# NOTES.

A Gas Circulating Pump. By GUY BARR.

A LARGE number of pumps for the circulation of gas through a closed system have been described in the literature, the intermittent motive power being supplied by an electrical solenoid, a motor, a vacuum pump, etc. The form which is the subject of this note is actuated by water pressure and appears to be capable of many applications in physico-chemical work. An earlier design was inspired by the apparatus described by Maass (*J. Amer. Chem. Soc.*, 1919, **41**, 53), which is operated by a filter-pump; the consumption of water was, however, reduced to little more than the volume of gas moved, by making a direct connexion to the water-main at T and allowing the water to run to waste through tap 2 (Fig. 1, *loc. cit.*). A pump was assembled, on these lines, so as to vary the height of the mercury by some 2 inches only and has been found to be quite satisfactory in operation when a circulation of gas up to about 50 c.c. per minute against a negligible resistance is required. A few simplifications appeared possible and these were incorporated in a second pump which has been constructed to work against heads of several inches of water for some experiments requiring the gas to be circulated through wash-bottles.

At A (see fig.) water from the mains enters a vertical tube, R, at the bottom of which there is an amount of mercury sufficient to fill the narrow tube B when displaced into it. (The bore of B must not be more than about 3·5 mm.) Water flows at the same time into the outer tube of C, which is half full of mercury, and as the pressure rises, this mercury is pushed up the inner tube of C.

The pressure increases until the column of mercury in B is, fairly suddenly, blown out into D; water is then free to escape through B and D to the exit E, so that the pressure in C is released and the " piston " of mercury in the inner tube of C falls. At the beginning of the cycle the U-tube F, connecting R and D, is full of mercury to about the level GG : during the rise of pressure this mercury is of course moved towards D and at the moment of release of pressure the mercury from B is added to the top of the column in D. When the pressure in R and C has fallen sufficiently owing to the escape of water through B, mercury from D siphons over into R through the small tube H at the top of F, and seals B once more. The cycle is then repeated. The figure shows the positions of the mercury levels at a certain stage during the up-stroke of the " piston."
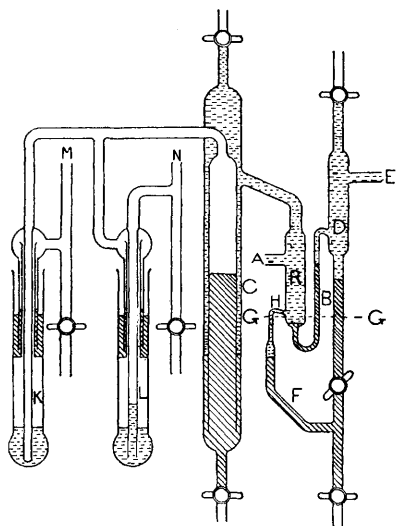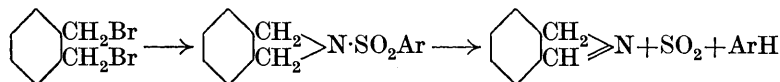

The liquid non-return valves or wash-bottles K, L operate in the usual manner, gas being bubbled through K as the mercury rises in the inner tube of C and sucked through L as it falls. The bottles are detachable for convenience, mercury seals providing a gas-tight connexion with the rest of the apparatus : the washing liquid may therefore be analysed if required. (Alternatively the bottles may be fused on, in which case a tap at the bottom is desirable for addition or removal of the liquid.) Connexion with the apparatus in which gas is to be circulated is made at M and N, the taps below being used for admission and removal of gas. Other stop-cocks are provided for release of air from the water supply, for adjustment of the quantities of mercury in C and F, and for regulation of the rate of fall of the mercury from D during the " blow-off " period. Constriction of the lower end of the inner tube of C would tend to equalise the suction and delivery speeds. The mean position of the mercury in C, and hence the mean pressure in the system beyond M and N, may be varied during an experiment, not only by manipulation of the appropriate taps, but also by adjustment of the position of the discharge end of a piece of rubber tubing attached to E.

The apparatus will circulate up to 100 c.c. of gas per minute against a head of an inch of water, using approximately the same volume of water per minute. Against higher heads the rate of circulation is diminished by wasteful compression in the dead space above the mercury piston. The principle involved may obviously be applied to many other purposes, *e.g.*, to the lifting of mercury in Sprengel or Töpler pumps if sufficient water pressure is available and suitable precautions are taken to prevent the mercury from retaining water.—NATIONAL PHYSICAL LABORATORY. [*Received, October 12th, 1928.*]

An Attempt to Prepare ψ-isoIndole. By GEOFFREY WILLIAM FENTON and CHRISTOPHER KELK INGOLD.

HOLMES and INGOLD having discovered (J., 1926, 1305) that the aromatic sulphonyl derivatives of benzylamine bases, on treatment with concentrated alkalis, yield the corresponding benzylidene-imines, sulphur dioxide, and the appropriate aromatic hydrocarbons, we attempted to exploit this novel reaction for the preparation of ψ-*iso*indole, several more conventional methods of synthesis having already failed to yield this compound. The proposed scheme was as follows :

$$\text{C}_6\text{H}_4\!\!\begin{matrix}\text{CH}_2\text{Br}\\\text{CH}_2\text{Br}\end{matrix} \longrightarrow \text{C}_6\text{H}_4\!\!\begin{matrix}\text{CH}_2\\\text{CH}_2\end{matrix}\!\!>\!\!\text{N·SO}_2\text{Ar} \longrightarrow \text{C}_6\text{H}_4\!\!\begin{matrix}\text{CH}_2\\\text{CH}\end{matrix}\!\!\gg\!\!\text{N}+\text{SO}_2+\text{ArH}$$

o-Xylylene dibromide (26·4 g.) was added to a cold suspension of *p*-toluenesulphonamide (17·0 g.) and anhydrous sodium carbonate (10 g.) in a solution of sodium ethoxide (sodium, 4·5 g.) in ethyl alcohol (150 c.c.). The mixture was gently warmed, then boiled for 2 hours, cooled, mixed with water, and nearly neutralised with acetic acid. The precipitated solid contained some unchanged *p*-toluenesulphonamide, which was removed by crystallisation from alcohol; 2-p-*toluenesulphonyldihydro*iso*indole* was then obtained (13 g.) as prisms, m. p. 176° (Found : C, 65·8 ; H, 5·65. $C_{15}H_{15}O_2NS$ requires C, 65·9 ; H, 5·5%). The 2-*benzenesulphonyl* derivative, prepared similarly, formed needles, m. p. 140° (Found : C, 64·6 ; H, 5·3. $C_{14}H_{13}O_2NS$ requires C, 64·9 ; H, 5·0%).

The *p*-toluenesulphonyl compound, on distillation in an atmosphere of nitrogen with concentrated aqueous potassium hydroxide (optimum concentration, 85% ; range investigated, 70— near 100%), gave a distillate consisting of toluene and, in small yield, a basic product ; and sulphite, but not *p*-cresol, was identified in the alkaline residue, which also contained some tar. The *picrate* of the base separated from alcohol in greenish-yellow leaflets, m. p. 196—197°

(decomp.) after discoloration from about 175°. Analysis indicated that this was the picrate, not of ψ-*iso*indole, but of dihydro*iso*indole (Found : C, 48·8, 48·8, 48·8, 48·6; H, 3·68, 3·69, 3·73, 3·51; N, 16·12, 16·08. $C_{14}H_{10}O_7N_4$ requires C, 48·5; H, 2·91; N, 16·19%. $C_{14}H_{12}O_7N_4$ requires C, 48·3; H, 3·45; N, 16·10%). The benzene-sulphonyl derivative, on corresponding treatment, gave a closely similar picrate, m. p. 195—198° (decomp.) with previous discoloration (Found : C, 48·4, 48·4; H, 3·58, 3·30; N, 16·24, 15·97%). Both preparations were extremely similar to, and almost certainly identical with, the picrate derived from an authentic sample of dihydro*iso*indole prepared as described by v. Braun (*Ber.*, 1922, **55**, 2062).

To obtain confirmation of this remarkable result we turned to the corresponding 1-methyl homologues, since in this case methods for the production of both the ψ-*iso*indole and its dihydro-derivative have been reported (Gabriel and Neumann, *Ber.*, 1893, **26**, 705). The picrate from 1-methyl-ψ-*iso*indole, prepared as described by these authors, decomposed from 135° upwards (Found : C, 50·3; H, 3·7. Calc. : C, 50·0; H, 3·4%). Our specimen of the picrate of the dihydro-derivative had m. p. 151°, and the nitrosoamine had m. p. 100°. By digestion in the cold with an acetone solution of p-toluenesulphonyl chloride and 10% sodium hydroxide in aqueous acetone, the dihydro-base was quantitatively converted into 2-p-*toluenesulphonyl*-1-*methyldihydro*iso*indole*, which crystallised from aqueous alcohol in rhombic prisms, m. p. 93° (Found : C, 66·8, 67·0; H, 6·03, 6·32. $C_{16}H_{17}O_2NS$ requires C, 66·8; H, 5·96%).

On distilling this substance in nitrogen with potassium hydroxide (optimum concentration, 75% ; range investigated, 70— near 100%), toluene, sulphite, a volatile base, and a tar, but no p-cresol, were again produced, and in the basic product 1-methyldihydro*iso*indole was definitely identified by the preparation of its nitrosoamine and p-toluenesulphonyl derivative.

Hence, although the formation of two of the expected products $(SO_2$ and ArH) seems to show that the reaction hoped for must occur, the third, namely the ψ-*iso*indole, undergoes extensive reduction during the process. We have not proved that this reduction is complete, and we have not identified the source of the hydrogen. Our general conclusion is that ψ-*iso*indole must be much less stable than indole, and that this difference is connected with the more symmetrical distribution of the three elements of unsaturation in

the heterocyclic ring of the latter : . This indicates that

the aromatic sextuple valency association is essentially peripheral (see Goss and Ingold, this vol., p. 1268).

We wish to thank the Chemical Society for a grant in aid of this investigation.—THE UNIVERSITY, LEEDS. [*Received, October 26th,* 1928.]

Note on the Paper by Hartley and Barrett on " The Determination of the Density of Liquids." * By JOHN GRINDLEY.

Sir Harold Hartley and W. H. Barrett (J., 1911, **99**, 1072) have made a careful study of the conditions under which the densities of liquids can be measured with an accuracy of ± 0.000005 when relatively small quantities of the liquids are available. The method they recommend seems entirely suitable for determining the densities of dilute aqueous solutions at temperatures differing little from room temperature, to which attention is specially devoted in their paper, but leads to appreciable errors when the densities of liquids having a larger temperature coefficient of expansion are being determined at temperatures differing by five or more degrees from room temperature. They recommend that the pyknometer be weighed against a counterpoise, equal in volume to that of the full pyknometer, and neglect buoyancy corrections except when the pyknometer is weighed empty. This assumes that the full pyknometer, when in the balance case, has a definite volume, whereas its volume depends first on the coefficient of expansion of the liquid it contains, and secondly on the difference between the temperature at which it was filled, *i.e.*, the temperature at which densities are being determined, and that of the balance case. If the pyknometer be first filled with water and then with some more expansible liquid, both say at 0° or 30°, the volume of the full pyknometer in the balance case at room temperature, say 15°, will be different in the two cases and the buoyancy corrections cannot be entirely neglected. It is not essential that the counterpoise be of exactly the same volume as that of the full pyknometer (permissible differences are discussed by Hartley and Barrett), but it is important that the difference between their volumes remains constant throughout a series of experiments. If, for example, a pyknometer of 25 c.c. capacity, whose glass occupies 4 c.c., be filled with water at 0°, its volume at 15° will be 29·018 c.c.; if it be then filled with butyric acid ($d_4^{0°} = 0.97844$, $d_4^{15°} = 0.96344$) at 0°, its volume at 15° will be 29·390 c.c.

If the volume of the counterpoise be 29·018 c.c., the buoyancy correction is zero when the pyknometer is full of water; when full of butyric acid, its volume is greater than that of the counterpoise by 0·372 c.c., which (at 760 mm. pressure) leads to a buoyancy correction of 0·00048 gram, sufficient to alter the calculated density by 0·000015.

To correct this error, the formula given by Hartley and Barrett must be modified :—

Let V_w and V_l = the volumes of the water and of the liquid, respectively, in the pyknometer at the temperature of the balance case, δ_w' and δ_l' = the densities of water and of the liquid, respectively, at the temperature of the balance case, and let the other symbols used by Hartley and Barrett have the same significance as before; then, instead of their equation (2), read :

$$(2) \qquad W_2 = W_p + \delta_w V_p - \Delta_2(V_{pg} + V_w) - (W_c - \Delta_2 V_c),$$

and instead of their equation (3) read :

$$(3) \qquad W_3 = W_p + \delta_l V_p - \Delta_3(V_{pg} + V_l) - (W_c - \Delta_3 V_c).$$

Since $\qquad \delta_w V_p = \delta_w' V_w$ and $\delta_l V_p = \delta_l' V_l$

and if $\qquad\qquad V_c = V_{pg} + V_p,$

combination of the above equations (2) and (3) with equation (1) of Hartley and Barrett gives :

$$\delta_l = \delta_w \frac{W_3 - W_1 + \Delta_1(V_c - V_{pg}) + \Delta_3 V_p\left(\frac{\delta_l}{\delta_l'} - 1\right)}{W_2 - W_1 + \Delta_1(V_c - V_{pg}) + \Delta_2 V_p\left(\frac{\delta_w}{\delta_w'} - 1\right)},$$

which approximates closely to the more convenient expression

$$\delta_l = \delta_w \frac{W_3 - W_1 + \Delta_1(V_c - V_{pg}) + \Delta_3 V_p\left(\frac{\delta_l}{\delta_l'} - \frac{\delta_w}{\delta_w'}\right)}{W_2 - W_1 + \Delta_1(V_c - V_{pg})}$$

As can be seen, the added term $\Delta_3 V_p\left(\frac{\delta_l}{\delta_l'} - \frac{\delta_w}{\delta_w'}\right)$ becomes negligible both when densities are determined at temperatures close to room temperature, i.e., $\delta_l/\delta_l' = \delta_w/\delta_w' = 1$, and when the liquid studied has an expansibility similar to that of water, i.e., $\delta_l/\delta_l' = \delta_w/\delta_w'$, in both of which cases the simpler expression of Hartley and Barrett suffices.

The symbol δ_l in the added term can be evaluated with sufficient accuracy by the simpler equation, and δ_l' can be found by interpolation from the densities determined over a range of temperatures.

—THE EDWARD DAVIES CHEMICAL LABORATORIES, UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH. [Received, September 5th, 1928.]