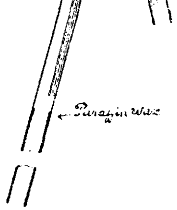
NOTES.

A Simple Form of Automatic Syphon. By DOUGLAS CREESE HARRISON.

FIG. 1.



THE syphon is made of glass tubing of diameter not greater than 5 mm. About eight capillaries of diameters varying between about $\frac{1}{4}$ mm. and 1 mm. and about 20 cm. long are drawn from the same tubing and placed inside the glass tube near one end. The tube is then heated not too strongly and bent to form the syphon, with the capillaries inside the bend and projecting about 7 cm. into the shorter limb of the syphon. The longer limb (which should extend well below the ends of the capillaries) is warmed and molten paraffin wax is drawn into it to within about 4 cm. of the ends of the capillaries. The wax is allowed to run down and the excess shaken out, so that, when cool, a thin, even layer remains on the inside of the tube. The wax serves to retain the drops of liquid drawn through the capillaries by surface tension, until, within a few seconds, they have accumulated to form a column of liquid heavy enough to draw liquid over the bend of the large tube. The height to which the liquid can be raised in starting the syphon will depend, of course, on the surface tension of the liquid and the cross-section of the capillaries. It is advantageous to use a number of capillaries of various diameters, since the liquid will rise more rapidly and to a greater height in the smaller capillaries and, as the liquid begins to accumulate in the longer tube, the pull exerted by gravity will assist the syphoning of the liquid in the larger capillaries. In this way the flow will become faster and faster until the liquid is drawn over the bend and syphons in the large tube. The capillaries occupy only a small part of the tube and so allow a rapid flow of liquid through the syphon.—SHEFFIELD UNIVERSITY. [*Received, August* 18*th*, 1927.]

The Preparation of Triacetonamine Hydrate. By FRANCIS FRANCIS.

THE following method was devised some years ago, but was not described at the time, since it was desired to investigate the other products of the reaction and to increase materially the yield of the base.

Into a mixture of 2½ kg. of acetone and 800 g. of fused calcium chloride in a large round-bottom flask provided with an efficient condenser, ammonia is passed at intervals until the whole of the chloride has been converted into a liquid complex. After 3 days the product is gently boiled on a water-bath until the liquid calcium chloride–ammonia compound has decomposed and resolidified, ammonia being evolved. The dark, strongly smelling liquid is then decanted from the solid or pasty chloride, and distilled until a thermometer in the vapour registers 75°; the distillate consists chiefly of acetone. The residue is placed in a freezing mixture of ice and hydrochloric acid, and when the temperature has fallen to 1—2° an amount of water is added, with vigorous stirring, corresponding to a yield of 28% of triacetonamine calculated on the acetone used, *i.e.*, the amount taken less that distilled off. Triacetonamine hydrate separates in a crystalline condition as the temperature falls; after being pressed between filter-paper and recrystallised several times from undried ether, it is obtained in large, well-formed, slightly yellow crystals (yield, 20—26%, calculated on the acetone used).

The conversion of the hydrate into nitrosotriacetonamine is carried out in the usual manner and the yield is quantitative. The extreme ease with which this nitrosoamine is decomposed catalytically by alkalis, giving a nearly quantitative yield of phorone, renders this an elegant method for the preparation of this unsaturated ketone (J., 1912, **101**, 2358).—THE UNIVERSITY, BRISTOL. [*Received, September* 15*th*, 1927.]

7-*Hydroxy*-3-*phenylcoumarin*. By WILSON BAKER.

AN attempt was made to synthesise 3-phenylchromones (*iso*flavones; Baker and Robinson, J., 1925, **127**, 1981; 1926, 2713) by condensing ethyl α-formylphenylacetate with resorcinol or phloroglucinol in presence of phosphoric anhydride. By analogy with ethyl acetoacetate and its derivatives, chromones should be produced (see papers by Simonis and collaborators, *Ber.*, 1913, **46**, 2015; 1914, **47**, 692, 2229, etc.), but the first condensation gave only 7-hydroxy-3-phenylcoumarin, which has also been prepared (Dey and Row, *J. Indian Chem. Soc.*, 1924, **1**, 121; Bargellini, *Gazzetta*, 1927, **57**, 459) from resorcylaldehyde, sodium phenylacetate, and acetic anhydride.

Jacobson and Ghosh (J., 1915, **107**, 1057) and Ghosh (J., 1916, **109**, 114) describe the reactions between ethyl α-formylphenylacetate and resorcinol, in presence of acetic acid and zinc chloride, and between formylphenylacetonitrile and resorcinol in presence of phosphoryl chloride, and the isolation in both cases of a substance, m. p. 131°, described by them as 7-hydroxy-3-phenylchromone. Since such condensations are now known to give coumarins (Baker and Robinson, J., 1925, **127**, 1981; Baker, *ibid.*, p. 2349; Bargellini, *Gazzetta*, 1925, **55**, 945), and the substance, m. p. 131°, could not be identical with 7-hydroxy-3-phenylcoumarin, which melts at 207—208°, the experiments were repeated, with the result that both gave the same product, m. p. 207—208°, identical in all respects with 7-hydroxy-3-phenylcoumarin. The product, m. p. 131°, is, therefore, not the product of these condensations, and its description is doubtless due to confusion of specimens in the laboratory.

7-*Hydroxy*-3-*phenylcoumarin*.—Ethyl α-formylphenylacetate (15 g.), xylene (75 c.c.), and resorcinol (50 g.) were heated at 160° for 2 hours, phosphoric anhydride (50 g.) being gradually added. The product, boiled with water to expel the xylene, was converted into the acetyl derivative, which, after twice recrystallising from acetic acid (charcoal), separated in colourless, flat prisms, m. p. 184—185°. No trace of an *iso*flavone could be detected in the mother-liquors. Hydrolysis produced 7-hydroxy-3-phenylcoumarin, which separated from alcohol in prisms, m. p. 207—208°, containing alcohol of crystallisation. The methyl ether, prepared by the action of methyl sulphate, crystallised from alcohol in colourless, nacreous plates, m. p. 124° (Bargellini, *loc. cit.*, gives m. p. 118—120°) (Found :

C, 76·0; H, 4·6. Calc.: C, 76·2; H, 4·8%). These compounds give yellow solutions in concentrated sulphuric acid, which exhibit an intense bluish-green fluorescence.

Condensation of Ethyl α-Formylphenylacetate with Phloroglucinol.—The two substances (15 g. of each), treated as previously described, gave an *acetyl* derivative (0·6 g.) which crystallised from acetic acid in hair-like, colourless needles, m. p. 255—256° (Found: C, 73·7, 73·6, 73·7; H, 4·2, 3·8, 4·6%; *M*, by Rast's method, 434, 416). Hydrolysis with potassium carbonate in 50% alcohol gave a phenolic substance which crystallised from alcohol in pale yellow prisms, m. p. 308—310° (decomp.) (Found: C, 72·2; H, 4·5%). This compound of high molecular weight is not identical with the 5 : 7-dihydroxy-3-phenylcoumarin prepared by Bargellini (*loc. cit.*). A number of empirical formulæ agree with the analyses, but without further experiments the selection of a definite formula is not possible. The phenolic *compound* gave with ferric chloride in alcoholic solution a yellow colour, and, like its acetyl derivative, dissolved in concentrated sulphuric acid to a bright yellow solution devoid of fluorescence.—THE UNIVERSITY, MANCHESTER. [*Received, September 13th*, 1927.]

A Double Compound of Chromic and Hydrogen Chlorides.

By JAMES RIDDICK PARTINGTON and SIDNEY KEENLYSIDE TWEEDY.

IF a concentrated solution of dark green chromic chloride is mixed with an equal volume of ether and slowly saturated with hydrogen chloride at 0°, the dark green chloride is precipitated. If the saturation is rapid, however, and the cooling bath is dispensed with, the solution becomes warm and besides dark green chromic chloride a heliotrope substance is precipitated. If the mixture is filtered with the aid of a pump, the green chloride often forms a layer of remarkably fine crystals on top of the heliotrope substance. The latter compound may be obtained in a fairly pure state if the stream of gas is stopped when the liquid is homogeneous and brownish-green, and after a while collects at the bottom of the vessel. The mother-liquor is decanted, the residue mixed with a large excess of ether, and after filtration the substance is air-dried. A further crop may be obtained by passing more hydrogen chloride into the mother-liquor, but after three such precipitations the product becomes largely contaminated with dark green chromic chloride. The substance may conveniently be washed with dry ether in a Soxhlet extractor (Found: Cr, 17·8, 17·3; Cl, 44·7, 44·9%. Constant values could not be obtained, showing that the product was never pure).

When freshly precipitated violet chromic chloride is washed with acetone in a Soxhlet extractor, if the acetone is warm when it falls upon the salt the surface of the latter becomes covered with a layer of the heliotrope substance, which in turn becomes covered with a layer of dark green chromic chloride. It would appear, then, that the heliotrope compound is also formed by the action of hydrogen chloride on the violet chloride when warm, since this acid is present in the freshly precipitated chloride.

The analyses agree roughly with the formula $CrCl_3,HCl,6H_2O$, which requires Cr, 17·2; Cl, 46·9%. Contamination with green or violet chromic chloride would cause the chromium content to increase and the chlorine content to decrease. No salts of this general formula have been described, but Larsson (*Z. anorg. Chem.*, 1920, **110**, 153) prepared two salts of composition $CrCl_3,MCl,5H_2O$, where M = Cs and Rb. A compound of this formula with M = H would require Cr, 18·2; Cl, 49·8%. The analyses will not fit in with any other type of double chloride formed by chromic chloride. Until the heliotrope substance can be prepared in a pure state, it can only be said that it is probably a double compound of the formula $CrCl_3,HCl,xH_2O$, where $x = 5$ or 6. The analyses and the method of preparation support the value $x = 6$.

Recoura (*Compt. rend.*, 1886, **102**, 922; *Ann. Chim. Phys.*, 1887, **10**, 49) records that when hydrogen chloride is passed into a chromic chloride solution for some days the latter turns brown and then red, and a soluble compound $CrCl_3,xHCl$ is formed, where x is greater than unity. On addition of ether, however, it is precipitated in unstable, green needles.

The heliotrope substance is insoluble in methyl and ethyl alcohols and dissolves in water to give a pink solution which immediately turns green, although of a different shade from that given by solutions of dark green chromic chloride. If a fragment of the substance is treated with a drop of water and observed under the microscope, it is seen that the process of solution is accompanied by very vigorous turbulence and agitation. It is not proposed at present to investigate the compound any further.—EAST LONDON COLLEGE, LONDON, E. 1. [*Received, October 6th*, 1927.]

The Viscosities of Chromic Anhydride Solutions. By JAMES RIDDICK PARTINGTON and SIDNEY KEENLYSIDE TWEEDY.

CHROMIC anhydride prepared and purified by the authors' method (J., 1926, 1142) had m. p. 193°. Melting points between 170° and 196° have been recorded in the literature. Both capillary-tube and test-tube methods were employed and the thermometer was compared with a standard instrument before use. Groschuff states (*Z. anorg. Chem.*, 1908, **58**, 108) that chromic anhydride supercools to the extent of 26°; our specimens, however, all solidified sharply within a degree or so of the m. p.

The viscosities of solutions of the anhydride were determined with an Ostwald viscometer as modified by Martin (*Bull. Soc. chim. Belg.*, 1925, **34**, 81). The instrument was standardised with conductivity water, and similar water, which had been stored in a Pyrex flask, was used for preparing the solutions. These were obtained by successive dilution. w is the weight of anhydride in 100 g. of water, η is the viscosity of the solution, and η_{H_2O} that of water (in dyne/cm.^{2}).

w.	η/η_{H_2O}.	η.
	Temp. 0°.	
111·4	1·482	—
72·86	1·195	—
51·38	1·110	—
29·59	1·057	—
	Temp. 18°.	
98·98	1·5116	0·01616
71·01	1·2849	0·01373
67·22	1·2674	0·01355
49·59	1·1628	0·01243
35·92	1·1017	0·01178
25·63	1·0581	0·01131
16·71	1·0349	0·01106

w.	η/η_{H_2O}.	η.
	Temp. 25°.	
147·4	2·3360	0·02130
89·40	1·4880	0·01357
62·60	1·2480	0·01138
46·60	1·1600*	0·01058
42·68	1·1360*	0·01036
31·67	1·0880	0·009923
24·36	1·0560	0·009631
12·05	1·024	0·009339
	Temp. 40°.	
111·4	1·328	0·008980
72·86	1·164	0·007871
51·38	1·1055	0·007475
29·59	1·053	0·007120
21·60	1·041	0·007039
16·55	1·027	0·006945

The readings marked with asterisks appear to be 1—2% too high; they do not lie on the smooth curve passing through the other points. The figures for 40° are probably less trustworthy than those at the lower temperatures, as the thermostat was not automatically controlled at this temperature.

The absolute viscosities, η, were calculated with the aid of Leroux's values for the viscosity of water (*Ann. Physique*, 1925, **4**, 163). If these values are plotted on a very large scale, it is seen that Leroux's results for 2·5° (0·01648) and 7·5° (0·01419 dyne/cm.^{2}) are probably too high by about 0·00015 and 0·0002 dyne/cm.^{2}, respectively. The following equation, which is of the type proposed by Slotte (*Ann. Physik*, 1888, **34**, 28), represents the curve with fair accuracy between 10·9° and 30°:

$$\eta_{H_2O}\,(\text{dyne/cm.}^2) = \frac{0{\cdot}633161}{T - 241{\cdot}307} - 0{\cdot}00207155$$

where $T = t + 273$, t being in degrees Centigrade. The closeness of the observed and calculated values is of the order accepted by Thorpe and Rodger (*Phil. Trans.*, 1894, *A*, **185**, 397):

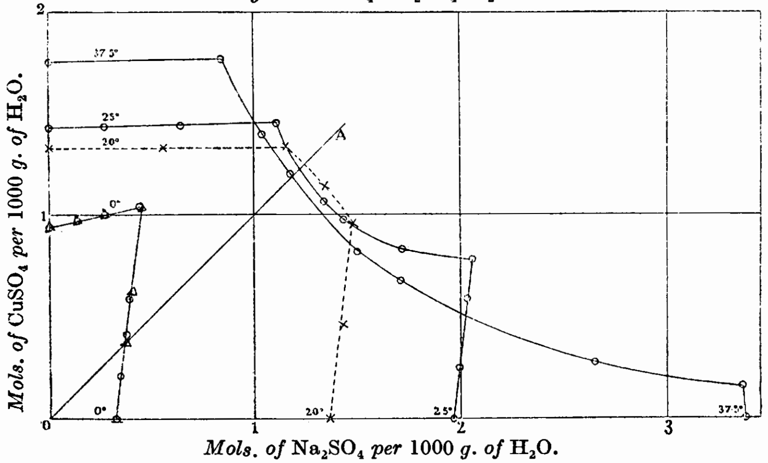
t.	η_{H_2O} (obs.).	(calc.).	t.	η_{H_2O} (obs.).	(calc.).
10·9°	0·01276	0·01279	20°	0·01018	0·010177
14	0·01175	0·01178	23·2	0·00949	0·00946
16	0·01121	0·01120	26·4	0·00883	0·008828
18	0·01069	0·01067	30	0·008198	0·008192

—East London College, London, E. 1. [*Received, October* 6*th*, 1927.]

Equilibrium in the System $CuSO_4$–Na_2SO_4–H_2O *at* 0°, 25°, *and* 37·5°. *A Correction.* By Robert Martin Caven and William Johnston.

An error appears in the figures relating to mols. of Na_2SO_4 per 1000 g. of H_2O (this vol., p. 2363), owing to the use of a wrong value for the molecular weight of sodium sulphate. The correct figures are obtained by multiplying those given by the factor 0·838.

System $CuSO_4$–Na_2SO_4–H_2O.



Diacon's results at 0° *are indicated thus* △.

Massink's results at 20° *are indicated thus* ×, *and the isotherm by a broken line.*

0A *is the line of equimolecular proportions to show solubility of double salt.*

Fig. 4 on the same page needs a corresponding adjustment, and the correct figure is shown above.

The error now corrected does not invalidate the conclusions drawn in the paper.—Royal Technical College, Glasgow. [*Received, October* 15*th*, 1927.]

Change of Properties of Substances on Drying. By Herbert Brereton Baker.

My attention has been directed to a paper by D. Balarew (*J. pr. Chem.*, 1927, **116**, 57). The author sealed up various liquids in

U-tubes, a liquid in one limb and sublimed phosphorus pentoxide in the other, and kept them for 3½ years. He states that subsequent examination of all the liquids, which included hexane and benzene, showed the presence of phosphoric acid, and he suggests that the rise in boiling point which I have found may be due to the presence of this substance or its esters. Apart from the fact that the rise in boiling point which I mentioned (26° in the case of benzene, lately increased to 38°) could not be accounted for by the presence of such an impurity, it was distinctly stated in my paper (J., 1922, **121**, 572) that "In every case the liquid distilled from the dried apparatus was tested for the presence of phosphoric acid, and no trace could be detected." If Balarew's phosphorus pentoxide were not free from the volatile trioxide, his results could be understood.—IMPERIAL COLLEGE, LONDON, S.W. 7. [*Received, November 3rd*, 1927.]

*The Dimorphism of 2-Chloroaceto-*p*-toluidide.* By MAURICE SCHOFIELD.

2-CHLORO-*p*-NITROTOLUENE (80 g.), m. p. 62·5°, obtained by chlorinating *p*-nitrotoluene (100 g.) at 57—59° in presence of anhydrous ferric chloride (4 g.) and in absence of sunlight and moisture, isolated by pouring the product into water, and crystallised from methylated spirit, was reduced at 60—70° with water (350 c.c.), iron powder (in slight excess; added during 2½ hours), and a little hydrochloric acid. The 2-chloro-*p*-toluidine thus obtained, b. p. 238—240°, m. p. 18°, was acetylated with acetic anhydride and acetic acid. The 2-chloroaceto-*p*-toluidide obtained (Found: C, 58·8; H, 5·5; N, 7·5. Calc. for $C_9H_{10}ONCl$: C, 58·8; H, 5·6; N, 7·6%) crystallised from benzene, alcohol, carbon disulphide, ether, and toluene in needles, m. p. 83°. This form, however, crystallised from light petroleum (b. p. 60—80°), in which it was sparingly soluble, in plates, m. p. 104°, and even when it was refluxed with a small quantity of this solvent a bulky, feathery mass, m. p. 104°, was obtained (Found: C, 58·7; H, 5·6; N, 7·7%). The reverse change was effected by crystallising the 104° form from benzene. After the molten 83° form had been kept at 120° for several minutes, solidification occurred at 93° after super-cooling to 89°. No crystallisation took place above 93° if the melt had been kept at 120° for longer periods. Freezing points up to 101° were given by a melt kept under similar conditions and seeded with the 104° form.

Kunckell and Lillig (*J. pr. Chem.*, 1912, **86**, 517) describe 2-chloroaceto-*p*-toluidide as crystallising from benzene in needles, m. p. 104°. —WOLVERHAMPTON AND STAFFORDSHIRE TECHNICAL COLLEGE, WOLVERHAMPTON. [*Received, October 8th*, 1927.]