	0.45	44.2
	56	60.9	3.65	0.65	47.2
12	2	47.2	7.8	0.7	31.2
	25	48.6	7.35	0.4	31.6
	56	48.35	7.45	0.75	33.0

The diagram fig. 3 represents the above results. When the mixture is such that the upper layer contains about 48 per cent. of potassium ethyl di-propyl-malonate, the three iso-thermals are very close together, and hence at this concentration it is evident that the effect of temperature on the mixture is very small.

An attempt was made to find out the temperature at which the two solid phases and the two liquid phases were present at the same time, but owing to the extreme viscosity of the liquid this was not successful, though it was found to be probably in the vicinity of 46° C.

A sample of sodium ethyl di-propyl-malonate was also made, and its solutions were found to have the same properties with regard to a solution of sodium or potassium carbonate as the potassium ethyl salt had to either of these solutions.

CHEMISTRY DEPARTMENT,
UNIVERSITY OF EDINBURGH.

(Issued separately July 14, 1910.)

REPRINT FROM THE

PROCEEDINGS

OF THE

ROYAL SOCIETY OF EDINBURGH.

SESSION 1909-1910.

VOL. XXX.—PART VI.—(No. 36.)

Specific Volume of Solutions of Tetra-propyl-
ammonium Chloride.

By J. W. M'David, B.Sc.

EDINBURGH :

PUBLISHED BY ROBERT GRANT & SON, 107 PRINCES STREET, AND
WILLIAMS & NORGATE, 14 HENRIETTA STREET, COVENT GARDEN, LONDON.

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Price Sixpence.

XXXVI.—Specific Volume of Solutions of Tetra-propyl-ammonium Chloride. By J. W. M'David, B.Sc., Carnegie Research Scholar. Communicated by Professor JAMES WALKER.

(MS. received June 7, 1910. Read July 4, 1910.)

DURING the investigation of the viscosities of aqueous solutions of tetra-propyl-ammonium chloride, Taylor and Moore* noticed that the density of a concentrated solution was less than that of a dilute solution at the same temperature. The following investigation, undertaken at the suggestion of Dr W. W. Taylor, shows how the density depends on the concentration and temperature of the solution.

Tetra-propyl-ammonium chloride was prepared from tetra-propyl-ammonium iodide. Silver chloride was added to an aqueous solution of the iodide and the mixture allowed to stand in the dark for some time. The tetra-propyl-ammonium chloride solution which was formed was then filtered off from the solid silver iodide and evaporated to dryness in a vacuum desiccator. The solid so obtained was a white crystalline substance which was very deliquescent. It was tested and found to be free from iodide.

A number of solutions of various concentrations were then made up. By titrating with a standard solution of silver nitrate the concentration of each solution was obtained. Its density was next determined at four different temperatures, viz. 0° C., 25° C., 35° C., and 56° C., by means of a Sprengel pycnometer. The density of each solution was deduced from the formula

$$d_p = \frac{W'D}{W} - \frac{0.012(W' - W)}{W}$$

The values for the density of water were taken from Landolt and Börnstein's Tables, pages 37 and 38.

The concentrations of the various solutions and their respective densities at each temperature are as follows:—

Concentration gms. per 100 gms. Solution.	Density.			
	0°.	25°.	35°.	56°.
0.0	.9999	.9971	.9942	.9853
0.93	.9997	.9968	.9938	.9850
1.73	.9995	.99645	.9933	.98465
3.12	.99915	.99595	.9928	.9839
6.87	.9991	.9952	.99195	.9826
9.75	.99895	.99445	.9908	.98155
10.90	.9992	.99465	.9910	.98155
15.69	.99965	.9940	.9901	.9798
23.98	1.0030	.99465	.9902	.9786
27.70	1.0055	.9959	.9909	.9792

* *Proc. Roy. Soc. Edin.*, xxviii. p. 470 (1908).

From the above table it is seen that at all temperatures the density of a dilute solution is less than the density of water at the same temperature. As the concentration increases the density gradually diminishes up to a certain point, depending on the temperature, and then begins to increase. By drawing four isothermals to represent the connection between the concentration and density of the solutions (fig. 1), it will be noticed that in each case the curve has a minimum, and that the minimum point moves away from the origin as the temperature increases. For example, the concentration of the solution of minimum density at 0° C. is about 7 per cent., at

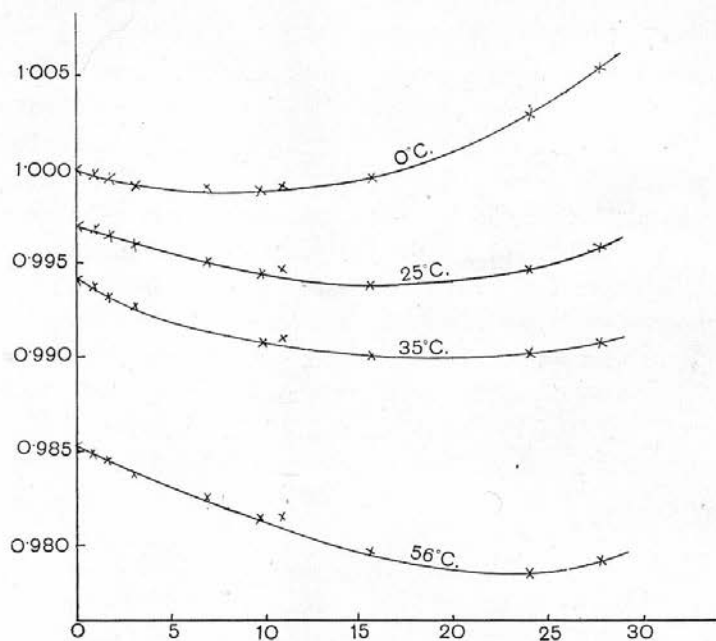


FIG. 1.—Concentration.

25° C. it is 16.5 per cent., at 35° C. 19 per cent., while at 56° C. it is approximately 22.5 per cent. It will be noticed that it is possible to obtain two solutions of different concentrations which have the same density. Thus at 25° C. a solution whose concentration is 3.12 per cent. has the same density as a 27.7 per cent. solution at that temperature. If now these two solutions are mixed, the resulting solution would have a smaller density. Similar results are obtained at the other temperatures.

Generally the density of a solution of a solid increases considerably as the concentration increases. It has been found, however, that the density of a solution of ammonium chloride* increases very slowly with the

* Landolt and Börnstein's Tables.

concentration. A 5 per cent. solution has a density of 1.058, while the density of a 25 per cent. solution is 1.0730. In the case of tetrethyl-ammonium chloride* the increase of density with concentration is even smaller, 4.14 per cent. and 16.30 per cent. solutions having densities of .9971 and .9994 respectively, while in the present case of tetra-propyl-ammonium chloride under certain conditions the density actually decreases as the concentration increases.

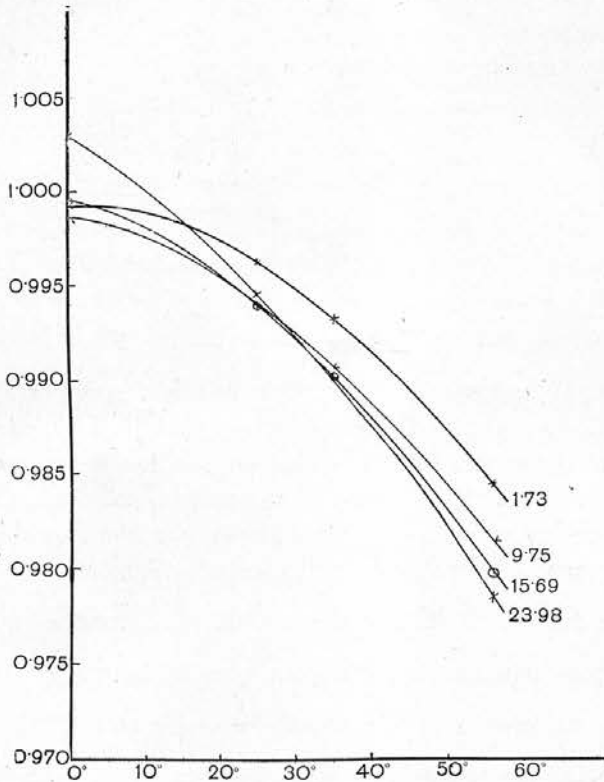


FIG. 2.—Temperature.

The curves in fig. 2 show the connection between density and temperature for solutions whose concentrations are constant.

Since the density of a dilute solution is less than that of water, it is evident that there must be expansion on solution. In order to find out whether the volume of a solution was greater than the combined volumes of solid and water, it was necessary to determine the density of the solid. To do this the method of floating was employed, the density being

* Taylor and Moore, *loc. cit.*

determined at two temperatures, viz. 2° C. and 13° C. The liquids used were bromonaphthalene and toluene. A mixture of these liquids was placed in a small test-tube and a few small crystals of tetra-propyl-ammonium chloride were introduced. The density of the liquid was adjusted by adding a few drops of bromonaphthalene or toluene until the crystals remained suspended in the liquid. The density of the mixture was then determined at 13° C.: this was found by means of the Westphal Balance, while at 2° C. the density of the liquid was determined by means of a pycnometer.

The following results were obtained :—

	3° C.	13° C.
	1·0329	1·0290
	1·0330	1·0295
	1·0344	1·0300
Average	1·0334	1·0296

The values 1·0341 and 1·0255 were taken as the density of the solid at 0° C. and 25° C. respectively, these values being obtained by extrapolation.

In order to determine the expansion on solution, it was necessary to determine the volume of unit mass of the various solutions, the volumes which the water in that unit mass would occupy at the same temperature, and also the volume of the solid in unit mass of each solution.

If d be the density of the solution at t° C., $\frac{1}{d}$ = volume 1 gm. solution at t° C. Suppose now that c is the concentration in gms. of solid per 100 gms. solution, and that Δ is the density of water at t° C., then $\frac{1-c/100}{\Delta}$ is the volume that the water in 1 gm. of solution would occupy if it were free.

If δ be the density of the solid, then $\frac{1}{\delta} \times \frac{c}{100}$ is the volume of solid in 1 gm. of solution.

The expansion on solution will be given by the formula

$$\frac{1}{d} - \left\{ \frac{1-c/100}{\Delta} + \frac{c/100}{\delta} \right\}.$$

The following table gives the results calculated for five of the foregoing solutions :—

Concentration gms. per 100 gms. Solution.	Tempera- ture t° C.	Density gms. per c.c.	Vol. of 1 gm. Solu- tion at t° V ₁ .	Vol. of Water in 1 gm. Solution.	Vol. of Solid in 1 gm. Solution.	Vol. of Water + Vol. of Solid in 1 gm. Solution V ₂	Expansion on Solution V ₁ - V ₂ .
1.73	0	.9995	1.0005	.9828	.0167	.9995	.0010
"	25	.9964	1.0036	.9856	.0169	1.0025	.0011
10.90	0	.9992	1.0008	.8911	.1054	.9965	.0043
"	25	.99465	1.0054	.8936	.1063	.9999	.0055
15.69	0	.99965	1.0004	.8432	.1517	.9949	.0055
"	25	.9940	1.0060	.8456	.1530	.9986	.0074
23.98	0	1.0030	.9970	.7603	.2319	.9922	.0048
"	25	.99465	1.0054	.7624	.2338	.9962	.0092
27.70	0	1.0055	.9945	.7231	.2679	.9910	.0035
"	25	.9959	1.0041	.7250	.2701	.9951	.0090

The figures in the last column of the table show that in all cases there is expansion on solution, *i.e.* the volume of solution is greater than the combined volumes of the solid and water in that solution. It will also be noticed that at 0° C. the expansion at first increases with concentration and

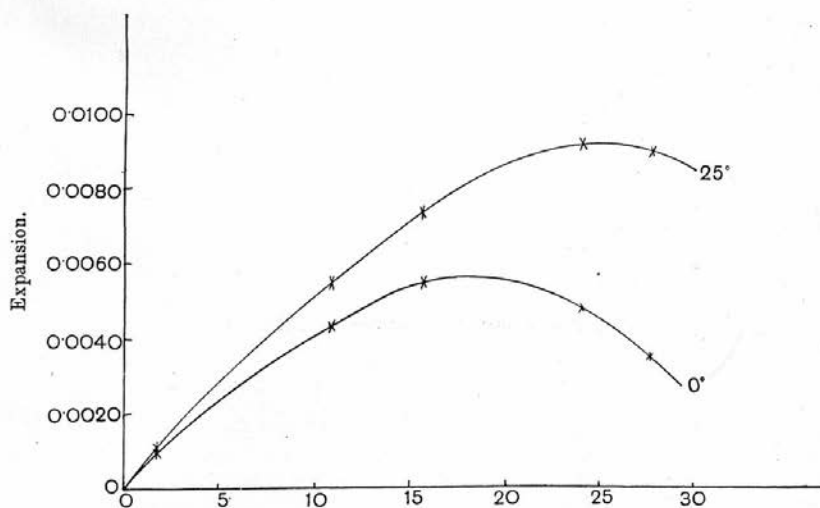


FIG. 3.—Concentration.

then decreases. Generally when a solid dissolves in water there is a slight contraction, *i.e.* the volume of the solution is greater than the volume of water in that solution, but less than the combined volumes of water and solid. There are, however, a few exceptions, of which the present case is one. Braun * mentions the chloride, bromide, and iodide of ammonium,

* *Zeit. f. physik. Chem.*, i. p. 259 (1887).

tartaric acid, and magnesium chloride hexahydrate as being solids which give expansion on solution.

On the other hand, Carse* found that in the case of dilute solutions of certain hydroxides the volume of solution was less than the volume of water it contained.

The curves in fig. 3 show the connection between the expansion on solution and the concentration at the two temperatures 0° C. and 25° C. At 0° C. a solution whose concentration is about 18.5 per cent. has the maximum expansion. At 25° C. a 26 per cent. solution evidently has maximum expansion. It will also be observed that the expansion increases considerably as the temperature is raised.

Similar results were calculated for the temperatures 35° C. and 56° C., but, owing to no allowance being made for the expansion of the solid, their accuracy could not be guaranteed, hence they have been omitted.

CHEMISTRY DEPARTMENT,
UNIVERSITY OF EDINBURGH.

* *Proc. Roy. Soc. Edin.*, xxv. p. 286 (1904).

(Issued separately September 7, 1910.)