

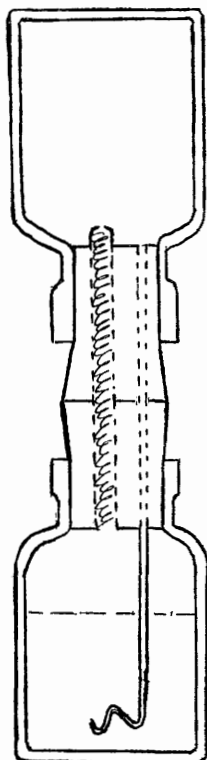
NOTES.

An Apparatus for the Determination of Solubility. By
ALAN N. CAMPBELL.

IN some very accurate work on the physical properties of optical antipodes (*Nature*, 1929, **124**, 792), it became necessary to determine solubilities with great accuracy, and any such method as the removal of samples from a bottle in the thermostat by means of a warmed pipette was obviously out of the question. Previous work with Goldschmidt's apparatus (*Z. physikal. Chem.*, 1895, **17**, 153) had shown that, although this embodies the important principle of filtering in the thermostat, it had certain objections: (1) it is too cumbersome; (2) suction is employed, whereby, if the solid is fine or slimy, it becomes clogged in the filter-plug and the apparatus has to be cleaned out. Accordingly the apparatus shown in the diagram was designed. It possesses the advantages of compactness and simplicity, for when it is inverted in the thermostat, filtration takes place.

The bottles are of the ordinary wide-mouthed 1-oz. type, except that the mouth of the top one is ground. Glass tubes pass through the bungs as shown. The wider tube (of 3 mm. internal diameter)

is constricted at the top and packed with glass wool. The other (quill) tube is drawn out to a capillary and bent into an S. As the liquid entering this tube at the beginning is pure solvent, which would dilute the saturated solution when subsequently expelled by the air pressure from below, it is advisable to arrange that all the immersed tube is of capillary diameter. The very small amount of pure solvent then expelled (perhaps 0.1 c.c.) is negligible in comparison with the total volume, especially when it is remembered that the whole solution then passes slowly through a layer of the solid.



× One-half.

The lower bottle is charged with solid and solvent and the apparatus fixed in a vertical position on the horizontal paddle of the thermostat stirrer. When dissolution is complete, the apparatus is inverted in the thermostat, and the solution filters through the plug, air being displaced into the upper chamber through the narrow tube. The double bend at the mouth of the latter prevents the entrance of solid matter into the lower bottle. The apparatus is then removed from the thermostat and the appropriate (weighed) bottle closed with a ground-glass plate.

The apparatus works perfectly, and should be very suitable for phase-rule studies, involving the analysis of the wet solid phase. The slight increase of gas pressure in the apparatus at the temperature of the thermostat prevents the leaking in of thermostat water. At high temperatures the apparatus should be enclosed in a grip to prevent the increased pressure forcing out the bungs.—UNIVERSITY OF ABERDEEN. [Received, December 9th, 1929.]

2'-Nitro-2- and -4-aminodiphenyl Sulphides and 4'-Nitro-2- and -4-aminodiphenyl Sulphides. By HERBERT HENRY HODGSON and WOLF ROSENBERG.

THE requisite diaminodiphenyl sulphide (25 g.) was dissolved in alcohol (200 c.c.), and sodium wire (5 g.) added at a rate sufficient to maintain regular ebullition (under reflux); after boiling for one hour, the mixture was treated with *o*- or *p*-chloronitrobenzene in slight excess of the amount required for the condensation

$\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SNa} + \text{C}_6\text{H}_4\text{Cl} \cdot \text{NO}_2 \longrightarrow \text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 + \text{NaCl}$, then boiled 2 hours longer and filtered hot. Only 4'-nitro-4-amino-diphenyl sulphide crystallised from solution on cooling; in the other cases alcohol, unchanged chloronitrobenzene, and any chloroaniline formed as by-product were removed by steam distillations and the tarry residue was crystallised three times from alcohol (charcoal). Constitutions were confirmed by reduction to the known diamino-diphenyl sulphides.

	M. p. and % S ($\text{C}_{12}\text{H}_{10}\text{O}_2\text{N}_2\text{S}$ requires S, 13%).	Colour of alcoholic solution.	Colour change of alcoholic solution with		Dry product with conc. sulphuric acid.
			chlorine water.	bleaching powder.	
Diphenyl sulphide.					
2'-Nitro-2-amino- (bright yellow plates)	81.5°; 13.2	Greenish- yellow	Brown with light sal- mon flocks	Pale brown	Yellow
2'-Nitro-4-amino- (golden-brown plates)	102°; 13.2	Brown- yellow	Light brown with brown flocks	Pale brown	Deep red changing to blue and violet on heating
4'-Nitro-2-amino- (brown-yellow prisms)	93°; 12.9	Greenish- yellow	Pale brown with sal- mon-pink flocks	Pale brown	Orange
4'-Nitro-4-amino- (bright orange-yellow leaflets)	143°; 13.2	Greenish- yellow	Light brown with yel- low flocks	Pale brown	Red-orange
		(compare Kehrmann and Bauer, <i>Ber.</i> , 1896, 29, 2362)			
2: 4'-Diamino- (colourless prisms from dilute alcohol)	62.5°; 15.0	(Calc. 14.8)			
		(compare Nietzki and Bothof, <i>Ber.</i> , 1894, 27, 3261; 1896, 29, 2774)			

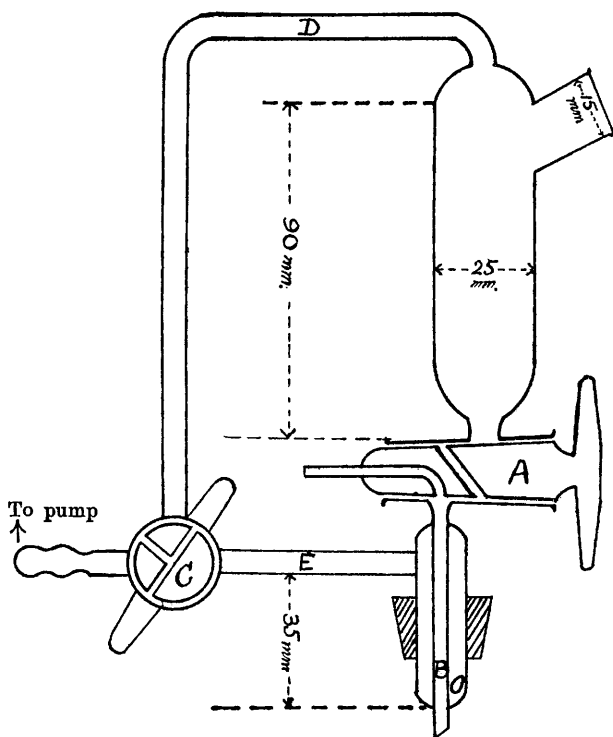
The authors desire to thank the British Dyestuffs Corporation for gifts of chemicals.—TECHNICAL COLLEGE, HUDDERSFIELD. [Received, November 13th, 1929.]

The Solubility of Sodium Thiocyanate in Alcohol. By JAMES RIDDICK PARTINGTON.

In a recent communication (Hughes and Mead, *J.*, 1929, 2282) the authors state that, for the solubility of sodium thiocyanate in alcohol, "no data are at present available." This statement is incorrect, since Dr. F. E. King and I published a series of experiments on this subject some little time ago (*Trans. Faraday Soc.*, 1927, 23, 522). The method of preparation of the salt was the same as that described by Hughes and Mead; their value for the solubility at 25° is, however, somewhat lower than ours, which may be due to the fact that the salt used by them was somewhat purer than ours, or, equally possibly, to some other cause. It may be mentioned that several experiments on the solubilities of salts in non-aqueous solvents have been published from this laboratory, and that several more are in progress.—EAST LONDON COLLEGE, UNIVERSITY OF LONDON. [Received, November 29th, 1929.]

An Improved Receiver for Vacuum Distillation. By GEORGE ARMAND ROBERT KON.

THE accompanying figure illustrates a form of receiver for vacuum distillation which has been in use in these laboratories for some time. It is simpler and cheaper than the ordinary "Perkin triangle," as it has only two taps instead of three; another advantage is that when air is admitted through the tap *A* to the lower portion of the apparatus



atus in order that the receiving flask may be changed, the last few drops of distillate remaining in the tube *B* are blown into the receiving vessel, thus minimising waste. The three-way tap *C* enables connexion to be made between the pump and either or both halves of the apparatus. It is, of course, possible to construct the apparatus with two rubber joints at *D* and *E* to allow receivers of different sizes to be used, but the all-glass apparatus illustrated is preferable, and as it is very compact, breakages are rare.*—IMPERIAL COLLEGE OF

* The apparatus described can be obtained from Messrs. Howard Rawson & Co., Pond Place, Fulham Road, London, S.W. 3.

SCIENCE AND TECHNOLOGY, SOUTH KENSINGTON, S.W. 7. [Received, December 11th, 1929.]

Preparation of 4- and 6-Hydroxy-3-nitrophenylarsinic Acids.

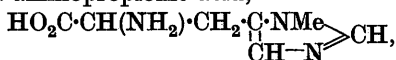
By ISIDORE ELKANAH BALABAN.

CLAUS and STIEBEL (*Ber.*, 1887, 20, 1379) reduced 2:4-dinitrochlorobenzene and obtained a mixture of 4- and 6-chloro-3-nitroaniline consisting almost wholly of the 6-chloro-compound: no yields are stated. These bases can be readily obtained by West's method (*J.*, 1925, 127, 494), the yields being 23.0% and 45.0% of 4- and 6-chloro-3-nitroaniline respectively.

When the bases are submitted to the Bart-Schmidt reaction, 4-chloro-3-nitrophenylarsinic acid (yield, 32.4%) and 6-chloro-3-nitrophenylarsinic acid (yield, 32.9%) are obtained (compare Balaban, *J.*, 1928, 809); and when these acids are boiled under reflux with 25% aqueous sodium hydroxide (10 c.c. for each gram) for 3 hours, they are converted into 4-hydroxy-3-nitrophenylarsinic acid (yield, 45.6%) and 6-hydroxy-3-nitrophenylarsinic acid (yield, 73.0%).—RESEARCH LABORATORY, MESSRS. MAY & BAKER LTD., WANDSWORTH, S.W. 18. [Received, December 7th, 1929.]

Anserine. By FRANK LEE PYMAN.

LINNEWEH, KEIL, and HOPPE-SEYLER (*Z. physiol. Chem.*, 1929, 183, 11) have recently shown that anserine yields on hydrolysis β -aminopropionic acid and an *N*-methyl derivative of *dl*-histidine. On distillation with soda-lime, anserine gave a dimethylglyoxaline which they identified with the dimethylglyoxaline obtained by Jowett (*J.*, 1903, 83, 438) by distilling *isopilocarpine* with soda-lime, since it gave a chloroaurate, m. p. 220—225°, Jowett giving m. p. 214—215°. They have overlooked the fact that the constitutions of the 1:4- and 1:5-dimethylglyoxalines have since been determined (Pyman, *J.*, 1910, 97, 1814; 1922, 121, 2616; Burtles, Pyman, and Roylance, *J.*, 1925, 127, 581), and that it has been shown that the chloroaurates melt at 137—138° and 218—219° respectively. Their dimethylglyoxaline is thus 1:5-dimethylglyoxaline and consequently their methylhistidine is *dl*- β -(1-methylglyoxalanyl-5)- α -aminopropionic acid,



and not the 1:4-isomeride formulated in their paper. The relative positions of the side chains and the *N*-methyl groups are thus the

same in anserine and pilocarpine.—RESEARCH LABORATORIES, MESSRS. BOOTS PURE DRUG CO. LTD., NOTTINGHAM. [Received, December 18th, 1929.]

The Mechanism of Cyanoacetamide and Cyanoacetic Ester Condensations. By CHRISTOPHER KELK INGOLD.

BARDHAN'S account (J., 1929, 2233) of the author's views on the condensation of ethyl cyanoacetate and similar substances with keto-enolic compounds requires adjustment. The only reference given by Bardhan in this connexion is to a paper (1921) by the author in which the conclusion was drawn that, since tendency to enolisation bears a close relation to tendency to condensation, the latter reaction involves the enol. Kohler and Corson's later demonstration (1923) that, notwithstanding the experience of previous observers (Thorpe, 1905; Haworth, 1908), condensation is possible with a ketone incapable of enolisation was naturally accepted by the author as proving that his former view was inadequate as a general conception, and in 1926, with Cooper and E. H. Ingold, he again discussed the Michael and aldol reactions in terms the application of which to cases of the type considered by Bardhan is that the cyanoacetamide or ethyl cyanoacetate anion may unite with the acetylacetone analogue either at C_α (electron-displacements α ; aldol reaction) or at C_γ (displacements M ; Michael reaction),

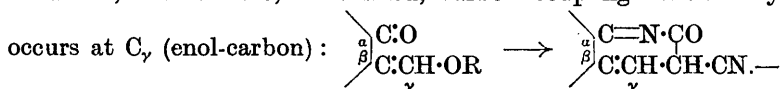
$\text{HO}\cdot\overset{\text{M}}{\text{C}}=\overset{\alpha}{\text{C}}-\overset{\alpha}{\text{C}}=\overset{\alpha}{\text{O}}$, and that a similar statement should apply to ketones generally, unless the second alternative disappears because

the unsaturated system is insufficiently extended to admit of displacements M . It is also part of the theory that tendency to condensation (aldol reaction; or Michael reaction, if constitutionally

possible) and tendency to enolisation, $\text{H}-\overset{\alpha}{\text{C}}-\overset{\alpha}{\text{C}}=\overset{\alpha}{\text{O}}$ (if constitutionally possible), are different manifestations of the same electron-attraction of carbonyl oxygen—which is why the two phenomena are related. The omission by Bardhan of any reference to this and subsequent cognate papers, together with his consistent use of the present tense in ascription to the author of the older views which these papers modify and supersede, are misleading features in his account.

With regard to the decision between C_α - and C_γ -carbon-coupling (where both possibilities are open, as in enolising 1 : 3-dicarbonyl compounds), a method of envisaging such problems has been advanced by Burton and the author (1928), and a mass of consistent

empirical observation is available. It is therefore surprising that Bardhan, whose own observations on the reaction between cyanoacetamide and enolising 1 : 3-dicarbonyl compounds are indecisive in the absence of knowledge of the direction of enolisation, nevertheless contends that carbon coupling at C_α (carbonyl carbon) is the general mode of reaction in this and allied condensations. No reference is made to the large body of significant contrary indications—even to such as directly relate to the particular reaction studied, as, for instance, the observations of Errera (1900), Simonsen (1908), and Sen-Gupta (1915) that in the condensation of cyanoacetamide with hydroxymethylene-ketones, in which the direction of enolisation is beyond doubt, and with ethoxymethylene-ketones, in which, furthermore, it is fixed, carbon coupling consistently



THE UNIVERSITY, LEEDS. [Received, November 6th, 1929.]
