THE DENSITY AND COMPRESSIBILITY OF PHOSPHINE; THE ATOMIC WEIGHT OF PHOSPHORUS.

by

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CONTENTS.

INTRODUCTION.

Phosphorus is an element of which the recognised atomic weight is subject to some uncertainty. The last Report on Atomic Weights issued by the Chemical Society (J.C.S., 1929, 218) adopts the Aston value of 30.98 (2), based on results obtained by the mass-spectrograph (Proc. Roy. Soc., 1927, 115A, 487); but the Report of the German Commission on Atomic Weights (Ber., 1929, 62, 1) still shows adherence to the older and higher value of 31.02, derived mainly from chemical analysis. (Baxter and Jones, Analysis of Silver Phosphate, J.A.C.S., 1910, 32, 298; Baxter, Moore and Boylston, Analysis of Phosphorus Trichloride, J.A.C.S., 1912, 34, 259; Baxter and Moore, Analysis of Phosphorus Tribromide, J.A.C.S., 1912, 34, 1637). These values differ by more than 0.1%.

In addition to the above-mentioned methods of determining the exact atomic weights of the elements, namely the mass-spectrograph method, based on positive-ray analysis, and the chemical or dynamic method, based on chemical analysis, there exists the physico-chemical or static method, based on Avogadro's principle, and depending on the determination of the densities and compressibilities of gases.

The present investigation is an attempt to determine the density and compressibility of the gas phosphine, /

phosphine, undertaken in the hope that the results obtained would be of value in assisting the determination of the more correct value for the atomic weight of phosphorus.

Although the compressibility coefficient of phosphine is not a small one, the gas is suitable in that it contains only a small proportion of the lightest element, hydrogen, in its composition; the error involved in deriving the atomic weight of phosphorus from the molar weight of phosphine is thus negligible. As far as can be ascertained, however, the published values for both density and compressibility are few in number and not concordant.

For the purposes of a molar weight determination, both density and compressibility require to be determined under standard conditions, for comparison with the known corresponding values for the standard gas oxygen. The normal density is defined as the weight of the normal litre, i.e., the weight of a litre of gas at 0°C., at 760 mm. pressure, at sea-level and Lat. 45°. The determination of compressibility requires a series of pv values at different pressures, all at 0°C., leading by extrapolation to a limit value for pv at zero pressure. It is usual to take the ratio of the pv products at zero pressure and at one atmosphere as equal to the factor $(1 + \lambda)$; $(1 + \lambda)$ can then be taken as a measure of the compressibility.

Pickering,/

Pickering, in the International Critical Tables, 1928 (vol.III,p.3), gives the Normal Density of phosphine as 1.5294, this figure being presumably based on the value 1.5293 given by G.T. Gazarian (J. Chim. Phys., 1909, <u>7</u>, 337) and by M. Bretschger (cf. Mellor's Inorganic and Theoretical Chemistry, vol.VIII, pp.807 and 820). This value is the one cited in the Landolt-Börnstein Tabellen. Earlier values are noticeably discordant, 1.52058 being given in Abegg's Handbuch (1907) and 1.5315 by Berthelot (Compt. Rend., 1898, <u>126</u>, 1415) based on experiments by Leduc (Compt. Rend. 1897, <u>125</u>, 297).

The figures for compressibility show a similar variation, not only in the results themselves, but in the methods employed to obtain these results. No figure is given in the International Critical Tables. The methods can be divided into two groups - one derived by semi-empirical calculation from critical data, the other depending on the more or less direct measurements of pressure, volume or density. Leaving aside the derivation of compressibility from the critical data, the following formula can be employed:-

$$1 - \frac{(p_2v_2)}{(p_1v_1)} = A^{p_2}_{p_1} (p_2 - p_1) ,$$

where/

where p and v represent the pressure and volume occupied by a given mass of gas under the differing conditions. The coefficient $A_{p_1}^{p_2}$ is a measure of the compressibility between the two pressures p_1 and p_2.

If the standard conditions are now applied, i.e. p_1 = zero pressure, and p_2 = 1 (unit) atmosphere,

$$1 - \frac{(pv)_1}{(pv)_0} = A_0^1 ,$$

or, taking $\frac{(pv)_0}{(pv)_1} = 1 + \lambda$, as above,

$$1 + \lambda = \frac{1}{1 - A_0^1} .$$

Gazarian, (loc.cit.) gives, with reference to phosphine gas, the value

$$A_0^1 = \frac{A_1^2}{1 + 4A_1^2} = 0.00828,$$

this being derived from direct measurements of Leduc, (Compt. Rend., 1897, 125, 297), whence

$$1 + \lambda = 1.0084.$$

Other values given by Gazarian, based on critical data by Leduc and Sacerdote, and by Briner, are

$$A_0^1 = 0.00939 \quad \text{(L \& S)}$$

$$A_0^1 = 0.00967 \quad \text{(B)}$$

whence/

whence $1 + \lambda = 1.0094$ (L. & S.)

and $1 + \lambda = 1.0098$ (B)

Berthelot (Compt. Rend., 1898, <u>126</u>, 1415) gives $A^1_o = .00937$, (also based on Leduc's values for T_c and p_c) whence $1 + \lambda = 1.0095$.

Enough has been said to show that the values obtained by such methods are of little use in the accurate determination of the molar weight of phosphine. The method employed in this investigation is the common "indirect" method of finding the density under pressures varying from one atmosphere to as near zero pressure as is consistent with accuracy. If a certain weight of gas W occupies a volume v under a pressure p, then the density per unit pressure is equal to $\frac{W}{pv}$. For a perfect gas $\frac{W}{pv}$ would be independent of the pressure since the product pv would then be constant; for an actual gas such as phosphine, the values obtained for the density per unit pressure are inversely proportional to pv and can therefore be conveniently employed in determining the departure of the gas from Boyle's Law. In particular, the ratio $\frac{(pv)_o}{(pv)_1}$ can be calculated, so that, from the values relating to the normal density and compressibility of phosphine, the molar weight of the gas and the atomic weight of phosphorus can be determined.

GENERAL DESCRIPTION OF METHODS AND APPARATUS.

Both the density and compressibility were determined by the density-globe method, i.e. by weighing a known volume of gas under known conditions of temperature and pressure. Density determinations were carried out at four distinct pressure-levels, viz. one atmosphere, three-quarters atmosphere, one-half atmosphere, and one-quarter atmosphere, the temperature in every case being that afforded by crushed and moistened ice. Two density globes of the ordinary stop-cock type were employed throughout the experiments, each of roughly 350 c.c. volume and each provided with a counterpoising bulb whose external volume differed from that of the corresponding globe by less than 0.2 c.c. These counterpoises were as far as possible subjected to the same treatment as the globes. They were constructed of the same glass and in their final forms were about 3 grams lighter in weight than the corresponding globes. Each globe weighed about 80 grams, and was constructed of ordinary soft glass, fairly thick in the wall to reduce the correction for contraction when evacuated. The actual contraction per atmosphere was about 0.02 c.c.

The weight of the empty globe was found by weighing/

weighing the globe with a known internal pressure of about 1 mm., accurately measured by means of a McLeod gauge; so that from a knowledge of the approximate density at low pressures, a sufficiently exact figure was obtained for the weight of gas remaining in the globe. It was assumed that at 0°C. the total gas adsorbed on the inside walls of the globes remained sensibly the same, from a weight point of view, at 760 mm. as at 1 mm.; the pressure was not reduced below 0.5 mm. in any actual experiment.

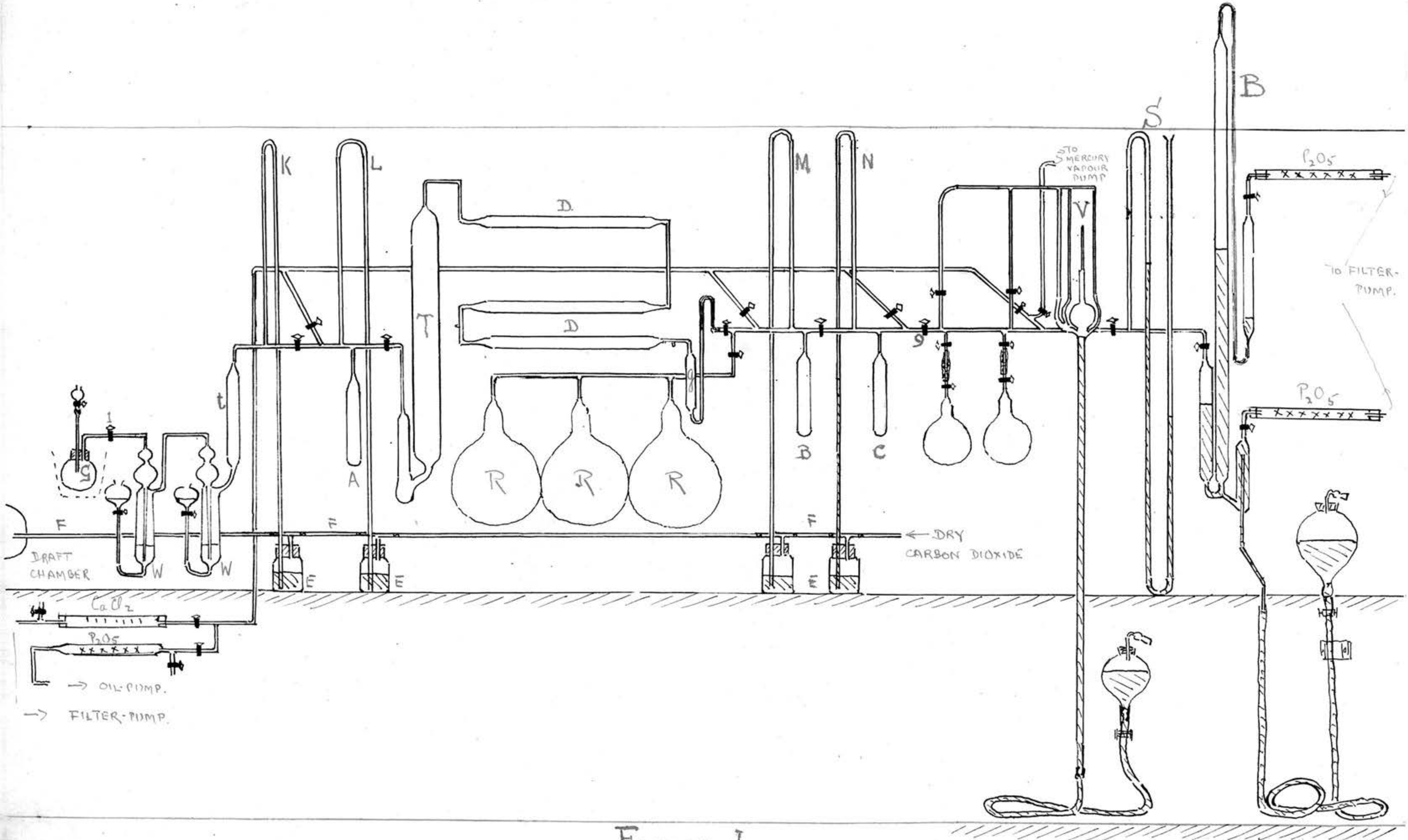
The higher pressures of 760 mm. etc., were measured by means of a manobarometer attached directly to the apparatus, the mercury levels being observed by a cathetometer reading nominally to 0.05 mm. This barometer was also employed to check the readings of the vacuometer.

Weighings were carried out by means of a Staudinger balance (formerly used by Dittmar and later by Crum Brown) with an accuracy of 0.02 or 0.01 milligram. The weight of gas involved ranged from 0.52 gram at one atmosphere to 0.13 gram at one-quarter atmosphere. At least 15 hours were allowed to elapse from the removal of the globes and counterpoises from the ice (with the consequent wiping and washing) and the actual time of weighing. Weighings were, in general, repeated twice.

The weights employed in the actual density determinations/

determinations and in the volume-standardisations of the globes were carefully calibrated against each other. The fractional weights were of platinum. It is not essential that the weights should be standard weights, provided the units of weight and volume are concordant.

The following pages contain a description of the apparatus and procedure in connection with each section of the work. It is highly desirable that in such a series of determinations full details should be given; where minute descriptions of experimental procedure are provided, it is thought that the omission of such procedure, in an experiment, would definitely render the results inaccurate.


K
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E
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DRAFT CHAMBER
← DRY CARBON DIOXIDE
TO MERCURY VAPOUR PUMP
P_2O_5
P_2O_5
TO FILTER-PUMP.
$CaCl_2$
P_2O_5
→ OIL-PUMP.
→ FILTER-PUMP.

FIGURE I

DESCRIPTION OF APPARATUS.

Given opposite (Fig. 1) is a diagram of the actual apparatus employed. It is constructed entirely of soft glass, with the exception of the rubber stopper of the generating flask G and the rubber joints used to attach the density globes. Briefly, phosphine was prepared from phosphonium iodide crystals and dilute potassium hydroxide solution in the flask G, passed through potassium hydroxide solution in the wash-bottles W, over solid potassium hydroxide in the small tower t, and collected in the solid form by means of liquid air in bulb A. The gas was then distilled through the drying tubes T and D, the former containing potassium hydroxide lumps and the latter phosphorus pentoxide, and was collected in bulb C as before. Glass wool in g prevented the transference of mechanically carried particles from the phosphorus pentoxide, and the millimetre capillary tube which followed served to check any sudden change in the rate of flow of the gas through the drying tubes. The gas after drying was distilled several times between bulbs B and C, first and final fractions being rejected, and was finally collected in bulb B; so that the first part of the apparatus up to tap 9, served for the preparation of the pure and dry gas. The rest of the apparatus served for the filling of the/

the density globes, at $0^{\circ}C.$, and at a known pressure, indicated approximately by the manometer S, and measured exactly by the vacuometer V or the mano-barometer B.

The three globes R, each of about 700 c.c. volume, acted as reservoirs for gas prepared and purified but not used in a filling, any such gas left over from one experiment being of course subjected to further fractional distillation before being used.

The safety manometers K, L, M, and N, dip into mercury in the closed bottles shown, a slow current of dry carbon dioxide being passed along the outlet tube into the fume cupboard. 3/16" glass tubing was employed generally except in the globe and vacuometer sections where ¼" tubing was used; it is perhaps preferable to have the manometer tubes L, M, and N, of even smaller diameter, these dimensions being referred to later when considering the phosphine fractionations.

The tap-grease used throughout the experiments on all stop-cocks was a rubber grease which proved most satisfactory. It did not appear to be noticeably attacked by the phosphine gas; a slight thickening in consistency was the only change after months of use. Globe stop-cocks were regreased once during the actual density experiments.

For evacuation purposes, three pumps in all were employed, /

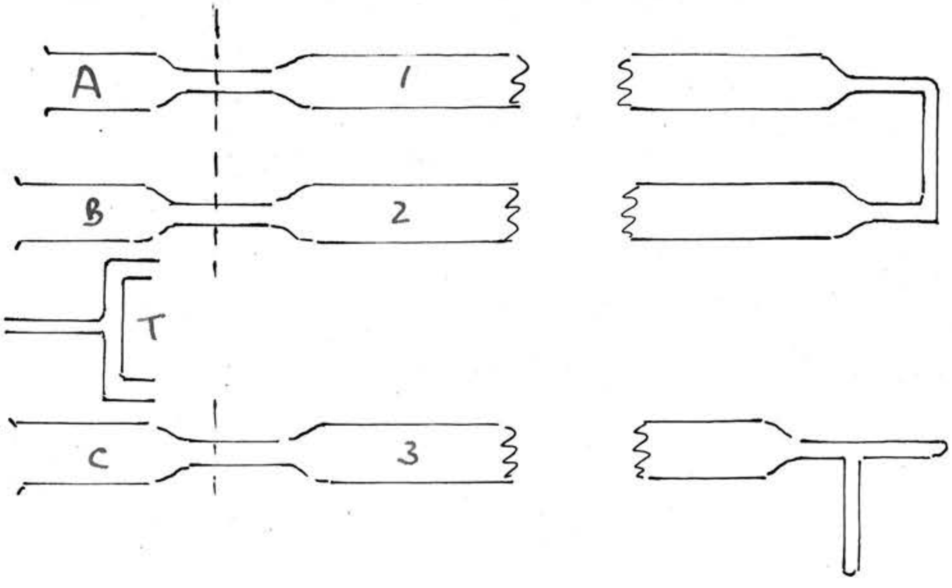
employed, an ordinary water filter-pump, a rotary oil pump driven by an electric motor, and a mercury-vapour pump. The oil pump was capable of producing a pressure of less than 0.001 mm. in a very short period of time, but of course could not be employed generally for the removal of phosphine gas. Where possible, the filter-pump was applied, the oil pump being only used occasionally on phosphine when the pressure was very low. Liquid air was employed as far as possible for such a reduction in pressure; the vapour pressure of solid phosphine at the temperature of liquid air is about 0.05 mm. The mercury-vapour pump was only employed for the removal of the last traces of air.

<u>Phosphorus Pentoxide Tubes.</u> In view of the importance of obtaining a thoroughly dry gas, particular attention was paid to the filling and sealing into position of the drying tubes. These were of a total length of from four to five feet and of 15 mm. diameter. In preliminary experiments for the preparation of dry air, these tubes had simply been filled with phosphorus pentoxide with glass-wool plugs at each end. By the too-abrupt opening of the end tap, a small quantity of phosphorus pentoxide had been carried past the final glass-wool plug into the tube beyond; it was observed that this phosphorus pentoxide was gradually converted into a syrupy liquid of/

of acids of phosphorus, even although the entering air had passed over solid potassium hydroxide before reaching the phosphorus pentoxide (cf. Morley, Smithsonian Contributions to Knowledge, 1898, Volume XXIX, p.21; Cooke, Amer. Chem. Jour., 1889, 11, 509; Noyes, Amer. Chem. Jour, 1890, 12, 441).

As suggested by Morley, therefore, the phosphorus pentoxide was interspersed every two inches with one inch lengths of glass wool, and this form of drying tube was used in the actual density determinations. The phosphorus pentoxide was packed fairly tightly into the tubes to offer as large a surface as possible to the moving gas. The three tubes were replaced after about six experiments.

In filling and sealing into position these drying tubes, it is especially important to prevent the presence of any moisture *after* the last glass-wool plug. The method adopted was as follows, the complete glass apparatus required being shown in the diagram:-



Tubes 1 and 2 (1 being the tube first traversed by the gas to be dried) were joined permanently together, while filling-tubes A, B, and C, were temporarily attached by means of three-inch lengths of ¼" glass tubing. Tube 3 was similarly constructed except that a small closed T-piece was attached at one end. The tubes were heated to remove any moisture and then filled while warm, especially in the case of No. 3, whose closed end must be free from all water. The filling-tubes A, B, and C, were cut squarely off (dotted line), after the inside surfaces of the narrow tubes had been cleaned of all phosphorus pentoxide as well as possible; if the cut glass surfaces remain untouched, joining up is without difficulty. Otherwise, phosphorus pentoxide or acids of phosphorus on the join renders the glass brittle and the seal itself unreliable. Tubes 2 and 3 were thus sealed together by means of the T-tube T, the small T-piece being used for blowing purposes, a three feet length of phosphorus pentoxide tube being inserted between the T-joint and the blower. Tubes 1 and 3 were sealed to the apparatus in a similar way; after a join, the T-tubes were at once drawn out and sealed off.

After these drying tubes were placed in position, it was essential that they be kept for as long as was convenient at as low a pressure as possible, thus/

thus serving the double purpose of testing for leaks and of freeing the phosphorus pentoxide of adsorbed or entrapped air. Noyes (Amer. Chem. Jour., 1889, 11, 156) mentions also the possibility of the glass wool consisting of glass tubes from which air might only be slowly removed. Even after three or four days evacuation, some such air always seemed to be present, since on standing with phosphine, the pentoxide acquired very slowly (after a month or so), a yellowish tint, and some gas was produced, not condensed by liquid air and therefore probably hydrogen. For this reason, a "drying" distillation cannot be regarded as so efficient as a "simple" distillation, unless special precautions have been taken; it is to be expected also that the yellow coating on the pentoxide particles will prevent proper drying of the gas.

Mano-barometer. Since the whole success of an experiment depends on the accurate measurement of the pressure, the construction of the mano-barometer is an operation to which the greatest attention must be paid. The instrument was constructed entirely of soft glass, being of the type described by German (J. Phys. Chem., 1915, 19, 437, J. Chim. Phys., 1914, 12, 78)(cf. Fig. 2.). The dimensions used were sensibly the same as those adopted by him, the internal diameter of the main short/

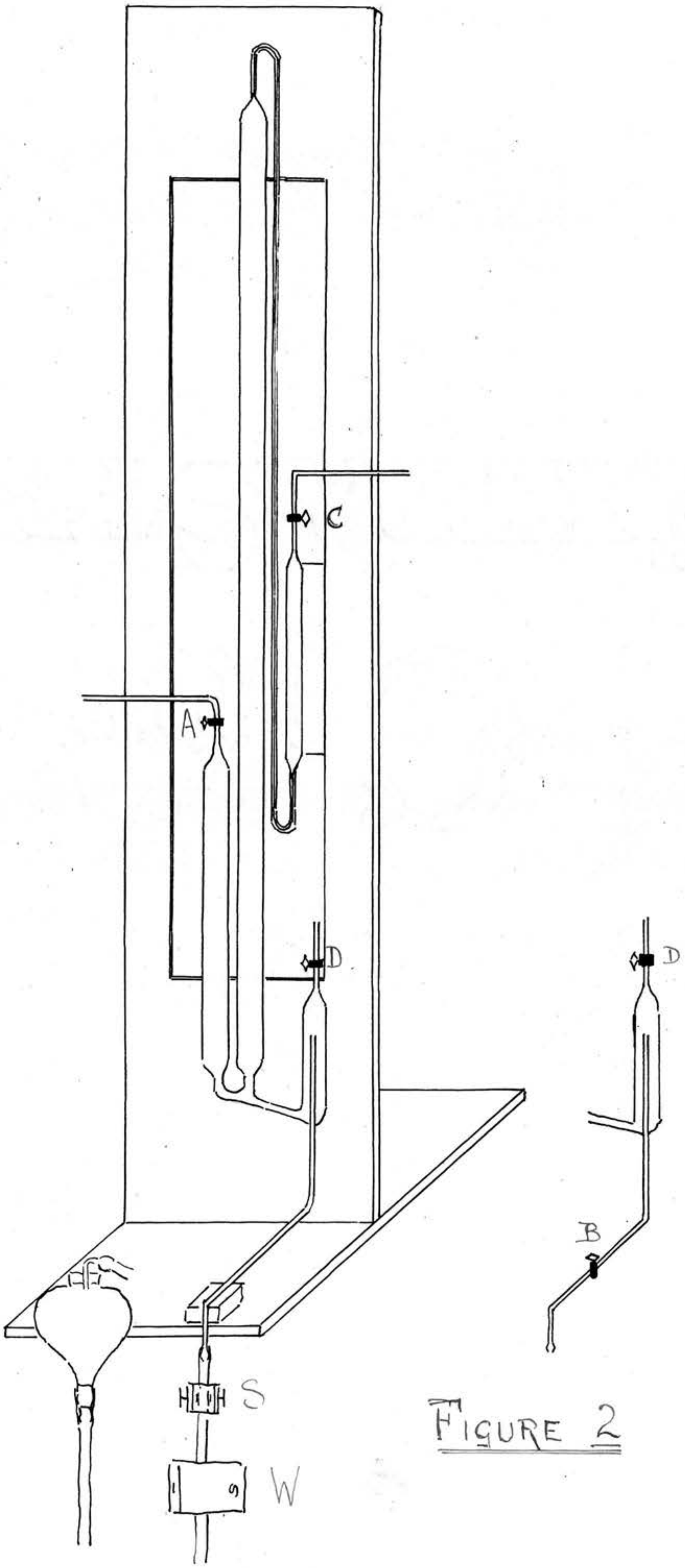


FIGURE 2

short and long limbs being 18 mm. Both limbs were constructed from the same glass tube, and as observations were carried out after causing the mercury to rise slightly in both limbs simultaneously, no meniscus correction need be applied. The capillary tube attached to the upper end was 0.8 mm. internal diameter, and about 90 cm. in vertical height.
No stopcock was employed between the air-trap and the rubber tubing leading to the moveable mercury reservoir; in this way the barometer may be filled and used without the mercury coming in contact with any greased surface - a very desirable precaution. The air trap was sealed into position in such a way that the internal seal was well below the foot of the manometer proper; in this way complete and proper evacuation can be given. Two clamps were employed on the rubber tube of the mercury reservoir, one a large wooden clamp, W, two inches wide, which also served to support the rubber tubing, and the other a small metal screw-clip, S, used in the final adjustment of the mercury surfaces. The best heavy-pressure rubber tubing was used for the connection. The whole apparatus was supported on a strong wooden frame, being held in position on plaster of Paris supports by brass and rubber strips.

Cleaning, drying, and filling of the barometer.

In order to assist the various operations of cleaning and drying, a stopcock B was sealed into position below the air-trap. None of the taps A, B, C or D requires lubrication at this stage. The barometer was completely filled with chromic acid mixture, allowed to stand for two or three days, drained, washed with distilled water, and again filled completely with concentrated nitric acid containing a little potassium chlorate. This was removed after another two or three days, the apparatus drained and thoroughly washed (seven or eight times) with the best distilled water. After draining, the stopcock centres and bores were dried and lubricated with the rubber grease employed throughout. The barometer was then evacuated by the oil pump for three or four days, the final pressure being less than 0.001 mm. Only glass connections were employed, except for the final rubber connection to the pump itself. The capillary reservoir and the main limbs were connected separately to the main pump-tube, while leakage into the barometer at taps B and D was prevented by the addition of a little mercury at the open ends. After this preliminary drying, dry air free from carbon dioxide was allowed to flow in slowly by B until atmospheric pressure was obtained. After standing overnight, the subsidiary tap B was cut/

cut off and the glass extension piece, with rubber tube and reservoir attached, at once sealed on. Precautions must be taken at this point to prevent the entrance of moisture. The reservoir was supported horizontally, a little mercury added (see Fig. 3) and the open end tightly closed by a rubber stopper.

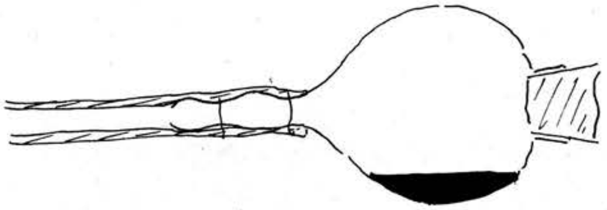


Fig. 3.

The oil pump was again applied,and after four or five hours' evacuation,a clip was fastened tightly on the rubber at a point near the barometer end. The reservoir was then tilted to allow the mercury to fill the tube as far as the clip: more mercury was added and the clip opened, the reservoir being in a suitable position, until the mercury just appeared in the glass tube entering the air trap.

The mercury-vapour pump was then inserted between the oil-pump and the barometer. Evacuation by this means was continued for two days, after which mercury was allowed to ascend into the air-trap until the main barometer limbs were isolated by mercury from the trap and reservoir. (See Fig. 4).

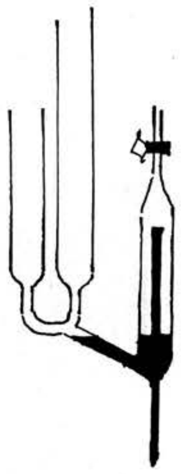


Fig. 4.

It is for this reason that the air-trap must be below the barometer proper. Evacuation by mercury-vapour pump was continued for five days; the filling with mercury was then begun.

As a preliminary, the mercury was allowed to rise until the smaller limb was about half full, this being accomplished by manipulation of the reservoir. A little dry air was then admitted by means of tap A, so that raising of the mercury still further at no time caused the mercury to come into contact with the grease of the tap. A similar procedure was undergone for the air-trap stopcock.

The main reservoir was then raised until the mercury completely filled the main limb, traversed the capillary, and began to fill the capillary reservoir; at this point the main reservoir was lowered and filling was complete. It remained then to attach the barometer to the main density apparatus, and to connect the/

the filter pump, with appropriate drying tubes, to the air-trap outlet and to the capillary reservoir; the latter normally was allowed to stand filled with dry air at a pressure of approximately one atmosphere. The mercury level in the capillary tube itself thus remained a few centimetres below the topmost bend of the capillary. The vacuum of the barometer can be tested from time to time by raising the main reservoir sufficiently; at no time, even after prolonged standing with the mercury levels in both main limbs the same, was more than a mere trace of gas to be obtained. On connecting the barometer "gas-space" to the mercury-vapour pump no difference in mercury levels in the two limbs could be detected by the telescope of the cathetometer: the barometer was therefore sufficiently accurate for the purpose.

The barometer itself was shielded on either side by large asbestos sheets; the temperature of the mercury was taken as that given by two standard thermometers reading to hundredths of a degree centigrade, hung by the side of the main limb, one with its bulb half-way up, the other slightly above the junction of the two limbs. (cf. fig. 2).

The mercury level in the gas-space is at the same vertical height as the centre of the globes; no correction on this account need be applied.

When the barometer is not in actual use, it

is/

is advisable to evacuate the gas-space. After allowing phosphine at one atmosphere pressure to stand for several weeks in the barometer gas-space, the pressure could not at once be reduced below 0.05 to 0.08 mm. At the same time, pressure readings by vacuometer were lower than readings by barometer. Continued evacuation, however, restored the levels; so that after each filling and measurement of pressure, the barometer gas-space was evacuated at once. The correct zero level was then attained immediately. The only explanation put forward is that the grease of the stopcock absorbs at first a small amount of gas, and that part of this gas, or of some decomposition product, can be removed slowly by exhaustion.

Cathetometer. This instrument consists of three parallel vertical brass bars mounted on a centre column and tripod. The millimetre scale is engraven on one of these brass bars and the telescope so attached that it can be adjusted vertically by a rough and fine motion. The telescope itself is provided with a spirit level and corresponding means of adjustment; the three bars, with the telescope, can be revolved horizontally.

The cathetometer was first of all adjusted vertically by means of the tripod adjustments until the telescope was exactly level in all horizontal directions. /

directions. This done, the whole accuracy of the readings depends on the treatment of the telescope and telescope stage; it is absolutely essential that at each reading, the telescope must be exactly level; at some positions on the scale the adjusting telescope screw must be employed. Provided these precautions are carefully observed, by practice, readings more accurate than the nominal 0.05 mms. can be taken; not only by reading the nearest vernier division, but by distinguishing half or even quarter divisions, a complete series of a dozen readings of the same pressure can be recorded without more than 0.05 mm. difference between the outside readings of the series. In this way, by averaging, an accuracy of 0.02 mm. is to be expected.

Behind the actual meniscus of the mercury column of the barometer a card was placed, sharply divided horizontally into two white and black sections (cf. Travers, Senter, Jacquerod, Phil. Trans. A., 200, 1903, p.111.)

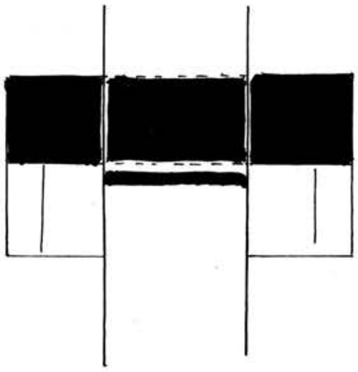


Fig. 5.

If the line of division be placed one or two millimetres above the meniscus, with the black section uppermost, (cf. Fig. 5) the mercury surface appears as a dead-black line, easily brought to exact coincidence with the cross-wire of the telescope. Two such cards were employed, one for each mercury surface; each was placed at the same distance above the surface (1-2 mm.), although no apparent difference in level could be observed, if for example, the dividing edge of the card were placed two millimetres instead of one millimetre above the surface.

Calibration of Cathetometer Scale. The scale of the cathetometer was calibrated by comparison with a standard metre (kindly supplied by Professor Sampson of the Blackford Hill Observatory, Edinburgh). This standard metre was given as correct at 0°C., the coefficient of linear expansion being 0.00001078. By experiment it was found that 725.00 mm. standard scale at 19°C. were equal to 725.17 mm. cathetometer scale at 20°C. i.e., 725.15 mm. standard scale at 0°C., were equal to 725.45 mm. cathetometer scale at 0°C., the coefficient of linear expansion of brass being 0.0000189. This involves a correction factor of $\frac{725.45}{725.15} = 1.0004(1)$, to be applied to the length of the cathetometer scale at 0°C. As, in the density determinations, the temperature of the cathetometer/

cathetometer scale ranged from 15°C. to 20°C., the actual correction finally applied to the observed reading at 15°C. was less than 1 in 10,000; from the above calibration 725.17 mm. cathetometer scale at 20°C. were equal to 725.15 mm. standard scale at 0°C.

Vacuometer. The vacuometer was of the standard McLeod type where 100 cc. gas at the original unknown pressure can be compressed into a graduated capillary of total volume 1.5 cc. This instrument, used to measure pressures of 0.5 mm. to 1.5 mm., always gave definite and constant results when employed with the necessary precautions. (cf. Baume, J. Chim. Phys., 1908, 6, 1; Travers,"Study of Gases" p.158; Baly and Ramsay, Phil. Mag., 1894, 38, 318).

The vacuometer, previous to its filling with mercury, was cleaned and dried in the same way as the barometer. Thorough drying is essential; during the operations no carbon dioxide was admitted to the apparatus. (cf. Baly, loc. cit.). It was normally kept at a pressure less than 0.5 mm. of phosphine, the main mercury reservoir being so adjusted that the gas was completely trapped by mercury in the main 100 cc. bulb. The chief precaution in its use appears to lie in the very slow rise of mercury when a reading is being taken. Otherwise gas appears to be trapped

by/

by the rising mercury on the sides of the bulb; an error of 0.03 mm. may be caused in this way. In general, with all precautions for the usual range of pressures from 0.5 mm. to 1.5 mm., the vacuometer gave readings of 0.01 to 0.04 mm. less than the corresponding readings by the barometer, this small discrepancy being apparently due to the above mentioned trapping of gas or to the tendency of the barometer to give high readings at low pressure (cf. p. 20). The average of all barometer and vacuometer readings was generally taken. The value so obtained cannot be far from the true one; in any case an error of 0.02 mm. in the reading corresponds to roughly 0.01 milligram of gas when applied to the weight of the globe taken at the reduced pressure.

<u>Mercury.</u> The mercury used in the various measuring instruments and manometers had previously been treated as follows. After filtration through muslin, it was twice passed through an ordinary Nitric Acid purifier, kept for some time at 80°C. and then twice distilled under a reduced pressure of about 12 mm. in a barometric still. Half of it was later re-distilled in the ordinary way with air-leak and air-condenser, the pressure being reduced by filter-pump. Pure and dry phosphine remains in contact with such mercury for an indefinite period without decomposition.

Rubber Joints were always used to attach the density globes to the main apparatus. They were cut from the best heavy-pressure rubber tubing and the talc, etc., removed from the inside surface as far as possible by moistening with water and rubbing with a glass rod cut squarely across. While moist, they were slipped into position on the apparatus, doubly wired on, the globes similarly put into position, and then all air and moisture thus introduced removed by thorough evacuation (30 mins. to an hour) by oil pump. The removal of the water is the most essential precaution; the importance of such exhaustive drying has been emphasized by Scheuer (Zeit. f. Phys. Chem., 1909, 68, 592). Treated in this way, such joints were always satisfactory, no leakage or other change of pressure being detected; the action of phosphine gas on the small area of rubber exposed would appear to be entirely negligible.

Seals. In order to prevent leakage into the globes during the drying period when the internal pressure is less than atmospheric pressure, seals were always applied. In the case of the very low pressures 0.5 to 1.5 mm., a short length of clean rubber pressure tubing, wired to an extension piece of glass tubing, was slipped on, all moisture being removed by oil pump as before, and then sealed off while evacuated. (Fig. 6)

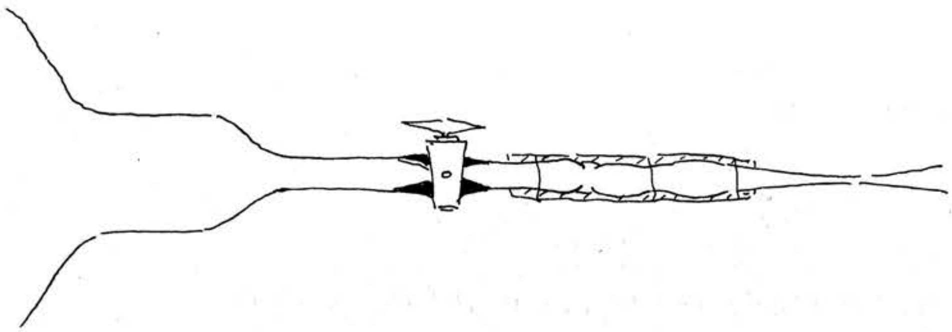


Fig. 6.

The pressure outside the globe in the tap-stem was thus less than 0.1 mm; leakage from the outside was effectively prevented, and if any pressure change at all occurred inside the globe, it would be the very small reduction due to leakage from the globe into the evacuated extension.

The same principle was employed for the other pressures (quarter atmosphere, etc.) except that after evacuation to remove moisture, dry air was allowed in until the pressure of air in the tap-stem was a few millimetres less than the pressure of phosphine in the globe.

Such seals were of course removed before weighing; during the period of weighing, inleakage, if any, was inappreciable.

STANDARDISATION OF THE DENSITY GLOBES.

The standardisation of the density globes can be considered in three sections: the determination of the contraction in volume on evacuation, the counterpoising, and the determination of the volume.

Contraction on evacuation.

As first stated by Rayleigh (Proc. Roy. Soc., 1888, 43, 362), it is necessary to determine the decrease in external volume of the globe on evacuation, since less air is then displaced by the globe than before, and the weight obtained is apparently too large. The method employed was the direct Travers method (Travers, 'Study of Gases', p.120; Germann, Jour. Phys. Chem., 1915, 19, 463; cf. Moles and Miravalles, Jour. Chim. Phys., 1924, 21, 1). The apparatus is outlined in Fig. 7. The globe was enclosed in a rigid glass container, placed in water at constant temperature. The upper half of the container carried a trebly-bored rubber stopper; through the first hole protruded the stem of the globe and through the second a calibrated capillary tube. By means of the third hole, the container was completely filled with water, and the lid clamped on so that the water stood at some convenient point in the/

the capillary. The globe was evacuated and the level of the water in the capillary noted together with the mercury levels of the manometer. Air was then allowed to fill the globe rapidly and the level of the water again noted. The volume of the capillary between the two levels gave the contraction of the globe.

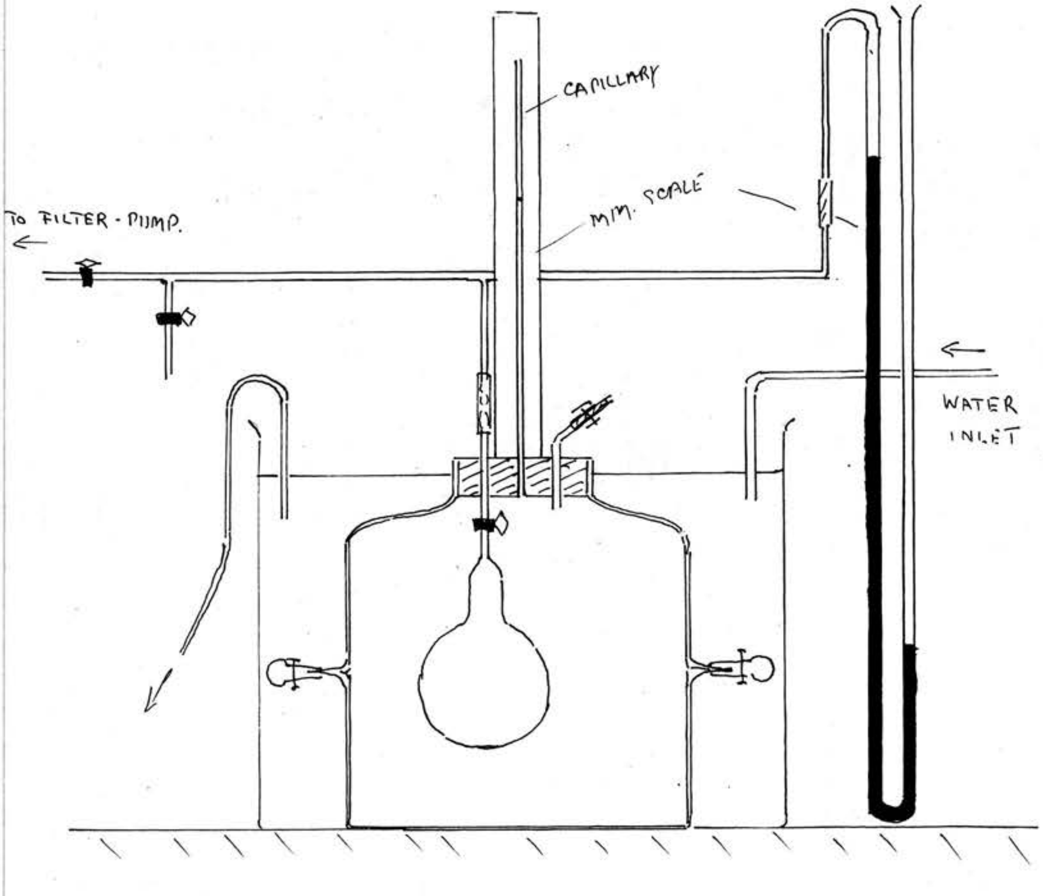


Fig. 7.

In view of the very small contraction found, full details of the experiment are not here given. The chief difficulty lay in the necessity for keeping the water used at a constant temperature, but by using/

using a continuous stream of tap water for the bath, only a very slight and steady change in capillary level was observed. The change in the period of time occupied in a determination was negligible as far as this was concerned. The capillary used had an internal diameter of 0.53 mm. and the fall in water level was about 8 cm. per atmosphere.

By varying the pressure to which the globe was evacuated it was found that

1. The contraction varied linearly with the reduction in pressure.
2. The contraction for Globe I was 0.017 c.c. per atmosphere, the corresponding figure for Globe II being 0.019 c.c. per atmosphere.

The correction applied to the weight of gas measured at one atmosphere pressure was thus 0.00002(0) grms. for Globe I and 0.00002(3) grms. for Globe II, the weight of 1 c.c. of air being taken as 1.2 mgrm. An error of 1 cm. in the reading of the capillary in the experiment is equivalent to a weight-error of 0.00000(25) grms.; it is very improbable that such an error is involved in the experiment.

Counterpoising.

The method adopted of finding the external volume of the globe or counterpoise was the usual one of weighing in air and weighing in water. The apparent loss in weight is equal to the weight of water displaced. In order to sink the globes and counterpoises a lead weight was attached by means of aluminium wire.

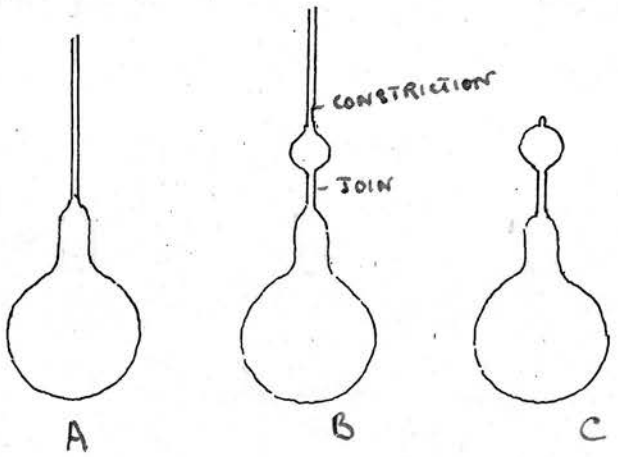


Fig. 8.

The original form of the counterpoise is given in Fig. 8 A; its volume was about 25 c.c. less than the corresponding globe. By a rough weighing, the difference in external volumes was obtained, and a small bulb roughly equal to this difference sealed to the stem of the counterpoise; on the further side of the bulb, the glass tubing was drawn out to a narrow constriction up to which the counterpoise was immersed when ascertaining the volume. By trial and

repeated/

repeated adjustment of the size of the auxiliary bulb, an almost exact volume-counterpoise was obtained. The tubing was then cut at the constriction, a little mercury added to adjust the relative weights of density-globe and counterpoise, and the counterpoise sealed off. A final series of weighings was then carried out to obtain the exact difference in volumes.

Thus for Globe 1 and Globe II, the difference in weight of displaced water between globe and counterpoise was respectively 0.14 grms. and 0.12 grms. Globes and respective counterpoises thus agreed in external volume to less than 0.2 c.c. The counterpoises were about three grams lighter in weight than the globes.

Volume of the globes.

Travers has mentioned the fact that density-globes, especially when newly constructed, have a distinct tendency to decrease in volume, ('Study of Gases' p.119; cf. Scheuer, Zeit.f.Phys.Chem., 1909, 68, p.588). Accordingly, both globes were kept in an exhausted condition for more than a fortnight in the hope that such a contraction would be thereby hastened and complete before the determination of the internal volume was begun.

The actual experiments were carried out on the/

the lines recommended by Germann (Jour. Phys. Chem. 1915, 19, 437; cf. Baume, Jour. Chim. Phys., 1908, 6, 1). The globes were weighed empty (evacuated), filled with pure distilled water at 0°C. and weighed full.

The globes were first cleaned by contact with chromic acid mixture for two or three days, followed by concentrated nitric acid for several hours, and were then washed out thoroughly with distilled water. At this stage practically no lubricant was employed for the globe tap, as it was difficult to prevent the entry of grease in the washing operations. The washing over, the tap key and barrel were cleaned and greased with the minimum quantity of grease. The globes were then dried by repeated exhaustion and filling with dry air. Evacuation was finally carried out to as high a limit as possible by the oil pump.

After removal from the pump, the tap-stems were cleaned and any exposed grease removed from the neighbourhood of the tap. Evacuated seals (cf. p. 25) were then attached. The globes were washed with distilled water, wiped carefully with clean moist muslin and again washed and sprayed with distilled water. Being touched as little as possible, they were suspended by aluminium wire in a closed cupboard containing a basin of phosphorus pentoxide.

Counterpoises/

Counterpoises were treated in an exactly similar way. After hanging for half-an-hour, any drops of water were removed from the bottoms of the globes and counterpoises by means of filter paper.

After fifteen hours, weighings were carried out to the nearest milligram after the seals had been removed and the tap stems cleaned with dry muslin. The balance used was the Staudinger balance, capable of taking 500 grams in each pan. Temperature and pressure were recorded at the same time.

Filling with water at 0^oC.

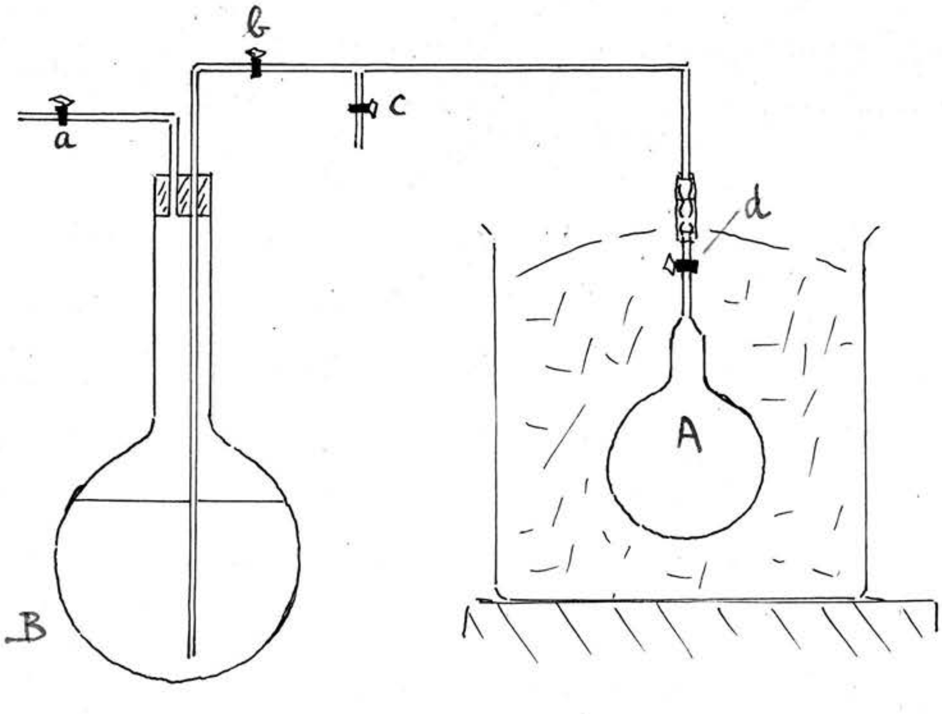


Fig. 9.

In figure 9, A is the density-globe to be filled. B is a round-bottomed Jena glass flask fitted with a two-holed rubber stopper as shown (Volume of A was about 350 cc., and volume of B about one litre).

The flask B was cleaned thoroughly and filled with the best distilled water obtainable; the water was boiled for about half-an-hour, no stopper or connecting tubes being in position. After this half-hour, these were put into position, taps a and b being open, and boiling continued. The long tube dipping into the flask was filled with water at the beginning of this second period by applying a flat piece of rubber or asbestos to the open end of a until the steam pressure drove water through tap b; tap b was then closed. Boiling was then continued for another half-hour.

The water in flask B having been boiled altogether for an hour as above and consequently considered free from dissolved gases, the flame was withdrawn and tap a closed as soon as steam ceased to be evolved. The water was then allowed to cool in contact with practically nothing but its own vapour. Meanwhile, the globe A, previously evacuated and weighed, was connected by pressure-tubing, wired on. The globe stopcock d was kept closed and the space between taps b, c, and d, evacuated by filter-pump through tap c.

When the water in flask B had cooled sufficiently, tap/

tap c was closed and tap b opened, when the space between b, c, and d, became almost entirely filled with water. Any air bubbles were removed by exhaustion through c (b closed). The warm water can easily be made to boil by the cold-water filter-pump. The connecting tubes having been satisfactorily filled, the globe tap d was partially opened and water allowed to enter the globe slowly; a quick stream tends to carry grease from the tap into the globe. Towards the end of the filling, it was necessary to open tap a and admit air, partially at least. The globe tap was then opened fully and any air bubbles removed as before.

The globe was now surrounded by melting ice, clean and finely crushed, and the whole allowed to remain for four to five hours to ensure equilibrium. Water was removed frequently by syphon from the ice bath, fresh ice being added as required and pressed well down round the globe. Towards the end of the cooling, tap b was closed and tap c opened to the atmosphere.

At the end of the cooling period, the connecting tubes and rubber joints were removed, the globe tap closed while the globe remained in ice as before, and the excess water removed from the globe stem, first by a thin capillary tube, then by filter paper or cotton wool on a wire. The globe tap was then opened/

opened and the globe removed from the ice. Careful and complete washing followed, moist muslin being used as before; the tap stem was then closed by a rubber end and the globe suspended in the drying-cupboard overnight. The counterpoise was treated similarly as to immersion in ice, washing and wiping; after half-an-hour's suspension, water drops were removed from the bottoms of the globes and counterpoises as already described. The globes were weighed next day, after replacing the rubber end by a small rubber tube and capillary, of known weight, to minimise evaporation of water during the weighing.

The greasing of the tap was perhaps the most important operation. Sufficient grease must be used to render the globe gas-tight when evacuated and suspended overnight before weighing empty. On the other hand, the slightest trace of grease at the ends of the capillary bore of the tap-key was almost invariably carried into the globe by the ingoing water. The globe was, therefore, usually re-evacuated and reweighed as a check, but only very occasionally was a definitely smaller weight recorded. Two experiments were usually carried out before a tap was regreased; the first of these usually resulted in a little grease being carried into the globe. Results would accordingly be slightly low. No objection could be taken to the second experiment on/

on this account; in a third experiment the globe was apt to leak when evacuated.

The globes were cleaned with chromic acid mixture and with nitric acid before each experiment; if a tap required to be regreased, this was done before cleaning. Alcohol and ether were also used as a preliminary.

Exhaustion of the globes was carried out to a pressure less than 0.1 mm., as measured by the vacuometer. The weight of the residual air was thus negligible, being less than 0.1 mgrm. for the 350 c.c. globe. The correction for contraction of the globe is of course negligible.

Some preliminary experiments were carried out with snow as the means of cooling; the results are given below.

Specimen Calculation.

Water boiled one hour, globe cooled in ice 5 hours. No grease visible in flask.

Weight of evacuated globe = 4.728 grms. (at 12.8°C. and 742 mm.)

Weight of re-evacuated globe = 4.728 grms. (13°C. and 742 mm.)

Weight of globe full = 340.297 grms. (13.1°c.& 741 mm.)

Hence, when the weights are corrected for buoyancy,

Weight full = 340.248 grms.

Weight empty = 4.728 grms.

$\therefore$ Weight of water = 335.520 grms.

Results for Globe I.

Snow	3¼ hrs.	335.549 grms.	
Ice	3½ hrs.	335.523 "	
Ice	4½ hrs.	335.518 "	(globe slightly greasy)
Ice	4½ hrs.	335.520 "	
Ice	5 hrs.	335.520 "	

Most probable value = 335.520 grms.

Results for Globe II.

Snow	3½ hrs.	341.297 grms.	
Ice	5½ hrs.	341.292 "	(globe slightly greasy)
Ice	4½ hrs.	341.294 "	
Ice	4½ hrs.	341.290 "	(globe greasy)
Ice	4 hrs.	341.292 "	

Most probable value = 341.293 grms.

Corrections to the vacuum standard are taken from the tables given in Felgentraeger's 'Hebelwage'.

The experiments in which snow was employed as the cooling medium seem to give a high figure as the result of inadequate cooling, partly because of the time given, partly because snow, even when moistened with water, cannot be packed closely round the globe satisfactorily. A semi-liquid mixture of snow and water would perhaps have been more suitable. Crushed and moistened ice, however, reproduces the conditions under which the actual density determinations were carried out. From four to five hours cooling by ice appears to be adequate for the size of the/

the globes employed; this period of time is the one recommended by Baume.

Leakage of the evacuated flask would give a low final value, inadequate cooling a high final value. It appears probable that under the given conditions both errors are small and tend to cancel out. In any case the maximum error between extreme values is less than 1 in 30,000.

The weight of water at 0°C. required to fill Globe I was therefore 335.52(0) grams and the corresponding figure for Globe II. 341.29(3) grams. These values refer to the corrected weights used, reduced to a vacuum standard, under the value of g, the acceleration due to gravity, at the laboratory.

Since the contraction in volume of the globe was about 0.02 cc. per atmosphere, the above figures were altered accordingly for the purposes of the calculation of the densities at the various pressures. The correction is a small one, being at the most of the order of 1 in 20,000.

At the conclusion of the density experiments, twelve months after the above calibrations, the volumes of the globes were redetermined. The values then obtained for the weight of water at 0°C. were for Globe 1, 335.502 grm. and for Globe II, 341.274 grm. These figures represent a decrease of about 1 in 15,000. The density experiments were carried out/

out at three distinct and approximately equal intervals of time, so that the actual figures employed in the density calculations were adjusted on the assumption that the decrease in volume was proportional to the time elapsing from the original calibration.

PREPARATION OF PHOSPHONIUM IODIDE.

The phosphonium iodide used for the production of the phosphine gas was prepared by a modification of the ordinary Hofmann method (Annalen, 1870, 155, 209). The reaction is generally represented by the equation

$$9\,P + 5\,I + 16\,H_2O = 5\,PH_4I + 4\,H_3PO_4\,,$$

The equation

$$13\,P + 9\,I + 21\,H_2O = 3\,H_4P_2O_7 + 7\,PH_4I + 2\,HI$$

is occasionally given as representing a subsidiary reaction.

The iodide was prepared in small portions of one hundred grams at a time, from 60 grams of white phosphorus and 100 grams of iodine. The yield obtained from these quantities in the ordinary way would appear to be about 70 grams; by the method finally adopted, the yield was always greater than 100 grams. The theoretical yield is 127 grams of iodide from 100 grams of iodine.

The required amount of white phosphorus (60 grams) was dried as far as possible by filter-paper and dissolved in 45 c.c. carbon disulphide, previously well shaken up with mercury to remove sulphur. The solution was allowed to remain for

two/

two or three days in contact with anhydrous sodium sulphate; at the same time 100 grams of iodine were dried in a dessicator containing phosphorus pentoxide.

Before the addition of the iodine to the solution, the sodium sulphate present was removed by filtration in the absence of air. The solution was allowed to syphon over into the receiving vessel, filtration being accomplished through fresh anhydrous sodium sulphate supported by a perforated Gooch disc resting on asbestos and glass wool. The syphoning action was started by means of carbon dioxide gas-pressure in the original vessel.

After filtration, the clear liquid was cooled in ice and the iodine added in small portions, the flask being kept cold during the operation. The carbon disulphide was then removed by distillation on the water-bath, first by heating the flask by immersion in slightly warm water and then by very gradually increasing the temperature from 40°C. upwards (b.p. $CS_2 = 46^{\circ}C.$). It appeared best to remove the solvent as soon as possible after the addition of the iodine. Due probably to the drying of the materials used, and aided by the slow evaporation, the carbon disulphide was removed without any 'bumping' or distinct evolution of hydriodic acid gas. After the disulphide appeared to be all over, the flask was heated by steam for a further two hours, the last

traces/

traces being removed by a slow current of dry carbon dioxide. Heating for one hour only appeared to cause the production of a noticeable quantity of hydrogen sulphide later. The whole distillation thus occupied from four to five hours.

The water condenser was then removed and replaced by a glass tube about fourteen inches long and one inch in diameter. (Fig. 10).

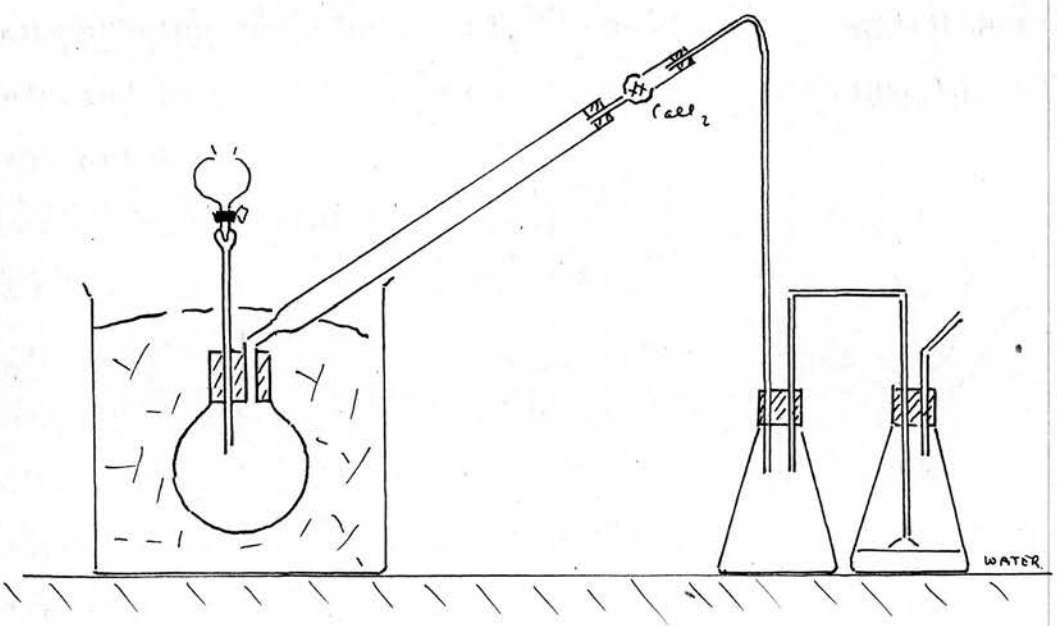


Fig. 10.

The flask and contents were thoroughly cooled in ice and 35 cc. of water added very slowly drop by drop; provided the addition of water be slow (3 to 4 hours) and the flask well cooled, all the phosphonium iodide should be retained in the flask, none appearing in the wide condensing tube. The generation of HI was small and only a trace of sulphur compounds discernible.

The/

The apparatus was then allowed to stand for two or three days.

To extract the iodide, the flask was heated by total immersion in water at 80° - 90°C. (Fig. 11).

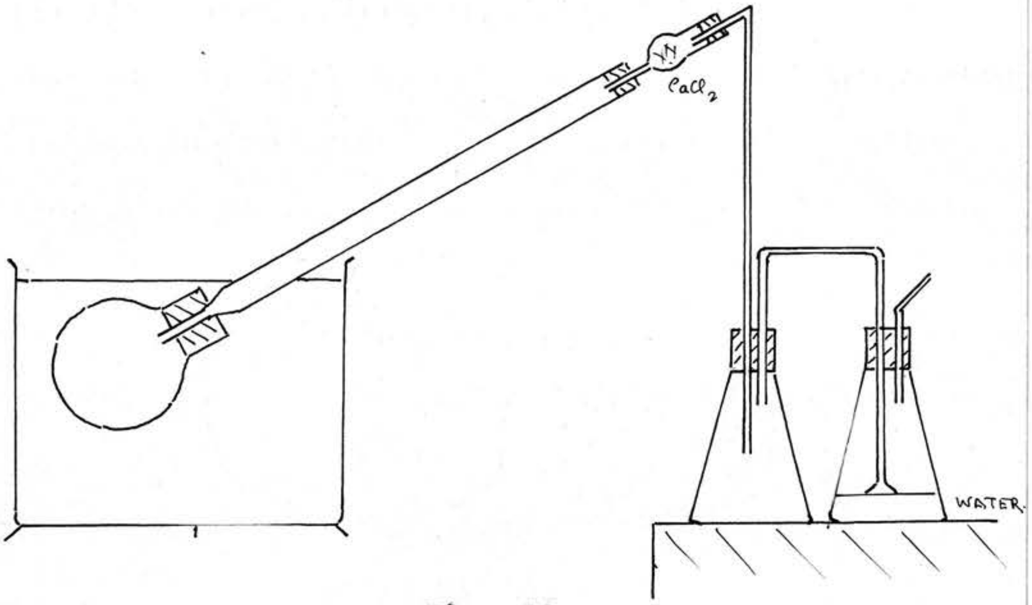


Fig. 11.

White crystals of phosphonium iodide appeared in the wide condensing tube, which was kept cool by moist filter paper wrappings. As the sublimation proceeded, these crystals appeared of a distinct yellow colour, becoming brownish-red towards the end of the operation. The flask was allowed to cool before the condensing tube was removed and its contents forced out. The iodide was always very difficult to remove, the more so if the layer of solid were a thick one; occasionally the glass tube had to be broken to obtain the product. The/

The yield at this stage was about 65 grams.

About 10 cc. water were again added to the residue in the flask, and after standing for three or four days, an additional 25 grams was obtained in the subsequent sublimation. Further addition of 5 cc. water, followed by standing for a week or more, yielded an additional 10 grams, the total yield of crude iodide being now greater than 100 grams.

The flask contained as a final residue a quantity of red phosphorus as well as crystalline phosphoric acid. The reaction would therefore appear to be expressed by the usual equation, the red phosphorus appearing as an unavoidable bye-product. The production of hydriodic acid gas cannot, however, be neglected, being especially noticeable if the reaction be carried out rapidly or the temperature be sufficiently high; while the ordinary equation expresses the theoretical initial materials and final products, the other subsidiary equation must in practice be considered.

Both these equations can be derived by assuming as one of the main reactions the reduction of phosphorous and phosphoric acids by hydriodic acid. The preparation would therefore appear to be summed up by saying that the hydrolysis of the phosphorus tri-iodide produces in the first instance phosphorous acid and hydriodic acid. Part of this phosphorous acid/

acid can decompose to give phosphine and phosphoric acid while the remainder with hydriodic acid gives phosphine and iodine. Assuming phosphoric acid to be similarly reduced, these equations can be gathered into one equation, the standard one

$$9\ P + 5\ I + 16\ H_2O\ =\ 5\ PH_4I + 4\ H_3PO_4.$$

The other equation can be derived on similar lines, assuming part of the phosphoric acid to lose water to give pyrophosphoric acid.

The increased yield of iodide obtained by allowing the residue to stand for several days is probably due to some slow reaction; it is suggested that the reaction in question is the reduction by hydriodic acid of the phosphorous and phosphoric acids. If the preparation be carried out as above, the evolution of hydriodic acid is not observed. The initial and final substances are given by the ordinary equation, the subsidiary equation given above representing a 'chain' reaction, easily observed by slightly altering the conditions of the experiment.

The orange-yellow tinge of the sublimed phosphonium iodide is probably due to the lack, at that stage of the preparation, of water vapour in the apparatus, as suggested by Holt and Myers (Zeit. f. Anorg. Chem., 1913, 82-83, 279). An experiment confirmed the fact that phosphonium iodide when distilled through phosphorus pentoxide is never obtained in the colourless or white form but always of yellow or/

or orange colour, even although the iodide is colourless to begin with. No free iodine is present to account for the colour, the explanation suggested being the dissociation of the iodide into phosphine and hydriodic acid followed by the dissociation of the hydriodic acid into hydrogen and iodine. The iodine then decomposes the phosphine to give a coloured iodide of phosphorus. Phosphonium iodide can thus be distilled in a somewhat moist atmosphere without discoloration; the water present decomposes the yellow iodide to give colourless products.

The iodide obtained above was resublimed under reduced pressure at 50° - 70° C, the apparatus shown in Fig. 12 being used. The bottle and tube were previously filled with carbon dioxide to prevent burning and explosion when the pressure was initially reduced.

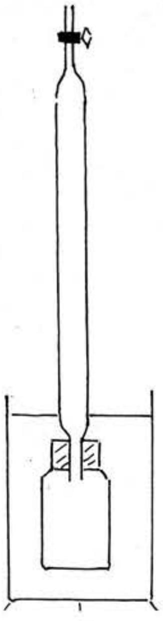


Fig. 12.

Only a small amount was sublimed at one time. Sublimation was fairly rapid, the product being obtained in transparent, cubical crystals. Very little material was lost in the operation, a slight brownish and moist residue being left behind.

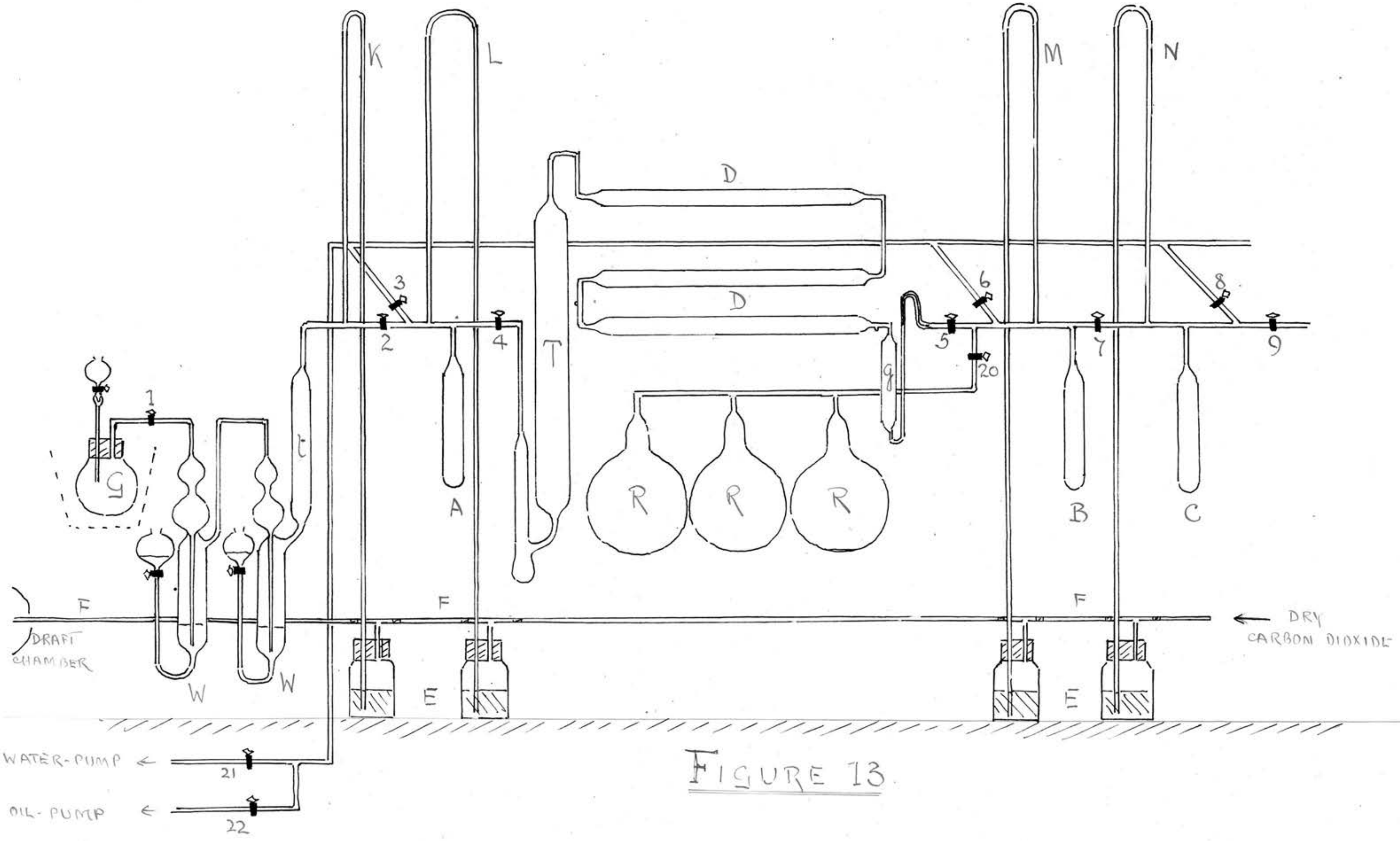
This 'purified' phosphonium iodide was used in the preparation of the phosphine gas for the density determinations; it was very hygroscopic and was kept in the dark in a tightly stoppered bottle.

PREPARATION OF PURE PHOSPHINE.

Under ordinary conditions, i.e. during a run of experiments, the different sections of the apparatus contained phosphine gas under varying pressures. Initially, however, after the apparatus had been set up and the density-globes attached, all sections following tap 1 were subjected to as high a degree of evacuation as possible, in the first instance to test for leaks and secondly to remove as much air and moisture as possible. This latter, of course, applies more to the sections following the drying tubes; these were washed out with dry air (free from carbon dioxide) several times before the final exhaustion was begun. New phosphorus pentoxide tubes were then sealed into position. On standing, the only increase in pressure was in these newly-filled tubes, an increase already referred to (cf. p 14).

Tap 1 having been closed (see Fig. 13), the generating flask G was removed from the apparatus and filled roughly with carbon dioxide gas. From forty to fifty grams of the 'purified' phosphonium iodide crystals were quickly introduced and the flask replaced, the carbon dioxide being removed as far as possible by filter-pump exhaustion by means of the tap of the dropping funnel. The use of carbon dioxide serves to prevent burning or explosion when the pressure is reduced.

In/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B
C
F
F
F
DRAFT CHAMBER
W
W
E
E
DRY CARBON DIOXIDE
WATER-PUMP
21
OIL-PUMP
22

FIGURE 13

In the first preparation of phosphine, as stated above, all the sections following tap 1 were evacuated as far as possible by the mercury-vapour pump, the wash-bottles w containing at that stage no potassium hydroxide solution. To introduce the solution, tap 2 was closed and tap 1 opened; solution was then run directly into the wash-bottles. For the other sections, gas was admitted as the operations proceeded; the descriptions that follow, apply in general to the ordinary cases where each section contained gas left over from a previous experiment.

Dilute potassium hydroxide solution (20%) was now added drop by drop to the solid iodide and phosphine gas was consequently evolved, at a rate easily observed by means of the mercury manometer K. The action was regular and easily controlled; the pressure remained practically steady whenever the supply of hydroxide solution was interrupted. Flask G was surrounded by ice to reduce as far as possible the percentage of hydrogen and other hydrides of phosphorus; for the same reason 20% potassium hydroxide was employed to liberate the phosphine itself. More concentrated solutions have been used in the preparation of phosphine by this method (50% solution being used by Sir Robert Robertson, Proc. Roy. Soc., 1928, 120, 128), but on one occasion when a 30% solution was employed by the author, the entrance of a small bubble of air produced slight burning, even when the flask had been well cooled in/

in ice. The same solution (20%) was used in the gas wash-bottles; this was replaced when necessary by means of filter-pump suction applied to the dropping funnels. The first wash-bottle was also cooled in ice, although the action of phosphine on potassium hydroxide solution is small (cf. Mellor's Inorganic and Theoretical Chemistry, Vol. VIII, p. 816).

The gas was collected in the solid form in the bottom of bulb A by means of liquid air contained in a Dewar flask. Taps 3 and 4 were, of course, closed, while tap 2 was kept only partially open. The pressure in the generating section was thus kept at a pressure of approximately three-quarters atmospheric pressure, the pressure in bulb A being generally very small. This pressure in A, as shown by the manometer L, tended to increase somewhat as the gas continued to collect in A, due to the presence of hydrogen or nitrogen. The vapour pressure of solid phosphine at the temperature of liquid air is about 0.05 mm.; the "excess" pressure, if large, was reduced at intervals by means of the filter-pump acting through taps 3 and 21. When no more gas could be obtained from the quantity of iodide used, tap 2 was closed; the contents of bulb A were then employed in the subsequent purification.

This preparation of phosphine was carried out as slowly as was convenient. For the quantities used, /

used, from two to three hours were usually given; otherwise, a yellow solid residue was left behind in bulb A after distillation. This residue could be almost entirely avoided if sufficient time were given to the preparation.

This "crude" phosphine was now ready for purification, but before this was begun the phosphine in the other sections of the apparatus (drying tubes, reservoirs and bulbs B and C) was also solidified in bulb A, being withdrawn through taps 6 and 3, taps 21 and 22 being, of course, closed. These other sections were then evacuated to as high a degree of exhaustion as possible by the oil-pump. All the phosphine in bulb A was now to be purified by drying and fractionation.

The solid phosphine was allowed to liquefy by lowering slightly the vacuum vessel containing liquid air. Total withdrawal with free exposure to the outside air may cause sudden and violent changes of pressure, especially if the solid phosphine be on the sides of the bulb instead of at the bottom. When all had assumed the liquid form and the pressure had reached about half an atmosphere, the first fraction of about one-fifth the total volume was allowed to evaporate and was rejected by means of the filter-pump through tap 3. Slow and steady evaporation was ensured by surrounding the bulb by

a/

a vacuum flask containing a little liquid air. Finally the manometer tube was washed out by allowing gas to escape by the mercury cup, a current of dry carbon dioxide being passed along the exit tube, F, at the same time; this prevented any possibility of explosion. The remaining phosphine was then re-solidified.

Distillation was then conducted through the drying tubes into bulb C. Since the gas was present in the solid form in bulb A at a very low pressure, connection was made to the evacuated drying tubes by fully opening tap 4. Tap 5 was kept closed at this stage. The pressure was then allowed to increase to about three-quarters atmospheric pressure by lowering slightly the liquid air vessel round bulb A. Meanwhile, bulb C was cooled in liquid air, tap 7 being open, taps 5, 6, 8, 9, and 20 being closed.

The actual distillation was then begun by partially opening tap 5. The pressure in the bulb A and in the drying tubes was always kept between three-quarters and one atmosphere, while that in the bulbs B and C always remained very small and close to the vapour pressure of solid phosphine at the temperature of liquid air. By closing tap 7, the rate of flow of gas through the control tap 5 could at once be observed by the slow fall of mercury level in the safety manometer M; in this way an exact control was kept/

kept of the process of the distillation. The distillation was continued until about one-fifth of the original volume in bulb A remained, when tap 4 was closed and the end fraction removed by means of the filter-pump through tap 3. The pressure in the drying-tubes was reduced generally to approximately one-half atmosphere by the liquid air round C, before tap 5 was finally closed and the "drying" distillation regarded as complete. The period of distillation was from six to eight hours; a perfectly colourless or white solid melting to a clear and colourless liquid was always obtained.

The process of "simple" distillation was then undergone backwards and forwards between bulbs B and C, the collecting bulb being well washed out with fresh gas before actual solidification was begun. Beginning and end fractions were rejected as before. In a distillation from, say, bulb B to bulb C, bulb C was kept surrounded by liquid air, tap 7 being kept only partially open, and the pressure, as indicated by the manometer N, being very low. The pressure in bulb B on the other hand, was kept at one-half to one-quarter atmosphere by suitably raising or lowering a flask containing a little liquid air; this pressure was also varied by means of the connecting stopcock 7. The number of such distillations given was usually three to four, followed by a fifth when actually filling/

filling the globes; it was found that after the second distillation, the vapour pressure of the solid phosphine at the temperature of liquid air reached a practically constant value. For the attainment of this constancy, however, certain definite precautions were necessary; such necessity was determined in the following manner.

In an attempt to increase the number of distillations by shortening the length of time given to each, the cooling vacuum vessel was removed entirely (after liquefaction of the solid) and the distilling bulb simply exposed to the air. The time of distillation was then about one hour. Unless there is solid phosphine present, the liquid does not boil but simply evaporates without disturbance. When, however, the distillate was examined, it was found to be no longer colourless, but dirty-looking when solid and of a slate-blue color when liquid. Black particles were observed to be floating throughout the liquid and it was at first thought that these particles had been in some way carried through from the drying tubes. Against this, however, was the fact that the distillate in the "drying" distillation was always perfectly colourless in the liquid form. Actually, the darkening in colour increased with the number of such "air-exposure" distillations, and while these solid particles were in the main left behind in a distillation,

a/

a small portion at least seemed to be carried over with the distilling gas. Correspondingly, it became more difficult to reach a constant vapour pressure of the solid phosphine; the effect was as if a non-condensable gas, such as hydrogen, were present in varying quantities.

The remedy, as suggested by comparison with the "drying" distillation, appeared to lie in the length of time given to a distillation, or rather to the temperature at which distillation was conducted. The distilling bulb was therefore kept cool by a vacuum vessel containing a little liquid air, while the distillation was conducted correspondingly slowly. The time thus occupied was from two to three hours. Otherwise, the varying temperatures and pressures occurring in the distillation would appear to hasten decomposition of the phosphine into hydrogen and some solid compound; under such conditions, therefore, no increase in the number of distillations given would improve in any way the purity of the product.

Reference may be made here to the method adopted in the rejection of the initial fraction. It had been originally intended to reject such gas by means of the overflow mercury cups closing the manometers. Unless these cups were well filled previously with carbon dioxide and a current of gas passed continuously, the phosphine rejected was liable to explosion; one/

one such explosion necessitated the complete replacement of that section of the apparatus. This liability of phosphine gas to spontaneous combustion in air appears to be determined by three conditions. Firstly, the gas is spontaneously inflammable if it contains, at a given temperature, more than a certain percentage of the hydride P_2H_4. When this percentage falls below the limiting value, the gas is not spontaneously inflammable, if the additional condition is introduced, that the gas be moist, i.e., that it have more than a certain percentage of water-vapour. This is the stage represented in the generating section of the apparatus; such gas was not, as a rule, spontaneously inflammable, in agreement with the observation of Rammelsberg (J. Chem. Soc., 1873, 601) that phosphine liberated from phosphonium iodide by dilute potassium hydroxide solution is not usually spontaneously inflammable but is occasionally so. Lastly, when dried by stick potassium hydroxide and phosphorus pentoxide, in the manner indicated, the gas was always spontaneously inflammable in the air. The rejection of gas from the apparatus was, therefore, as far as possible, carried out by means of the filter-pump, which moistened the gas sufficiently to render it non-inflammable. The conditions given above do not include many other complicating factors that are not mentioned; for example, a mixture/

mixture of phosphine, air, and water-vapour, which would be stable at, say, atmospheric pressure, might not be stable at one-quarter atmosphere pressure. This was occasionally made evident in the preparation of the gas, when the gas at the pressure in the generating section (three-quarters atmosphere) passed through tap 2 into a section kept at a low pressure by means of liquid air. Slight explosion was then evident if more than a trace of oxygen were present in the generating section.

The main bulk of rejected gas in a distillation was, therefore, withdrawn by means of the filter-pump. It was advisable, however, that the manometer outlets be employed occasionally; the hydrogen which appeared to collect in the top bends of these manometer tubes was otherwise difficult to remove satisfactorily. When a slow current of carbon dioxide is employed in the exit-tube, E, to sweep out such rejected gas, care must still be taken; a sudden reduction of pressure in any distilling bulb (by the application of liquid air, for example,) may draw sufficient air into the exit-tube to cause explosion. For this reason, as well as to reduce the quantity of hydrogen in the bulb, these manometers are best constructed of small diameter tubing.

Such are the main details in connection with the preparation of the pure and dry gas. In conjunction/

conjunction with a very slow distillation in the actual filling of the density-globes, the gas was considered free from hydrogen and the other impurities liable to be introduced in the actual preparation of phosphine. In addition, the solid phosphorus used in the original preparation of the phosphonium iodide was examined for arsenic, since arsine might be difficult to separate from phosphine by simple distillation. It is not likely, however, that arsenic would be carried past the phosphonium iodide stage of the preparation. By Marsh's test it was found that the arsenic content of the original phosphorus was less than ten parts per million and as such was not likely to affect the density figures.

It was originally intended to submit the gas to "barbotage", i.e. purification by bubbling the gas through liquid phosphine (cf. Reiman, J. Chim. Phys., 1917, 15, 292 and 345; Gray, J.C.S., 1905, 87, 1605). This was actually done on one occasion, but no increase in purity could be detected as judged by the density results in this experiment. Reliance was therefore placed on simple distillation for the purification.

EXPERIMENTAL PROCEDURE IN DENSITY DETERMINATIONS.

Preliminary Treatment of Density Globes.

As already described, the internal surfaces of the density globes were thoroughly cleaned by prolonged contact with chromic acid mixture, followed by nitric acid. Washing with distilled water followed, the greatest care being taken to prevent entry of grease into the globes. After draining, the stopcocks were carefully cleaned and re-greased: all exposed grease must be removed as completely as possible.

It is of the utmost importance that the inside surfaces of the globes be entirely free from moisture. To this end, repeated evacuation and filling with dry air was given, the mercury-vapour pump being used in the final stages. Lastly, the globes were subjected to mercury-pump exhaustion for three days; the surfaces were then considered to be in a suitable condition for saturation with the pure and dry gas. A supply of pure phosphine was prepared by the methods already described, and both globes were slowly filled with the gas until the internal pressure was roughly atmospheric. After closing all taps, the apparatus was left for four to five days in the hope that satisfactory equilibrium would be obtained in that period.

Evacuation.

The next step was to determine the weight of the 'empty' globe, i.e., to weigh the globe containing gas at a known pressure of about 1 mm. For this purpose, both globes were surrounded by cleanly crushed ice, which was kept at a level above the stopcocks of the globes; melted ice was allowed to run out through holes in the bottom of the ice-box. The counterpoises were embedded in the same ice. Globes and counterpoises were subjected to the same treatment in a "reduced-pressure" determination or "evacuation" as in a "filling" at atmospheric or other standard pressure, all such processes being duplicated as far as possible. The globes and counterpoises were, therefore, surrounded by ice one hour before filling or evacuation, followed by a period of two hours given to ensure thermal equilibrium before the final measurements of the pressure were begun.

The pressure was reduced to approximately one millimetre in all sections following tap 9, these sections (Fig. 14) being designated by the terms globe section, vacuometer section and barometer section. In order that no inleakage should occur during the period of time given for attainment of equilibrium, the sections adjacent were also reduced to roughly the same pressure. Evacuation was begun by/

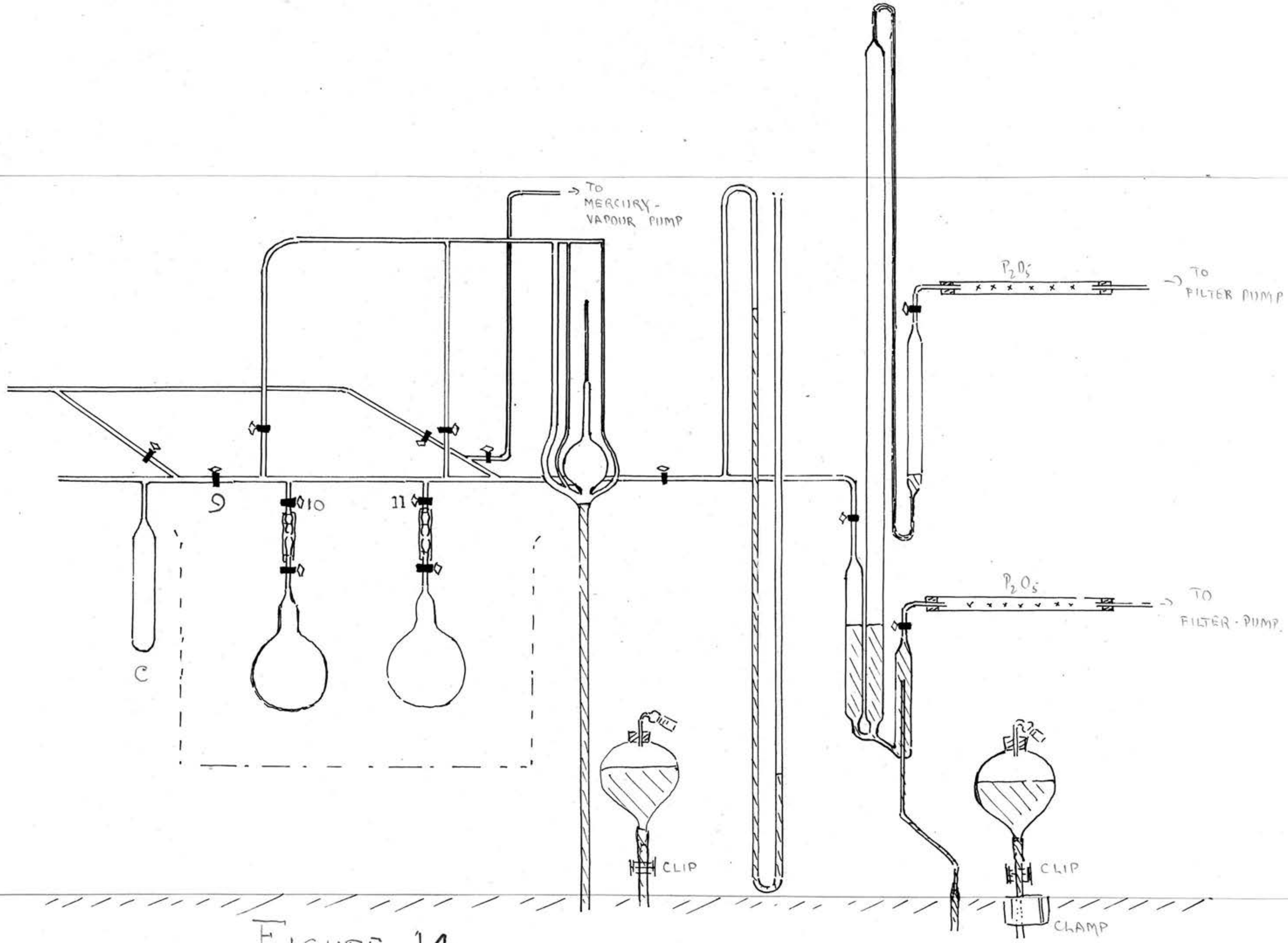
→ TO MERCURY-VAPOUR PUMP
P_2O_5
→ TO FILTER PUMP
P_2O_5
→ TO FILTER-PUMP.
9
10
11
C
CLIP
CLIP
CLAMP

FIGURE 14.

by means of the water-pump, the gas from the globes being used, if necessary, for "washing" purposes. All such removal or transference of gas was conducted slowly to avoid any mechanical effect on grease, etc. When the limit of evacuation by the water-pump was approached, liquid air was used for the final reduction in pressure. Bulb A was used for the purpose. The vacuometer and barometer section, previously exhausted by oil-pump, were connected on in the final stages of the reduction; the level of mercury in the vacuometer was adjusted so that it was just below the opening into the 100 cc. bulb. The apparatus was then left for two hours to attain equilibrium. This period of time was mainly given because such is the period required in the corresponding filling of the globes; in the present case, equilibrium appeared to be attained in a very much shorter time. At the end of one hour, the mercury surfaces of the barometer were subjected to the same upward movement; the clips were then tightly fastened on the rubber tube leading to the mercury reservoir. Near the end of the second hour, readings by vacuometer and barometer were taken alternately. Provided the experiment was carried out as above, no trouble was experienced; fluctuation in pressure can only be ascribed to improper drying of the rubber joints or to inleakage from adjacent sections.

After/

After a series of pressure readings, the globe stopcocks were finally closed and the pressure elsewhere reduced to approximately 0.05 mm. by means of liquid air. The oil-pump was applied to reduce the pressure still further: taps <u>10</u> and <u>11</u>, (Fig. 14) were then closed and the rubber connections to the globes cut off. The pressure of gas in the joints must be so reduced before admitting air, otherwise burning occurs with deposition of oxides and acids of phosphorus in the tap-stems of the globes. Following the cleaning of the tap-stems, outside and inside, of all sediment from the rubber joints, evacuated seals (cf. p. 25) were slipped into position, all air and moisture thus introduced being removed by evacuation. While evacuated, the connection to the pump was sealed off; globes and counterpoises were then wiped with moist muslin and sprayed with distilled water before being hung in the drying cupboard, prior to weighing. As before, after a short time, any drops of water were removed from the bottoms of the vessels, then a basin containing phosphorus pentoxide put inside and all allowed to remain undisturbed for at least fifteen hours before weighing.

The apparatus itself was always left with the globe section in the evacuated condition; any inleakage of air was not then accompanied by visible deposition of compounds of phosphorus.

Filling.

After the weighings of the "empty" globes were completed, the globes were reattached to the apparatus and the air and moisture thus introduced removed by thorough exhaustion by the oil-pump. Increase of pressure was then tested for by means of the vacuometer, over a period of time ranging from half-an-hour to an hour. The joints being pronounced satisfactory, the globes (and counterpoises) were surrounded by ice; everything was then in readiness for the filling.

The phosphine, dried and fractionated as already described, was held in the solid form in bulb B usually. After rejection of a large initial fraction, the globes were washed out three or four times with fresh gas, these "washings" taking the form of fillings to half-an-atmosphere pressure alternated by filter-pump evacuation. At this stage, also, the barometric vacuum was checked by driving over some mercury from the main limb to the capillary reservoir. Finally, the pressure in the globes was very slowly allowed to increase until the required pressure was attained; adjacent sections were similarly treated (with the exception of the vacuometer) before the apparatus was allowed to stand to attain equilibrium. After one and a half hours the mercury surfaces of the barometer were subjected to/

to the same upward movement; at the end of two hours, readings of the pressure were begun. During this period the ice used was kept well packed round the globes, being moistened occasionally with distilled water while the level of the ice was kept well above the stopcocks of the globes. A thermometer reading to hundredths of a degree was also placed in the ice; the temperature here recorded was in every experiment practically constant.

After the expiry of the two hours, the readings were begun, first by taking the temperature of the ice, followed by the thermometer readings on the barometer itself and on the cathetometer scale. The actual difference in mercury levels was then observed, repeated observations being taken (cf. p 21); after the final reading, the globe stopcocks were quickly closed and the temperatures again all recorded.

The globes were then cut off after evacuation of all other sections, including the barometer gas-space (cf. p. 20). Appropriate seals were applied to the globes, if necessary, i.e., if the internal pressure of the globes were one-quarter, one-half, or three-quarters atmosphere. Globes and counterpoises were then washed and hung away in the drying cupboard prior to weighing.

WEIGHINGS.

(cf. Manley, Phil. Trans. Roy. Soc., A, 1910, p. 210)

The procedure in connection with the weighings is one on which too much importance cannot be laid. It must be remembered that at one-quarter atmosphere pressure the weight of gas in the globe was only slightly greater than one-tenth of a gram; to attain an accuracy of one in ten thousand, therefore, weighings would need to be exact to 0.01 milligram, without taking into consideration the fact that the object actually on the balance-pan might not represent the true weight desired, by reason of grease, dust particles, and the like, picked up in the various stages of the experiment.

The balance used was the Staudinger balance previously employed in the determination of the volumes of the globes. The balance-case was partially covered with tin-foil to minimise the effects of unequal temperatures. The sensitivity with globe and counterpoise in position was about 1.5 scale divisions per milligram; a telescope was provided whereby readings of the resting-point could be taken to the nearest hundredth of a division. A thermometer, reading to hundredths of a degree, was hung inside the balance case in a central position, this being assumed to give the actual temperature during a weighing.

As mentioned previously, weighings were carried out after at least fifteen hours' suspension of globes and counterpoises in the drying cupboard. These weighings were checked twice, i.e., the first weighing was carried out in the morning after hanging overnight, the second in the late afternoon, and the third on the following day. The results obtained are considered later.

Without doubt, the most important factor in the determination of the weight of an object on the balance-pan is the factor of temperature. The temperature must be kept as constant as possible; anything likely to produce air currents or other disturbances must be avoided; radiators, windows, draft-chambers and the like must thus be attended to. In the actual weighings recorded, it was the exception, rather than the rule, that constant temperature was actually obtained; generally a slow rise was experienced, the presence of the observer in the weighing room being enough to cause an appreciable rise in temperature, sufficient to affect the resting-point of the balance. Manley (loc. cit.) recommends a suitable case for the balance beam or, failing this, a suitable time of swing in the closed balance case until temperature, flexure, knife-edges, etc., have all attained satisfactory equilibrium positions. A temperature coefficient can be obtained, whereby, for/

for a given load, the resting-point can be corrected to a given temperature - but it is to be remembered that weighings ought to be carried out under such conditions that such a correction may be as small as possible.

The globes and counterpoises were suspended in the drying-cupboard by means of aluminium wire, which was not removed at any time and which served to support the globes and counterpoises on the balance pans. For internal pressures less than atmospheric pressures, "seals" were in position and were, therefore, to be removed before weighing. These seals were cut off with as little disturbance as possible, the globes being held by means of silk finger covers; the tap-stems were very carefully cleaned by dry muslin; then all visible dust particles removed from the outside surfaces by touching lightly with a small brush. In this condition, transference to the balance case was then accomplished, the globe being placed on the left-hand pan and the counterpoise and necessary weights on the right-hand pan. The zero-point was determined with a twenty-gram weight on each scale pan, the weights being so distinguished that a particular weight always occupied the same pan. These weights were removed when the globe and counterpoise were introduced.

The actual routine finally adopted was as follows:

1. Insert zero weights; allow to remain for ten minutes, balance case closed.
2. Release beam; allow to swing for ten minutes. Meantime, remove the seal from the globe to be weighed.
3. Arrest beam; re-swing and read zero-point by repeated and continuous swings. Observe temperature.

Repeat.

This routine was repeated with the globe and counterpoise in position, the sensitivity being determined at the same time. After this reading of the resting-point, the zero-point was again observed.

These observations gave two zero-points at two corresponding temperatures, with a resting-point for the globe at an intermediate temperature. From the zero temperature-coefficient thus obtained, (always about -0.25 scale divisions per degree) the true zero-point at the intermediate temperature was calculated, from which by the sensitivity the required weight was obtained. The atmospheric pressure was also recorded for the purpose of reducing the weight obtained to the vacuum standard.

The seals were immediately replaced if repeat weighings were to be carried out later.

For/

For concordant readings of the resting point at the same temperature it was essential that release and arrestment of the beam be carried out with the greatest care. Sudden arrestment might alter knife-edges, etc., or alter the position of the rider on the beam. Sudden release might cause an appreciable difference in resting-point, due to a different position of the knife edge. The procedure adopted was to release the beam as gently as possible, no attempt being made to swing the beam; this was then accomplished by the temporary application of an additional rider. In this way alone could concordant results be obtained.

The weights used were calibrated against each other in air by the substitution method of Richards (J.A.C.S., 1900, 22, 144). Every attention was paid to such calibration, especially with regard to the fractional weights. The average of three determinations was here employed in calculating the final values; "outside" figures for a given weight, differing by more than 0.01 milligram, were seldom obtained.

Results of Repeat Weighings.

As has been previously mentioned, weighings were carried out in the morning of the day after the globes were washed, in the late afternoon of the same day, and on the morning of the following day. The following figures refer to weights obtained for a globe in regular use during a set of experiments and not to one which had been newly greased or otherwise altered from a previous condition.

After 16 hrs. weight = 3.53732 grms.
" 23 " " = 3.53731 "
" 48 " " = 3.53726 "

or again,

After 17 hrs. weight = 3.02086 grms.
" 23 " " = 3.02084 "
" 48 " " = 3.02081 "

The first set of weights are those of a globe weighed full of gas at one atmosphere internal pressure; the second set refer to the same globe weighed with gas at approximately one millimetre pressure. Whether the globes were full or "empty", therefore, both sets of weighings show a slight and regular decrease which was characteristic of every such weighing. In general, a further appreciable decrease was not observed; for example, the following figures represent/

represent weighings of one globe carried out on four consecutive days.

First day - 3.45333 grms.
Second day - 3.45328 "
Third day - 3.45327 "
Fourth day - 3.45325 "

When, therefore, the characteristic drop of 0.04 to 0.06 milligram was obtained in the second day's weighings, further weighing was not carried out. Corresponding weights were employed in the density calculations.

The only difference between a globe and its counterpoise lies in the existence of the tap grease; it is probable that the above decrease in weight is due to progressive drying of the grease previously moistened by contact with ice and then exposed to the dry air of the drying-cupboard. It must be emphasised that such regular variation in weight was not at once observed after the regreasing of a globe tap. Large variations may then occur to begin with, a decrease of as much as 0.3 milligram per day for four days being observed on one occasion. On the other hand, an increase in weight may be experienced, due perhaps to oxidation of the grease exposed to the air. Obviously, then, the greasing of a tap is an operation to which great attention must be paid. Excess grease must not be used and all exposed grease at the junction of tap-key and barrel completely removed. It was /

was found best to suspend, finally, the globe in the drying cupboard for a week or more before actual experiments were resumed.

For the purposes of the density calculations, the average of the "weights empty" before and after a "filling" was taken as the weight to be subtracted from the weight of the full globe. While such "zero" weights showed occasionally irregular variation, the difference was generally small and, as before, frequently fairly regular - e.g.,

2.92637 grms.
2.92641 "
2.92647 "
2.92650 "

Such an increase is probably to be attributed to some progressive change in the condition of the tap-grease.

THE NORMAL DENSITY OF PHOSPHINE.

The normal density is defined as the weight of the normal litre i.e., the weight of one litre of gas, at 0°C., at a pressure of 760 mm. of mercury, at sea level and latitude 45° ($g = 980.616$).

Outline of Calculation.

The experiments gave

(1) the weight of water at 0°C. required to fill the globe at 0°C., weighed with a certain set of weights, under the value of g for the laboratory,

(2) the weight of phosphine gas at 0°C. required to fill the same globe at 0°C., at a certain known pressure, the gas being weighed with the same set of weights under the same value of g for the laboratory.

The ratio of the weight of gas to the weight of water occupying the same volume under the same conditions, gives the density of the gas relative to water. Since the density of water under the standard conditions is known, the density of the gas can at once be calculated. The value of g for the laboratory need only be introduced in the reduction to standard conditions of the observed height of the mercury barometric column.

If W = weight of water,

w = weight of gas,

P_o = (reduced) pressure in mm.,

d = density of water in grams per millilitre
under standard conditions,

and L = density of the gas at the measured pressure,

then

$$L = \frac{w \times d \times 760}{W \times P_o} \times 1000.$$

It is usual to designate the factor $\frac{W}{d}$ as the "volume" of the globe.

If P_o be exactly 760 mm., then $L = L_N$ represents the normal density. If P_o be not exactly 760 mm., but have a value very close to 760 mm. then L_N can be calculated from L by means of an approximate knowledge of the coefficient of compressibility.

The following figures were employed in the calculations:-

Density of water = 0.999868 grams per millilitre.

Normal acceleration due to gravity = g_n = 980.616.

Laboratory acceleration due to gravity = g_1 = 981.531,

(calculated by the formula given by Germann, J. Phys. Chem., 1915, 19, 471).

Coefficient of cubical expansion of mercury = 0.0001818.

Coefficient of linear expansion of brass = 0.0000189.

Example of calculation.

In an experiment, the globe was weighed "empty", i.e., containing gas at a pressure of approximately 1 mm., then weighed "full", i.e., containing gas at approximately 760 mm., then again weighed "empty". The data for these three sections are given under the headings A, B, and C below, the figures being obtained in an actual experiment with Globe II.

$$\text{Volume of Globe II} = \frac{341.294 \text{ ml.}}{0.999868}$$

$$= 341.340. \text{ ml.}$$

A.

Residual pressure = 1.50 mm.

1st weight of "empty" globe = 2.93309 grm (after 15 hrs)

2nd " " " " = 2.99308 grm (" 20 ")

3rd " " " " = 2.93303 grm (" 30 ")

Therefore apparent weight of "empty" globe = 2.93303 grm.

(1) Correction for the buoyancy of the air on the weights.

The above weight was recorded under the atmospheric conditions of 15.9°C. and 744 mm. pressure, when 1 c.c. of air weighs 1.19 milligram. Taking 8.4 as the density of brass and assuming all the weights to be made of brass, since all weights were calibrated against a brass 10 gram weight in air (cf. Gray and Burt, J.C.S., 1909, 95, 1636), the weight of air displaced/

displaced was $\frac{2.933}{8.4} \times 0.00119 = 0.00042$ grm.

Therefore weight at vacuum standard = 2.93261 grm.

(2) <u>Correction for residual gas.</u>

Correction equals $1.51 \times \frac{1.50}{760} \times \frac{341.3}{1000}$

= 0.00102 grm.

The normal density of phosphine at very low pressures is here taken as 1.517 (cf. results later), the volume of the globe being represented by 341.3.

True weight of "empty" globe = 2.93159 grams.

B.

1st weight of "full" globe = 3.45345 grm.
2nd " " " " = 3.45345 "
3rd " " " " = 3.45340 "

Therefore apparent weight of "full" globe =

3.45340 grm. at 16.4° C. and 753 mm.

Buoyancy correction = 0.00049 grm.

Therefore weight of globe = 3.45291 "

C.

Residual pressure = 0.70 mm.

1st weight of "empty" globe = 2.93256 grm.
2nd " " " " = 2.93256 grm.
3rd " " " " = 2.93252grm. at

17.7° C. and 758 mm.

Buoyancy correction = 0.00042 grm.

Correction for residual gas = 0.00048 grm.

Therefore/

Therefore weight of "empty" globe = 2.93162 grm.

From A and C, average weight of "empty" globe =

2.93160 (5) grm.

From B, weight of globe "full" = 3.45291 grm.

Therefore weight of gas = 0.52130 (5) grm.

The correction for contraction of the globe on evacuation = 0.00002(3) grm.

Therefore true weight of gas in globe = 0.52133 grm.

The pressure of gas in the globe was given as follows.

Observed height of mercury column as measured by cathetometer scale = 759.85 mm.

Temperature of mercury = 16.01°C.

Temperature of scale = 16.5°C.

(1) Correction for cathetometer scale.

Reading reduced to 0°C. = $759.85 \times (1 + 16.5 \times 0.0000189)$

$= 759.85 \times 1.0003(1)$.

At 0°C., the cathetometer scale was too long, the correcting factor being $\frac{1}{1.0004\ (1)}$. (cf. p. 22).

Hence true length of mercury column = $\frac{759.85 \times 1.0003(1)}{1.0004\ (1)}$ mm.

(2) Correction for temperature of the mercury.

Coefficient of cubical expansion of mercury = 0.0001818

Correcting factor = $1 + (16.01 \times 0.0001818)$

$= 1.0029(1)$.

Hence/

Hence reading corrected to $0^{o}C. = \frac{759.85 \times 1.0003(1)}{1.0029(1) \times 1.0004(1)}$ mm.

(3) <u>Correction for gravity.</u>

$$\text{Correcting factor} = \frac{g_1}{g_n} = \frac{981.531}{980.616} = 1.0009(3).$$

Hence the true pressure is given by

$$P_o = \frac{759.85 \times 1.0009(3) \times 1.0003(1)}{1.0029\ (1) \times 1.0004\ (1)}$$

$$= 758.27 \text{ mm.}$$

$$\text{and Density} = \frac{0.52133 \times 0.999868 \times 760 \times 1000}{341.294 \times 758.27}$$

$$= 1.5307(8).$$

This value was finally corrected for the compressibility of phosphine gas between the pressure 758.27 mm. and the standard pressure 760.00 mm. The correction is very small, being given by

$$A = A^1_o \frac{(760.00 - P_o)}{760.00}$$

A^1_o was taken as 0.0090 (cf. later).

$$A = 0.000012 \times 1.73 = 0.000021.$$

The above density figure must be multiplied by the factor 1.00002.

The final value of the normal density is therefore

$$L_N = 1.5308(1).$$

<u>Summarised</u>/

Summarised Results for the Density of Phosphine.

In the following table, P_o represents the true pressure, all corrections having been made; G is the actual weight of gas required to fill the globe, and L_N the normal density.

Series	Globe	P_o	G	L_N
1.	[I.	758.27	0.51258	1.5311(1)]
	II.	758.27	0.52133	1.5308(1)
2.	I.	764.10	0.51648	1.5308(0)
3.	II.	760.03	0.52247	1.5307(4)
4.	I.	762.02	0.51504	1.5307(3)
	II.	762.02	0.52383	1.5305(4)
5.	I.	761.86	0.51490	1.5307(1)
	II.	761.86	0.52374	1.5307(3)
6.	I.	760.86	0.51422	1.5307(7)
	II.	760.86	0.52307	1.5308(0)
7.	II.	761.58	0.52250	1.5305(7)

Average L_N = 1.5307 (2)

The figures of Series 1, were obtained in the first experiment actually performed. Although the result by Globe II is in good agreement with the results following, the result of Globe I is distinctly high and was therefore rejected in the calculation of the average value. The cause would seem to be incomplete removal of moisture, either from the globe itself/

itself in the first instance, though this seems unlikely, (cf. p. 60), or from the rubber joint used to attach the globe to the apparatus. With reference to the former suggestion, it is not unusual for the first result of such a series of density determinations to be high (Guye, Compt. Rend., 1906, <u>143</u>, 1233; cf. Gray and Burt, J.C.S., 1909, <u>95</u>, 1641).

THE COMPRESSIBILITY OF PHOSPHINE.

The molar weight of a gas, as calculated by the original Avogadro hypothesis, is given by the formula

$$M = \frac{D_G}{D_O} \times 16 \times 2.$$

The required molar weight is here represented by M, the ratio D_G to D_O being the density of the gas relative to the density of the standard gas oxygen, and the basis of the whole system being $O = 16$. The employment of this equation involves the fundamental assumption that equal volumes of all gases under the same conditions of temperature and pressure contain an equal number of molecules. The molar weight is proportional to the relative density. In other words, the molar volumes of all gases are the same; under fixed conditions, the molar volume is a constant.

Actually, of course, this equation gives results that may be very far from accurate, i.e., when compared with the usually accepted values derived from analytical methods. The divergence is the more marked when the gas in question is one of the easily condensable gases of large compressibility, where the error may amount to as much as 2%, as in the case of sulphur dioxide. The Avogadro hypothesis in the above/

above form is therefore of little use in the accurate determination of molar or atomic weights.

According to the original theory, the ratio D_G to D_0 ought to be constant as long as the conditions under which the densities are measured are the same for the gas in question and for the reference gas. Actually of course, this is not the case; gas densities are usually given for the conditions 0°C. and 760 mm. pressure, but under these conditions the theoretical gas laws are not obeyed by actual gases and the gas in question will in general disobey these laws to a greater or less extent than is the case with the standard gas oxygen.

It appears, however, from actual experiments, more especially by Regnault and Rayleigh, that the more nearly the pressure approaches to zero, the more accurately are these gas laws obeyed. They are, in fact, limit-laws, only holding exactly when the pressure is zero. The molar volumes of all gases can then be taken as constant when considered, not at atmospheric pressure, but at zero pressure only. For the purposes of a molar weight calculation, it is therefore assumed that at zero pressure alone are the molar volumes constant.

The variation of relative molar volume undergone when the pressure rises from zero to one atmosphere finds its explanation in gas compressibility. Oxygen itself is/

is a member of the group of difficultly condensable gases - the so-called "permanent" gases - and its coefficient of compressibility per atmosphere is small. Although its relative molar volume changes with change of pressure, yet the change is a small one.

On the other hand, for an easily compressible gas such as phosphine, the molar volume suffers a much greater decrease with increase of pressure, and the density at one atmosphere is much greater than it would be if it were an ideal gas. Where, previously, it could be stated that at $P = 0$ the molar weight was proportional to the density alone, (the molar volume being constant) now, for $P = 1$ atm., the molar weight is proportional to the density multiplied by the new molar volume.

Molar weight $\propto$ (density) × (molar volume).

This statement is at the basis of Berthelot's method of calculation of molar weights from the corresponding densities, and this is the method which is now generally applied.

Compressibility in general can be expressed by means of the coefficient

$$A_{p_1}^{p_2} = \frac{1 - \frac{p_2 v_2}{p_1 v_1}}{p_2 - p_1} ,$$

where v_1 and v_2 represent the volumes occupied by the/

the same mass of gas under pressures p_1 and p_2 at constant temperature. Berthelot considered two gases under an infinitely small pressure p_0; according to the above ideas, their molar volumes were equal, and equal to v_0. The gases were then compressed to atmospheric pressure p_1 ; the molar volumes ceased to be equal and assumed the values v_1' and v_1'' . Substituting in the above formula, and taking the atmospheric pressure as unity, while p_0 becomes zero,

$$\frac{V_1'}{V_1''} = \frac{1 - A'^{\,1}_{0}}{1 - A''^{\,1}_{0}} ,$$

where $A'^{\,1}_{0}$ and $A''^{\,1}_{0}$ represent the coefficients of compressibility of the two gases. This is equivalent to saying that the molar volumes are proportional to $(1 - A^{1}_{0})$, and consequently the molar weights are proportional to $D(1 - A^{1}_{0})$, where D is the density of the gas at one atmosphere pressure. The product $D(1 - A^{1}_{0})$ is Berthelot's "limit-density". The molar weight of any gas relative to O = 16, is then given by

$$M = \frac{D_g\left(1 - A^{1}_{g_0}\right) \times 32}{D_O\left(1 - A^{1}_{O_0}\right)} ,$$

where D_G is the density of the gas at 760 mm.,

D_O is the density of oxygen at 760 mm.

$A^{1}_{G_0}$ = coefficient of compressibility of the gas between zero and one atmosphere pressure,

and/

and $A_{0_o}^{1}$ = coefficient of compressibility of oxygen between zero and one atmosphere pressure.

The whole question then resolves itself into the accurate determination of D and A_o^1 for both gases, D being the density at 760 mm. and A_o^1 the coefficient of compressibility as defined by the equation.

All such values are to be determined at the standard temperature 0^oC.

As stated earlier (p. 2), it is usual to define λ so that

$$1 + \lambda = \frac{(pv)_o}{(pv)_1}.$$

Since, from the general formula,

$$1 - \frac{(pv)_1}{(pv)_o} = A_o^1$$

it follows that

$$1 - A_o^1 = \frac{1}{1 + \lambda} .$$

If, therefore, L represent the weight of the normal litre of the gas in question, L_0 that of the normal litre of oxygen, and $(1 + \lambda)$ and $(1 + \lambda_o)$ refer to the corresponding compressibilities, then the molar weight of the gas, on the basis 0 = 16, is given by

$$M = \frac{L}{L_0} \frac{(1 + \lambda_o)}{(1 + \lambda)} \times 32.$$

The/

The actual determination of the product pv at zero pressure can only be carried out by means of extrapolation applied to values obtained at higher pressures where accurate experiments can be carried out. For the permanent gases it is generally assumed that pv is a linear function of the pressure and consequently $(pv)_o$ can be obtained without much error, but for the more compressible gases such as phosphine, it is doubtful whether such linearity can be assumed. It must be remembered that Berthelot's limit-density method of calculation is based on the obedience of all gases to the gas laws at zero pressure. If the gas laws are followed exactly, then $\frac{\Delta (pv)}{\Delta p}$ must be zero at zero pressure. It is very difficult to decide by direct experiment whether such is the case; the form of the isothermal ought to be determined at as many pressures as possible. Even then, the true form of the curve may not be obtained due to some error inherent in the method adopted; the most serious of these errors would appear to be connected with adsorption.

The formula employed in the calculation of the normal density was

$$L_N = \frac{w \times d \times 760}{W \times P_o} \times 1000.$$

The densities for the other pressures of three-quarters, one-half, and one-quarter atmosphere were calculated/

calculated by a similar formula; for example, the actual density at one-half atmosphere is given by

$$L = \frac{w \times d \times 380 \times}{W \times P_o} 1000,$$

where P_o is a pressure close to 380 mm. As indicated earlier, for the purposes of compressibility, these actual densities were converted to densities per unit pressure; in other words, referred to the standard 760 mm. as if the gas laws were actually obeyed. The difference from the normal density gives the divergence from the gas laws over the range of pressure considered. These densities per unit pressure are denoted by $L_{\frac{3}{4}}$, $L_{\frac{1}{2}}$, and $L_{\frac{1}{4}}$.

The following tables give the various results obtained for the densities at three quarters, one half, and one quarter atmosphere pressure. As before, P_o is the fully corrected pressure, G the actual weight of the gas in grams while the final column gives the calculated value of L, the density per unit pressure.

Three-quarters/

Three-quarters Atmosphere.

Series	Globe	P_o	G	$L_{\frac{3}{4}}$
1.	I.	570.30	0.38458	1.5273(9)
	II.	570.30	0.39116	1.5272(4)
2.	II.	569.48	0.39063	1.5273(2)
3.	I.	569.97	0.38428	1.5271(0)
	II.	569.97	0.39092	1.5271(7)

Average $L_{\frac{3}{4}}$ = 1.5272(4).

One-half Atmosphere.

1.	I.	378.76	0.25487	1.5240(5)
	II.	378.76	0.25919	1.5237(2)
2.	I.	378.80	0.25494	1.5242(3)
3.	I.	381.88	0.25690	1.5237(0)
	II.	381.88	0.26132	1.5235(7)
4.	I.	379.99	0.25555	1.5232(6)
	II.	379.99	0.26003	1.5237(6)
5.	I.	379.26	0.25514	1.5237(5)
	II.	379.26	0.25953	1.5237(5)

Average $L_{\frac{1}{2}}$ = 1.5237(6)

One-quarter/

One-quarter Atmosphere.

Series	Globe	P_0	G	$L_{\frac{1}{4}}$
1.	I.	189.00	0.12686	1.5203(8)
	II.	189.00	0.12903	1.5201(9)
2.	I.	188.52	0.12653	1.5202(2)
	II.	188.52	0.12871	1.5203(2)
3.	II.	189.72	0.12951	1.5200(6)
4.	I.	189.94	0.12750	1.5204(7)
	II.	189.94	0.12970	1.5204(7)

Average $L_{\frac{1}{4}} = 1.5203(1)$.

Mean Errors. The 'probable error' of the mean has been calculated in the usual way from the above tables of figures. The density results can then be summarised as follows:-

$L_N = 1.5307(2) \pm 0.0000(5)$.

$L_{\frac{3}{4}} = 1.5272(4) \pm 0.0000(4)$.

$L_{\frac{1}{2}} = 1.5237(6) \pm 0.0001(2)$.

$L_{\frac{1}{4}} = 1.5203(1) \pm 0.0000(5)$.

The mean error of a single experiment has also been calculated on the assumption that the following experimental errors are unavoidable:-

Normal density determination;

1. Calibration of volume, 3 in 300,000, or 0.1 in 10,000
2. Weighings, 2 in 50,000, or 0.4 in 10,000
3. Pressure, 3 in 76,000, or 0.4 in 10,000
4. Temperature, 1 in 27,300, or 0.37 in 10,000

Mean/

$$\text{Mean error} = \pm\sqrt{0.01 + 0.16 + 0.16 + 0.14}$$
$$= \pm\sqrt{0.47}$$
$$= \pm\ 0.7 \text{ in } 10,000.$$

Taking into account the fact that ten experiments are considered, the mean error becomes $\frac{0.7}{\sqrt{10}}$ or 0.22 in 10,000.

Similar calculations have been performed for the other series of determinations. The mean errors thus obtained are summarised as follows:-

One atmosphere pressure,	0.2 in 10,000.
Three-quarters atmosphere pressure,	0.4 in 10,000.
One-half atmosphere pressure,	0.4 in 10,000.
One-quarter atmosphere pressure,	0.9 in 10,000.

Calculation of $(1 + \lambda)$.

Since the density is inversely proportional to the volume, relative values of pv for the corresponding pressures are obtained by dividing L_N, the normal density, by L, the density per unit pressure. The value of pv at one atmosphere is here taken as unity. The values so obtained increase as the pressure decreases; the problem is to determine the value of pv at zero pressure. The last column of the table below gives the increase of pv per atmosphere calculated for the corresponding pressure-ranges of three-quarters, one-half, and one-quarter atmosphere. The pressure in atmospheres is denoted by P.

P.	L.	pv.	$\frac{\Delta(pv)}{\Delta p}$.
1.00000	L_N = 1.5307(2)		
0.75000	1.5272(4)	1.0022(78)	0.0091(12)
0.50000	1.5237(6)	1.0045(67)	0.0091(34)
0.25000	1.5203(1)	1.0068(47)	0.0091(32)

It appears from the figures of the last column, that the relationship between pv and p is linear with respect to p. The average value of 0.0091(25) is therefore adopted for $\frac{\Delta(pv)}{\Delta p}$. The factor $(1 + \lambda)$ for phosphine is then represented by the number 1.0091(25).

$$(1 + \lambda) = 1.0091(25).$$

THE MOLAR WEIGHT OF PHOSPHINE AND THE ATOMIC WEIGHT OF PHOSPHORUS.

The formula to be employed is

$$M = \frac{L(1 + \lambda_0)}{L_0 \ (1 + \lambda)} \times 32 \qquad \text{(cf.p. 86)}$$

The normal density of oxygen, L_0 , was taken as 1.4290(0) and the factor of compressibility, $(1 + \lambda_0)$, as 1.0009(6) (cf. Gray and Burt J.C.S., 1909, 95 , 1666; Batuecas, J. Chim. Phys. 1925, 22, 130).

$$L = 1.5307(2).$$

$$(1 + \lambda) = 1.0091(25).$$

The molar weight of phosphine is then given by

$$M = \frac{1.5307(2) \times 1.0009(6) \times 32}{1.4290(0) \times 1.0091(25)}$$

$$= 34.000.$$

Taking the atomic weight of hydrogen to be 1.0078, the atomic weight of phosphorus is 30.977.

DISCUSSION.

The question of adsorption of gas on the walls of the density globe is one which is very difficult to investigate experimentally. It is generally assumed that the gas film at 760 mm. pressure is sensibly the same as the gas film at 1 mm. pressure, an assumption which would appear to be justified in the case of the "permanent" gases. The standard gas oxygen is itself a "permanent" gas, and if any error through this cause does occur, practically the same error will be experienced in the case of any other permanent gas, so that both density and compressibility can be regarded as in error by very nearly the same amount. The results for molar and atomic weights should, therefore, on this account at least, show good agreement with the results obtained by other methods. In the case of the more easily condensable gases, however, such as phosphine, hydrochloric acid gas, sulphur dioxide and the like, the error arising in this way may be expected to be correspondingly greater. The normal density, calculated on the assumption that the gas films are equal for the two extremes of pressure, will be too large. It must be remembered, however, that in an experiment as ordinarily conducted, the time given for establishment of equilibrium/

equilibrium between gas and surface is not one in which equilibrium would be completely established. In the experiments with phosphine the period of time was usually not more than three hours, this being actually the time of immersion in ice of the density-globes. Again, it is usually considered advisable that such density determinations be carried out with globes that differ considerably in volume and therefore in surface exposed to the gas (cf Moles, Ber. 1926, <u>59</u>, 740; Scheuer, Zeit. f. Phys. Chem., 1909, <u>68</u>, 577). If such be the case, the smaller globe will give the higher density, since the surface per unit volume is greater; in general, however, an examination of density results yields no definite information on this matter, such variation being apparently overshadowed by the errors involved in the experimental manipulation. While, therefore, the possibility of such an error due to adsorption must be considered, it would appear probable that the error involved is a small one, an assumption which is borne out by the fact that atomic weights obtained by this method are generally lower, rather than higher, than the usually accepted values.

In the case of phosphine, that part of the experimental work which would appear to be of the greatest importance is the purification of the gas by fractional distillation. It has already been remarked that rapid/

rapid distillation at room temperature was accompanied by production of hydrogen gas and that no matter how many such distillations were given, the purity of the resulting product could not be considered to be improved. It is therefore to be expected that the figure for the normal density would, on this account, be low, an error which would tend to counterbalance the error of the opposite sign due to adsorption. It appears probable that Gazarian's result of 1.5294 (J. Chim. Phys., 1909, 7, 341) is low for this reason, as is suggested by Baxter and Jones (J.A.C.S, 1910, 32, 298). The most probable value for the normal density of phosphine, from the experiments here described, is not less than 1.5307.

In the case of the compressibility, the factor $(1 + \lambda)$ would not be affected by any small percentage of impurity, assuming such impurity to be of constant amount in all the density determinations. From the adsorption point of view, the density results at one-quarter atmosphere would be more accurate than those at the higher pressure of one atmosphere. The compressibility factor would accordingly be too large. The figure actually obtained for $(1 + \lambda)$ for phosphine in these experiments is 1.0091(25), on the assumption that the curve representing the variation of pv with p is a straight line. If the gas laws are accurately obeyed at zero pressure/

pressure, $\frac{\Delta pv}{\Delta p}$ will be zero. It is possible, of course, that such a zero coefficient will not make its appearance until the pressure is exceedingly low. In any case, the value for $(1 + \lambda)$ will again be too large. For these reasons, the most probable value of $(1 + \lambda)$ would appear to be not greater than 1.0091.

The final figure obtained for the atomic weight of phosphorus in this investigation is 30.97(7), which represents a difference of 1 in 6,000 from the value of 30.98(2) adopted by the Committee of the Chemical Society. The application of the foregoing considerations would tend to decrease this divergence.

SUMMARY AND CONCLUSION.

Determinations of the density of phosphine gas were carried out at the pressures of one atmosphere, three-quarters atmosphere, one-half atmosphere, and one-quarter atmosphere. The gas was prepared by the action of dilute potassium hydroxide solution on solid phosphonium iodide, and purified by fractional distillation. The value for the normal density thus obtained was

$$L_N = 1.5307,$$

and the factor for compressibility between zero and one atmosphere pressure was found to be

$$(1 + \lambda) = \frac{(pv)_0}{(pv)_1} = 1.0091.$$

The molar weight of phosphine is then 34.00(0), and the atomic weight of phosphorus 30.97(7).
The accuracy claimed is of the order of 1 in 10,000.

The author desires to thank Dr S.A. Kay and Sir James Walker for the kind interest shown and the valuable advice given during this investigation.

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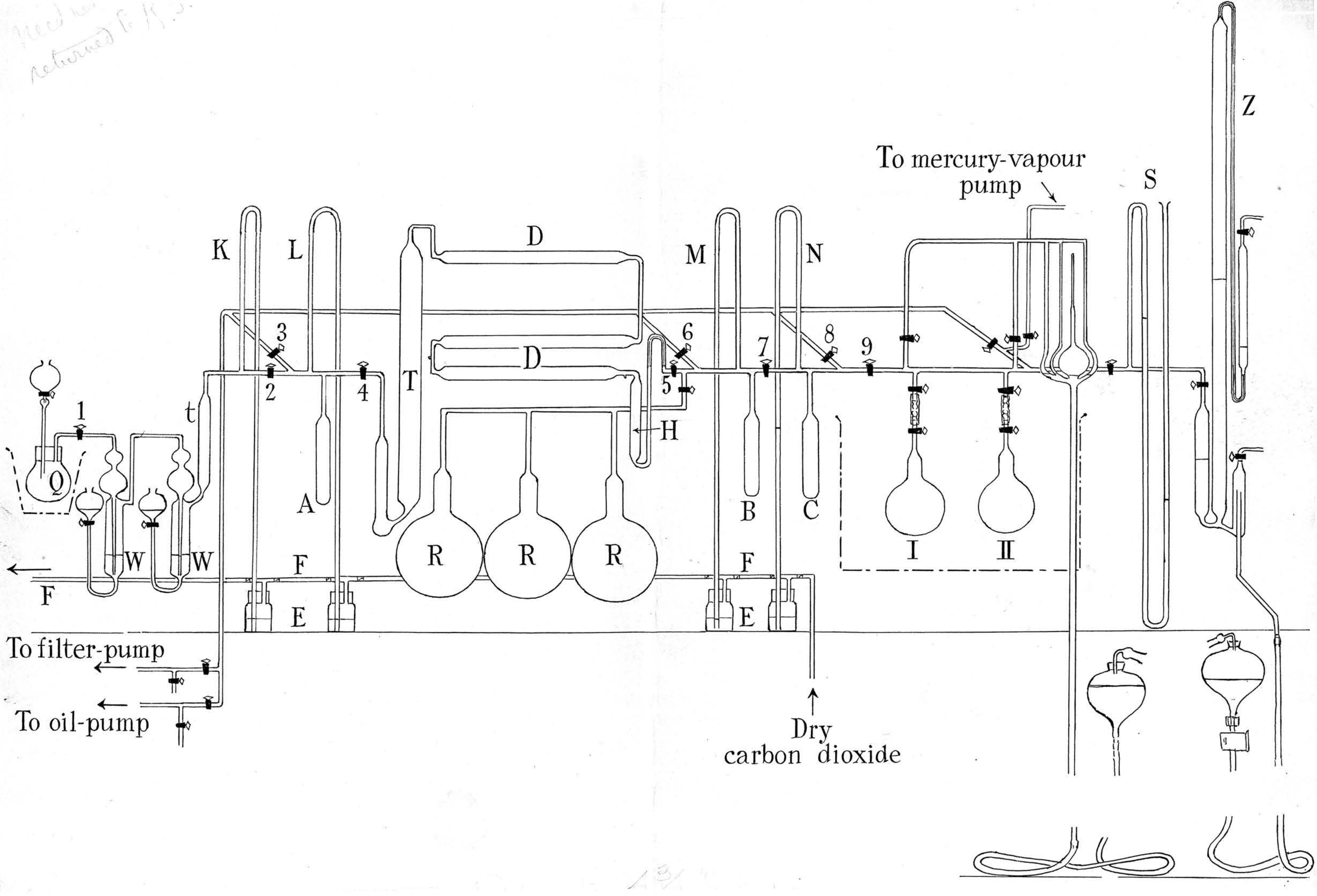

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