

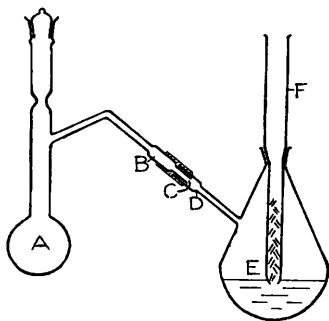
## NOTES.

*The Determination of Available Oxygen by the Bunsen Method.*

By THOMAS WALLACE PARKER and PERCY LUCOCK ROBINSON.

THE most recent investigation of the accuracy of the Bunsen method of determining available oxygen by liberation of chlorine appears to indicate that results may be as much as 0.5% low (for potassium

permanganate) owing to the reaction between chlorine and water (Rupp, *Z. anal. Chem.*, 1918, 57, 226). Difficulties attending accepted practice, viz., the tendency for the potassium iodide solution to be drawn back into the reaction flask and the necessity of transferring this solution to another vessel for titration (compare Wagner, *Z. anal. Chem.*, 1903, 42, 365), have been overcome by using the device shown in the figure.



The apparatus consists of a 50 c.c. flask, A, with a ground-in stopper, sealed by sulphuric acid, and a delivery tube of 8 mm. diameter, widened at B to 10 mm., the end, C, of which is inserted into the especially widened side tube of the absorption flask, rubber being used to complete the joints. The absorption flask, E, is a pear-shaped vessel, 18 cm. high and of 250—300 c.c. capacity, into the neck of which is fitted, by a ground-joint, the tube F, 22 × 2 cm., the rounded bottom of which is pierced with a small hole 8 mm. in diameter. The lower two-thirds of this tube is packed with glass beads. This apparatus is filled to such a height with potassium iodide solution that with the passage of gas the liquid is forced up

the tube 1—1.5 inches above the general level before the pressure is relieved and part of the liquid returns to the main bulk. With such an adjustment there is a continuous interchange of liquid in the bead column, and if for any cause the pressure in the system falls below atmospheric, air passes down the tube into the apparatus.

In carrying out an estimation 20 c.c. of pure concentrated hydrochloric acid were measured into the reaction flask, a fragment of porous pot was added, followed by a small test-tube containing a known weight of pure potassium dichromate, after which the stopper was immediately inserted and  $\frac{1}{2}$ — $\frac{2}{3}$  of the liquid was gently distilled into the potassium iodide. The absorption flask was then detached, the bead-packed tube removed after being well washed both inside and outside with potassium iodide solution and with water, and the liberated iodine was titrated with thiosulphate solution. Blank experiments with acid alone showed that there was a constant correction of about 0.45 c.c. of 0.04*N*-thiosulphate. The addition of magnesite for the purpose of displacing the last trace of chlorine from the reaction flask was without appreciable effect and the addition of potassium iodide to several lots of diluted residual liquor showed a complete absence of chlorine in all cases. Experiments made in an earlier apparatus, in which the delivery tube was fitted to the neck of the flask by a ground joint, showed that the washing-out of this tube does not raise the result. Lubrication of this ground joint with vaselin or with metaphosphoric acid gave slightly low, or higher but somewhat irregular, results, respectively.

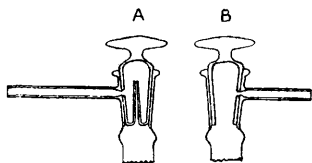
Ten experiments made with 0.1200 g.  $\pm$  0.2 mg. portions of potassium dichromate and titrated to  $\pm$  0.05 c.c. of 0.1*N*-thiosulphate, gave results agreeing among themselves to 1 part in 325 parts, but the mean was about 0.37% low.

In order to find whether the method is susceptible of a high degree of accuracy a second series of experiments was made in which the dichromate was weighed to  $\pm$  0.02 mg. and the chlorine was liberated under slightly less than atmospheric pressure and absorbed at 0°. The thiosulphate was standardised with 0.1*N*-potassium dichromate by means of a weight burette and an approximately 0.04*N*-thiosulphate solution was prepared by the same method. The weight burette was used for the 0.1*N*-thiosulphate in titrating the liberated iodine, the end point being finally reached by use of the weaker solution in a burette, and in this manner results to  $\pm$  0.02 c.c. of 0.1*N*-thiosulphate were obtained. The following figures, the first being the weight of dichromate (g.) and the second the available oxygen %, indicate a concordance of 1 part in 3,250 parts and the mean is 0.18% below the theoretical

value : 0.24653, 16.281 ; 0.24319, 16.283 ; 0.24681, 16.286 ; 0.12167, 16.285.—UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE, NEWCASTLE-ON-TYNE. [Received, February 22nd, 1929.]

*An Improved Calcium Chloride Tube.* By DOUGLAS VERNON NELMAR HARDY.

CALCIUM chloride tubes of many different designs have been employed for the absorption of water produced during combustions. Of these, the chief types in common usage are (i) the U-tube with two side-arms, one of which carries a water-trap, and (ii) the U-tube similar to that shown in the diagram but having both stopcocks of design B. The first type may be used many times with the same filling, but has the disadvantage that, while it is waiting to be weighed, rubber caps must be attached. The use of the second type involves frequent replacement of the filling. The advantages of both patterns are possessed by the U-tube shown (as to its upper part) in the diagram, in which stopcock A acts as an efficient water-trap. — UNIVERSITY COLLEGE, SOUTHAMPTON. [Received, February 26th, 1929.]



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*The Volatility and Structures of the Azides and Aliphatic Diazo-compounds.* By NEVIL V. SIDGWICK.

THE cyclic structures originally ascribed to these compounds have been generally abandoned in recent years in favour of the open-chain formulæ I and II (as expressed in modern symbols).



This is due mainly to the work of Angeli, Thiele, and Staudinger, who showed that they give derivatives containing these open chains. The proof that the azoxy-compounds and the *N*-ethers of the oximes have open-chain and not ring structures supported this view. The argument is, however, not very conclusive; it might be urged that the azides and diazo-compounds themselves contain closed rings, and that when these open, since the double link between nitrogen atoms (unlike that between carbons) is normally very strong, they must form unbranched chains.

Lindemann and Thiele (*Ber.*, 1928, 61, 1529) have shown that the parachors of a series of azides have the values to be expected for the ring structures. But this also is inconclusive, because the difference between the constitutive values calculated for the ring (38.6) and for the open-chain formula I (44.8) is only about 2% of

the total parachor; and though the observed value (mean, 40.3) is nearer to the former than to the latter, it might be maintained that these unusual structures involved a slight modification of the accepted parachor values.

It is to be expected that the volatility of the compounds will throw light on their structures. A co-ordinate link always causes a rise in the b. p., due to the external field of the resulting dipole, as is shown by the b. p.'s of the isomeric pairs  $\text{CH}_3\cdot\text{O}\cdot\text{NO}$ ,  $-12^\circ$ ;  $\text{CH}_3\cdot\text{N}\overset{\text{O}}{\underset{\text{O}}{\rightleftharpoons}}$ ,  $101^\circ$ :  $\text{P}(\text{O}\cdot\text{C}_2\text{H}_5)_3$ ,  $156^\circ$ ;  $\text{C}_2\text{H}_5(\text{C}_2\text{H}_5\cdot\text{O})_2\text{P}\rightarrow\text{O}$ ,  $198^\circ$ :  $(\text{CH}_3)_2\text{N}\cdot\text{O}\cdot\text{CH}_3$ ,  $30^\circ$ ;  $(\text{CH}_3)_3\text{N}\rightarrow\text{O}$ ,  $>180^\circ$ . If the azides and the aliphatic diazo-compounds have the ring structures, they should boil at about the same temperatures as the corresponding chlorides or bromides, whereas if they have open-chain structures with the co-ordinate link, their b. p.'s should be much higher, and nearer to those of the nitro-compounds.

In the following tables the published data are collected. The second column gives the pressure in mm. under which the b. p. of the azide or diazo-compound was observed: the values for the halides and nitro-compounds at this pressure have been found by interpolation, or by extrapolation by means of the Ramsay-Young formula; the latter is not very accurate, but the errors should not exceed a few degrees. Compounds whose b. p.'s are recorded at pressures below 10 mm. have been omitted, because of the uncertainty both of the measurements and of the necessary extrapolations.

TABLE I.  
Boiling Points of Azides.

	Press. (mm.).	X =				
		N <sub>3</sub> .	Cl.	Br.	I.	NO <sub>2</sub> .
CH <sub>3</sub> X .....	760	20°	-24°	+ 4.5°	43°	101°
CH <sub>2</sub> Cl-CH <sub>2</sub> X .....	25	45	24	32	68	77
CH <sub>2</sub> Br-CH <sub>2</sub> X .....	20	49	20	33	63	—
CH <sub>2</sub> I-CH <sub>2</sub> X .....	20	68	63	63	—	—
CH <sub>2</sub> ·CHX .....	760	26	-15	+17	—	—
CH <sub>2</sub> ·CH-CH <sub>2</sub> X .....	760	76	46	71	103	127
CH <sub>2</sub> X-CH <sub>2</sub> ·OH .....	20	73	50	65	78	105
CH <sub>2</sub> X-CH <sub>2</sub> ·OEt .....	25	49	19	35	56	72
CH <sub>2</sub> X·COCl .....	20	50	12	33	55	—
X·CO <sub>2</sub> Me .....	760	102	71	—	—	—
X·CO <sub>2</sub> Et .....	760	113	93	—	—	—
X·CH <sub>2</sub> ·CO <sub>2</sub> Et .....	20	70	52	73	81	101
CH <sub>3</sub> ·CHX·CO <sub>2</sub> Et .....	16	70	49	59	63	85
(CH <sub>3</sub> ) <sub>2</sub> CX·CO <sub>2</sub> Et .....	16	71	53	65	—	—
(CH <sub>3</sub> ) <sub>2</sub> CH·CHX·CO <sub>2</sub> Et .....	16	82	74	79	—	94
CH <sub>3</sub> ·CO·O·CH <sub>2</sub> ·CH <sub>2</sub> X .....	20	74	53	67	86	108
C <sub>6</sub> H <sub>5</sub> X .....	24	74	37	55	82	106
C <sub>6</sub> H <sub>5</sub> ·CH <sub>2</sub> X .....	23	108	77	95	—	121
(p)CH <sub>3</sub> ·C <sub>6</sub> H <sub>4</sub> X .....	15	78	33	48	69	86

TABLE II.

## Boiling Points of Aliphatic Diazo-compounds.

	Press. (mm.).	X =				
		N <sub>2</sub> .	H, Cl.	H, Br.	H, I.	H, NO <sub>2</sub> .
CH <sub>2</sub> X .....	760	-23°	-24°	+4.5°	45°	101°
CHX·CO <sub>2</sub> Me .....	760	132	130	144	170	203
CHX·CO <sub>2</sub> Et .....	760	143	145	169	180	216
CHX·CO <sub>2</sub> C <sub>6</sub> H <sub>11</sub> .....	760	164	190	207	—	—
CH <sub>3</sub> ·CX·CO <sub>2</sub> Me .....	13	54	38	48	—	—
CH <sub>3</sub> ·CX·CO <sub>2</sub> Et .....	41	67	72	80	87	112
CH <sub>3</sub> ·CH <sub>2</sub> ·CX·CO <sub>2</sub> Et .....	11	64	54	64	84	106
(CH <sub>3</sub> ) <sub>2</sub> CH·CH <sub>2</sub> ·CX·CO <sub>2</sub> Et ...	12	72	90	98	—	—
CH <sub>3</sub> ·CO·CX·CO <sub>2</sub> Et .....	12	103	100	103	—	—
CHX·CN .....	15	47	27	47	79	—

It will be seen that the b. p.'s of the azides lie near those of the bromides, or between these and the iodides (this was pointed out by Forster and Newman, J., 1910, 97, 2572, from whose paper several of the values are taken); the b. p.'s of the diazo-compounds lie very near those of the chlorides; those of the nitro-compounds are always much higher. These results seem to indicate that the ring formulæ should be retained for both of these classes of compound.—  
LINCOLN COLLEGE, OXFORD. [Received, April 8th, 1929.]

*The Preparation of Quinaldinic Acid.* By THOMAS WESTON  
JOHNS TAYLOR.

THE most convenient way of preparing quinaldinic acid is that of Reissert (*Ber.*, 1905, 38, 1610) in which the acid is obtained as its copper salt. The tedious operation of removing the copper with hydrogen sulphide can be avoided and the acid obtained much more readily by taking advantage of the low solubility of sodium quinaldinate in cold sodium hydroxide solution.

If the copper salt is boiled with an excess of such a solution (about 2*N*) until all the copper is present as oxide, and the hot solution filtered, sodium quinaldinate crystallises in about 85% yield on cooling. The sodium salt so obtained has the formula C<sub>9</sub>H<sub>6</sub>N·CO<sub>2</sub>Na, 1½H<sub>2</sub>O, and does not lose its water on standing in a vacuum over calcium chloride (Found: Na, 10.3, 10.4, 10.5. Calc.: Na, 10.4%). The water is lost by heating to 140–150°, or by drying over sulphuric acid in a vacuum (Found: Na, 11.9, 11.7. Calc.: Na, 11.8%). The hydrate of the sodium salt can be purified by recrystallisation from dilute sodium hydroxide solution or from 95% alcohol; in the latter case it first separates as a thick jelly which gradually breaks up into crystals. Rough solubility determinations showed that at room temperature it is about forty times less soluble in 1.5*N*-sodium hydroxide than it is in water.

The acid can be rapidly obtained from the sodium salt by making a paste of the latter with water and adding the theoretical amount of hydrochloric acid. After cooling, the acid can be collected and washed with ice-cold water.—THE DYSON PERRINS LABORATORY, OXFORD. [Received, April 17th, 1929.]

*The Viscosity of Ether at Low Temperatures.* By EDM. VAN AUBEL.

THE relation between the fluidity of a normal liquid and the temperature has been shown by the author (*Compt. rend.*, 1921, 173, 384) to be represented by the formula  $\phi = m + n \log(\theta - t)$ , where  $m$  and  $n$  are constants and  $\theta$  is the critical temperature. This formula was shown to represent satisfactorily the behaviour of several normal liquids above  $0^\circ$ . The recently published measurements of Archibald and Ure (*J.*, 1927, 610) on the viscosities of ether from  $0^\circ$  to  $-109.8^\circ$  give the opportunity of testing the validity of the formula at lower temperatures. The following table shows that good agreement is obtained down to  $-92.2^\circ$ . The constants used in obtaining the calculated values are: critical temperature of ether  $\theta = 193.8^\circ$ ,  $m = 4003.46$ ,  $n = -1599.7$ .

Temp.	Fluidity measured.	Fluidity calc.	Diff.	Temp.	Fluidity measured.	Fluidity calc.	Diff.
$0^\circ$	344.5	344.39	+0.11	$-53.9^\circ$	174.2	173.89	+0.31
$-10.2$	308.7	308.75	-0.05	$-64.5$	144.3	144.79	-0.49
$-20.2$	275.0	275.5	-0.5	$-75.4$	115.4	116.08	-0.68
$-30.1$	243.4	244.09	-0.69	$-84.4$	93.05	93.22	-0.17
$-32.1$	238.1	237.9	+0.2	$-92.2$	74.96	74.01	+0.95
$-43.0$	206.2	205.17	+1.03				

THE UNIVERSITY, GHENT. [Received, March 5th, 1929.]