Photographs of the original solution, of Fractions 3, 4 and 5, and of the residual solution are reproduced in Plate III. It will be noted that erbium concentrated chiefly in the first three fractions and that in the succeeding fractions its amount rapidly decreased. The atomic weight of the rare earths in the final fraction, No. 6, was 92, which demonstrates the rapidity of the concentration of yttrium by this method.

The results of the experiments here described upon the fractional electrolysis of different mixtures of the rare earths appear to warrant the statement that the method yields quite rapid separations of some of the rare earths, and that these separations can be effected with far less expenditure of time and labor than by the customary methods of fractional crystallization or fractional precipitation.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

VACUUM AND PRESSURE STOPCOCKS.[1]

BY MERLE RANDALL AND F. RUSSELL V. BICHOWSKY.

Received November 11, 1914.

The first essential of any stopcock of either hard or soft glass, no matter what its design, is that the glass be perfectly homogeneous and thoroughly annealed, as strains in either the key or frame will in time cause the stopcock either to jam or to leak. Unsymmetrical construction, whether due to poor design or poor workmanship, will, in general, have the same effect. Especially unfortunate is a lack of uniformity in the thickness of the walls of the frame.

Stopcocks of large taper in the key are easier to grind and polish than those of small taper, but are less satisfactory for the reasons that the key must necessarily be shorter, and that the lubricant has a greater tendency to float the key from the seat, especially when the stopcock is used under pressures slightly greater than that of the atmosphere. Careful grinding and very careful polishing are naturally essential.[2]

Probably the most serious defect of the ordinary straight-bore stopcock is the tendency of the bore to track bubbles and to scrape off the lubricant in its plane and thus allow leakage around the barrel.[3] The diagonal-bore stopcock does not allow direct leakage in this way and is, in a measure, self-sealing. It should be pointed out that the key of diagonal-bore stopcocks should be longer than that of straight-bore stopcocks of the

[1] This paper is written in response to several requests for the specifications of the stopcocks in use in this laboratory.

[2] Morley, Smithsonian Contributions No. 980, p. 89 (1895).

[3] This scraping and tracking can be partially prevented by proper construction of the apertures of the cross bore and frame.

same diameter, and that the slope of the bore should be sufficient to provide a wide ring of unscraped lubricant.[1]

Diagonal-bore stopcocks, when used with the key in a vertical position in apparatus through which liquids are passed, are likely to trap some liquid in the bore of the stopcock. This is especially inconvenient when mercury is used, as in gas measuring apparatus. It can, however, be entirely prevented by the convenient arrangement of the tubes shown for a two way vacuum stopcock (Fig. 1). The principle is applicable to all other types.

TABLE I.—ORDINARY ONE WAY STOPCOCKS WITH SOLID KEY.[2]

	Mm.	Mm.	Mm.	Mm.	Mm.	Mm.
Key:						
Bore of hole	1.0	1.0	2.0	2.0	3.0	6.0
Diameter, large end	6.5	11.0	11.0	11.0	15.0	20.0
Diameter, small end	5.3	9.0	9.0	9.0	12.0	17.0
Length of ground surface	17	32	32	32	36	47
Total length	25	42	42	42	48	65
Frame and Tubing:						
Inside diameter of tubing	1.0	1.0	2.0	3.0	6.0	12.0
Thickness of walls of tubing	1.0	2.0	2.0	1.5	1.5	1.5
Length of tubing	100	100	100	100	100	150
Distance between tubing A and base of key	6	12	12	12	13	15
Distance between tubing A and B	5.0	8.0	8.0	8.0	11.0	14.0

TABLE II.—ORDINARY TWO WAY STOPCOCKS WITH SOLID KEY.

	Mm.	Mm.	Mm.	Mm.	Mm.	Mm.
Key:						
Bore of hole	1.0	1.0	2.0	2.0	3.0	6.0
Diameter, large end	6.5	12.0	12.0	12.0	15.0	21.0
Diameter, small end	5.0	9.0	9.0	9.0	12.0	17.0
Length of ground surface	22	44	44	44	47	60
Total length	36	60	60	60	65	80
Frame and Tubing:						
Inside diameter of tubing	1.0	1.0	2.0	3.0	6.0	12.0
Thickness of wall of tubing	1.0	1.5	1.5	1.5	1.5	1.5
Distance between centers of tubing A and C	10.0	16.0	16.0	16.0	22.0	28.0
Length of tubing	100	100	100	100	100	150
Distance between tubing A and base of key	6	12	12	12	13	15

[1] Dr. C. A. Kraus of the Massachusetts Institute of Technology has used a large number of lubricants, and finds that, in general, the stiffer lubricants, such as the gutta percha lubricant recommended by Keyes (*Loc. cit.*), are the more satisfcatory. With pressure stopcocks it is necessary to use a very much heavier lubricant than usual. Dr. Kraus has also pointed out a number of desirable features in regard to stopcocks for which we extend our thanks.

[2] The stopcocks described in Tables I and II are analogous to those shown in Figs. 2 and 3.

Specifications for various convenient sizes of ordinary diagonal-bore stopcocks are given in Tables I and II. Stopcocks made to specification are only slightly more expensive than the stock designs and we have found them much more satisfactory.

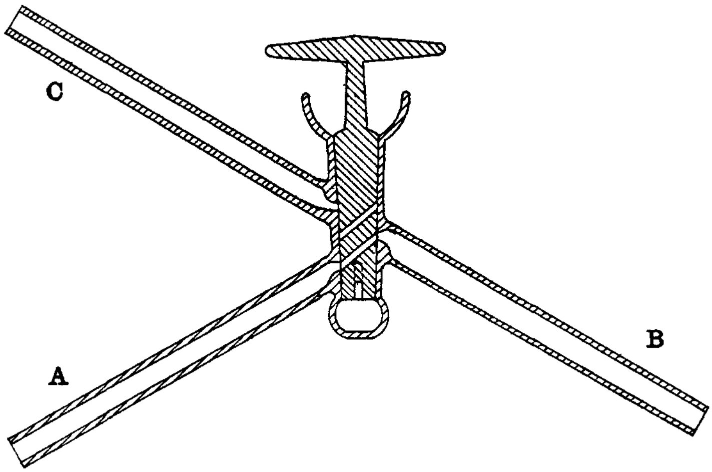


Fig. 1.—Self-draining two way vacuum stopcock. Keyes type.

Vacuum Stopcocks.—Of the various types of vacuum stopcocks only that described by Keyes[1] (Figs. 2 and 3) appears to be satisfactory.

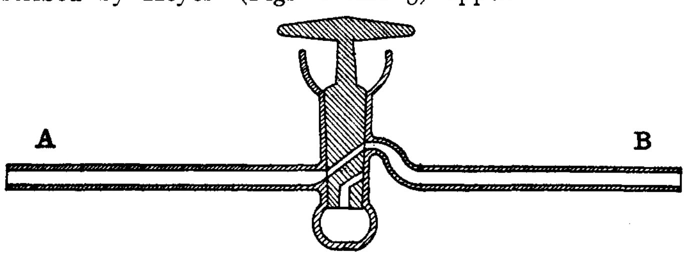


Fig. 2.—One way vacuum stopcock. Modified Keyes type.

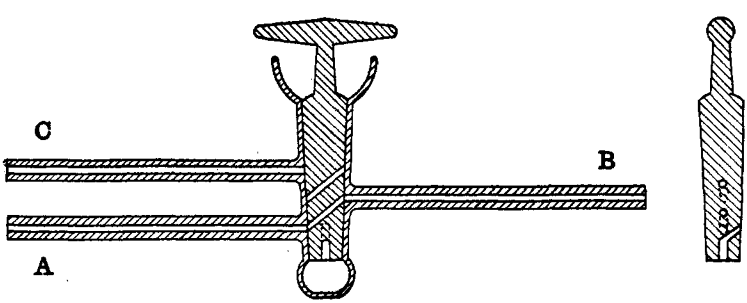


Fig. 3.—Two way vacuum stopcock. Keyes Type.

[1] Keyes, *Science*, **28**, 735 (1902); THIS JOURNAL, **31**, 1271 (1909).

In this type an extension of the small end of the frame is formed into a closed chamber which can be evacuated at will. Stopcocks having a similarly constructed chamber at the base, but having no means provided for evacuating it, are disadvantageous, as the air in the chamber is under a pressure slightly greater than that of the atmosphere and so tends to loosen the key and leak into the apparatus. Stopcocks of this type, however, can be readily converted into the Keyes type by boring suitable channels. Those stopcocks in which the small end of the barrel is formed into one of the connecting tubes are fairly satisfactory as long as this connecting tube is permanently connected with a vacuum, except that it has the disadvantages of the straight-bore type, is unsymmetrical, and is not as compact as the Keyes form. The cup that is left on the

TABLE III.—ONE WAY VACUUM STOPCOCKS WITH SOILD KEY; Cf. FIG. 2.

	Mm.	Mm.	Mm.	Mm.	Mm.	Mm.	Mm.
Key:							
Bore of hole	1.0	1.0	2.0	2.0	3.0	3.0	6.0
Diameter, large end	6.5	9.0	9.0	9.0	15.0	15.0	20.0
Diameter, small end	5.3	7.5	7.5	7.5	12.0	12.0	17.0
Length of ground surface	17	32	32	32	36	36	46
Total length	34	51	51	51	64	64	70
Frame and Tubing:							
Inside diameter of tubing	1.0	1.0	2.0	3.0	3.0	6.0	12.0
Thickness of wall of tubing	1.5	3.0	2.0	1.5	1.5	1.5	1.5
Depth of vacuum seat	6	.10	10	10	10	10	10
Length of tubing	100	100	100	100	100	100	150
Distance between tubing A and base of key	4	8	8	8	10	10	12
Distance between tubing A and B	5.0	7.0	7.0	7.0	11	11	14

TABLE IV.—TWO WAY VACUUM STOPCOCKS WITH SOLID KEY; Cf. FIG. 3.

	Mm.	Mm.	Mm.	Mm.	Mm.	Mm.	Mm.	Mm.
Key:								
Bore of hole	1.0	1.0	1.0	2.0	2.0	2.0	3.0	6.0
Diameter, large end	6.5	12.0	12.0	12.0	12.0	12.0	15.0	21.0
Diameter, small end	5.0	9.0	9.0	9.0	9.0	9.0	12.0	17.0
Length of ground surface	22	44	44	44	44	44	47	60
Total length	40	70	70	70	70	70	75	90
Frame and Tubing:								
Inside diameter of tubing A and C	1.0	1.0	2.0	2.0	3.0	3.0	6.0	12.0
Inside diameter of tubing B	1.0	1.0	2.0	2.0	2.0	3.0	6.0	12.0
Thickness of wall of tubing	1.5	2.0	2.0	2.0	2.0	1.5	1.5	1.5
Distance between tubing A and C	10.0	16.0	16.0	16.0	16.0	16.0	22.0	28.0
Depth of vacuum seat	6	10	10	10	10	10	10	10
Length of tubing	100	100	100	100	100	100	100	150
Distance between tubing A and base of key	5	7	9	9	9	9	10	12

top of the Keyes stopcock is not intended to be filled with mercury, but is merely to catch the excess lubricant that squeezes out, or it may be filled with a very soft lubricant.[1]

Specifications for various sizes of one and two way vacuum stopcocks are given in Tables III and IV.

Pressure Stopcocks.—No glass stopcock suitable for use under pressures has been described.[2] Professor G. N. Lewis and one of the writers have designed a pressure stopcock in which the taper of the key is reversed in direction and in which the base of the frame has been formed into a deep pressure seat (Fig. 4). This stopcock has been used in a number of investigations in this laboratory and has proven perfectly satisfactory when properly lubricated. The pressure is limited only by the breaking strength of the glass. The deep pressure seat and long handled stem are necessary in order that the stopcock can be properly lubricated.

The frame is first made with an extension M, (Fig. 4) which is afterwards sealed off at N as the last step in the process of assembly. The

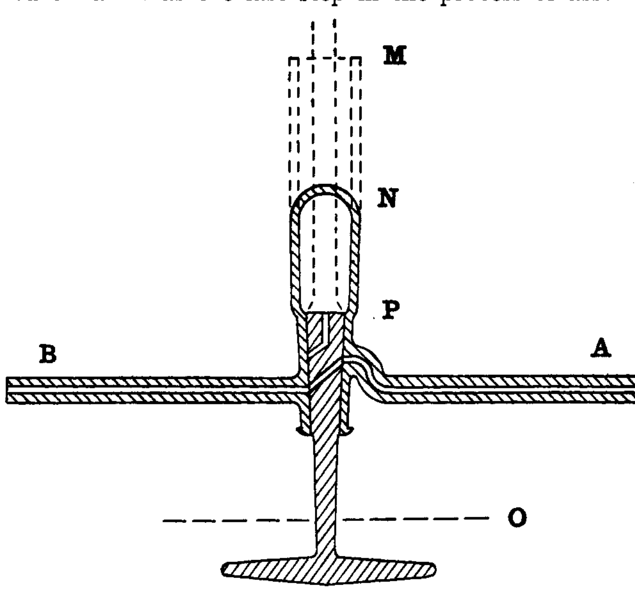


Fig. 4.—One way pressure stopcock. Lewis and Randall type.

[1] If it is desired, this cup may be filled with mercury, but it has been the experience of this laboratory that mercury does not increase the efficiency of a well ground and well lubricated stopcock, and is apt to float the key from the seat of one that is poorly made and lubricated.

[2] Since this paper was written, Professor W. A. Noyes has kindly called our attention to the fact that Dixon and Edgar (*Phil. Trans.*, (*A*) **205**, 169 (1905)) have described a pressure stopcock in which the taper of the key is reversed. This stopcock, in which the pressure chamber is formed into one of the connecting tubes possesses the same disadvantages as the similar vacuum stopcock already discussed.

key of the stopcock is made without the handle below O, but with a long stem on the large end of the key as shown by the dotted lines. By means of this stem the key is then ground into the frame. The extension of the key is cut off at P and the holes are then bored into the key so as to register with the bore of tubes A and B. The handle is then sealed on below O and the base of the barrel sealed off at N. It is usually more convenient to use this stopcock in the inverted position shown in the figure. The stopcock may be made self-draining by inclining the tubes A and B. It has been found convenient to insert a coiled spring between the barrel and the handle in case the stopcock is to be used for vacuum as well as pressure. Satisfactory dimensions are given in Table V.

TABLE V.—ONE WAY PRESSURE STOPCOCK WITH SOLID KEY.

	Mm.
Key:	
Bore of holes	1.0
Diameter, large end	9.0
Diameter, small end	7.0
Length of ground surface	30
Total length	70
Frame and Tubing:	
Inside diameter tubing	1.0
Thickness of wall of tubing	3.0
Thickness of wall of frame	3.0
Depth of bulb, on pressure seat	25
Length of tubing	100
Distance between tubing A and base of key	13
Distance between tubing A and B	7.0

Multiple Stopcocks.—The two way stopcock enables one to connect either of two parts of an apparatus separately to a third, but does not allow both to be connected at the same time with the third. Neither does it allow the first two parts to be connected. It is also sometimes desirable to connect more than three parts of an apparatus in various combinations. It is, of course, possible in most cases to accomplish this result by a more or less inconvenient arrangement of a number of one and two way stopcocks. The straight-bore multiple stopcock is unsuitable for careful work, and cannot be used in apparatus under pressure or vacuum.

It is perfectly possible to combine the fundamental principles discussed in the previous sections and make multiple stopcocks of the diagonal-bore ordinary, vacuum or pressure type, as in Fig. 5, which shows a multiple way vacuum stopcock. The essential feature of this design is that the connecting tubes, which may be as many as are desired, are symmetrically placed about the barrel but upon different horizontal planes. The connection, E, to the vacuum seat is bored so that it registers with the lower of the connecting tubes, A, and is at such an angle that none of the other holes register at the same time. Holes are then bored to a common center from the connecting tubes. The arrangement of these holes may

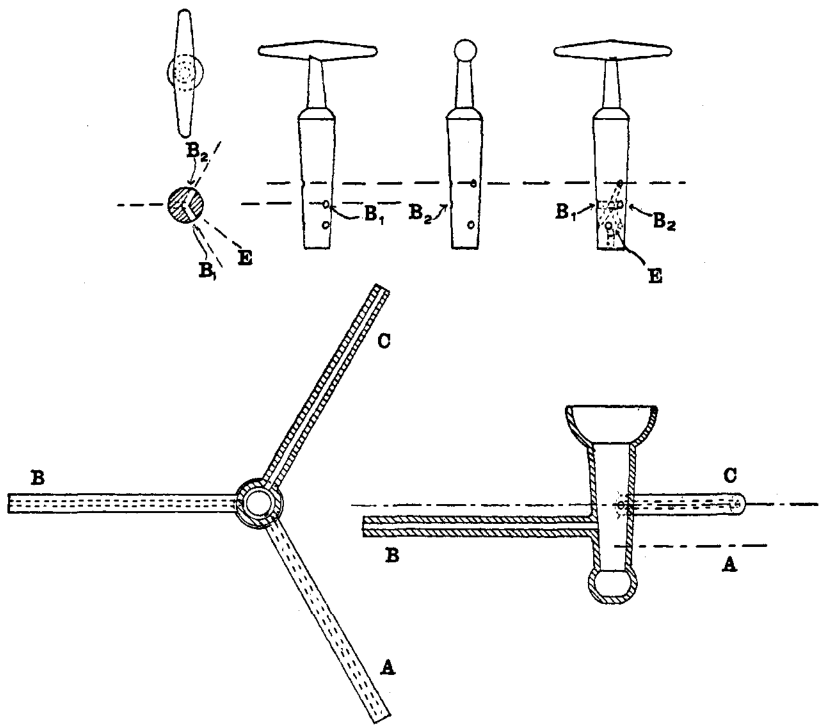


Fig. 5.—Multiple vacuum stopcock.

be varied to suit the particular purpose of the stopcock. In the stopcock shown, tube A, which is assumed to be connected to the pump may be

TABLE VI.—MULTIPLE VACUUM STOPCOCK WITH SOLID KEY.

	Mm.
Key:	
Bore of holes	1.0
Diameter, large end	12.0
Diameter, small end	9.0
Length of ground surface	44
Angle between A and B and C	120°
Angle between A and E	30°
Total length	70
Frame and Tubing:	
Inside diameter of tubing	2.0
Thickness of wall	2.0
Distance between planes A and B	6.0
Distance between planes B and C	6.0
Angle between A and B and C	120°
Depth of bulb	10
Distance between A and base	8

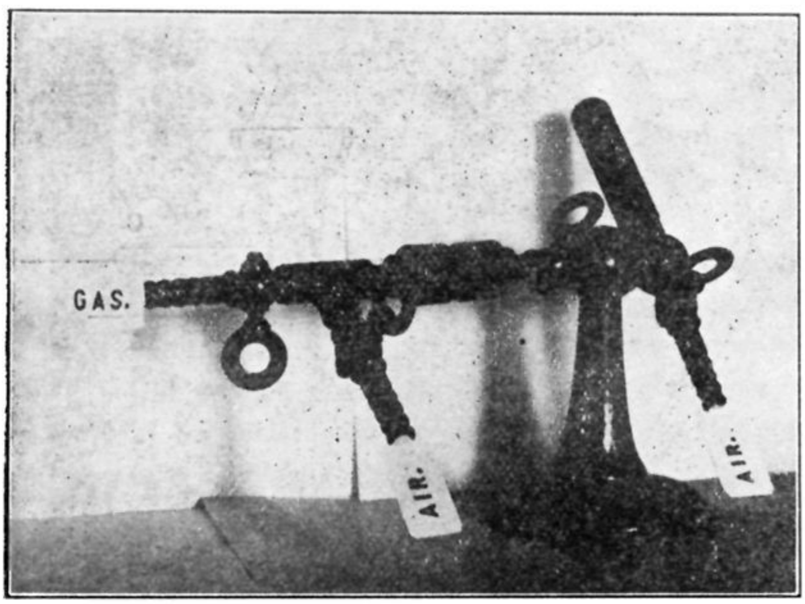
separately connected with tube B or C, or B and C may be themselves connected. If, when tubes B and C are connected, a hole is drilled from A to the center, the stopcock will operate as a multiple way stopcock connecting either B or C, or both, to A. The dimensions of this stopcock are given in Table VI.

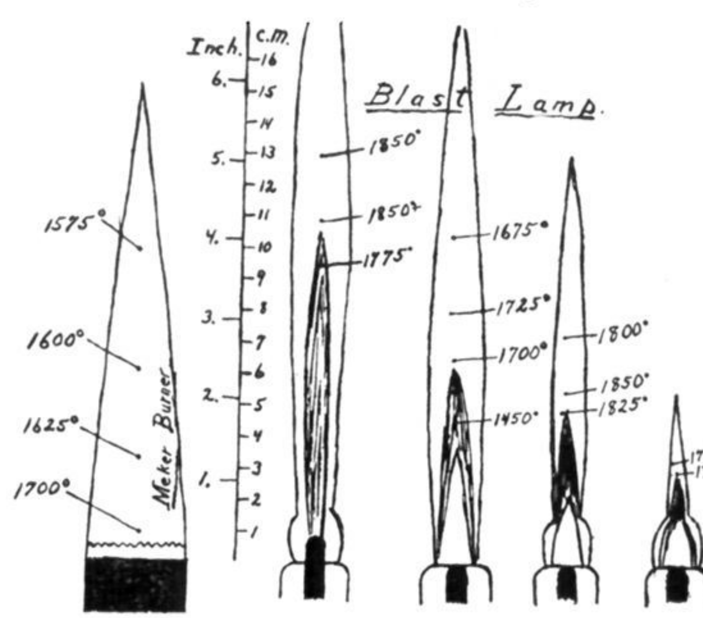
In conclusion, the authors wish to thank Professor G. N. Lewis and Mr. G. H. Fosdick for their kind suggestions.

BERKELEY, CALIF.

NOTES.

Blast-Lamp for Natural Gas.—The common blast-lamp may be rendered suitable for natural gas by connecting a T-tube to the gas inlet, so that sufficient air may be introduced with the gas to give a blue flame before blowing air through the regular air nozzle. For thorough mixing of the gases a small mixing chamber is desirable. The illustration shows a lamp so modified, that has been in operation in this laboratory for almost a year, being used by students for working glass as well as for heating crucibles. Flames of all sizes are secured almost as easily as with coal gas. Copper gauze was placed in the burner tube to prevent "flashing back," but later this precaution was abandoned, as our gas can not be made to "strike back" in any burner. A small thermocouple gave the flame temperatures indicated in the diagram.





JAMES C. MCCULLOUGH.

SEVERANCE LABORATORY OF OBERLIN COLLEGE.

A Modified Kipp Generator.—The diagram, Fig. 1, shows a gas generator which can be used to take the place of a Kipp. Especially adapted to individual student use in qualitative analysis, it ensures a ready supply of hydrogen sulfide gas at any moment.

Three gas bottles (ordinary gas collecting bottles will do just as well) are connected as shown. The reservoir bottle, *a*, which is free to move, contains a three hole stopper. A thistle-tube is inserted in one hole, a bent glass tube extending almost to the top of the bottle in the other hole, while through the third hole is inserted a short piece of glass tubing, *d*. A rubber tube (about 6 mm. bore) has one end attached at *d* and the other to the glass tube at *e* of the bottle *b*. Tube *f* extends almost to the bottom of the bottle *b*, and to the top of the stopper of bottle *c*. The other hole of the generating bottle *c* contains a piece of bent glass tubing closed by a pinch-cock, as shown.

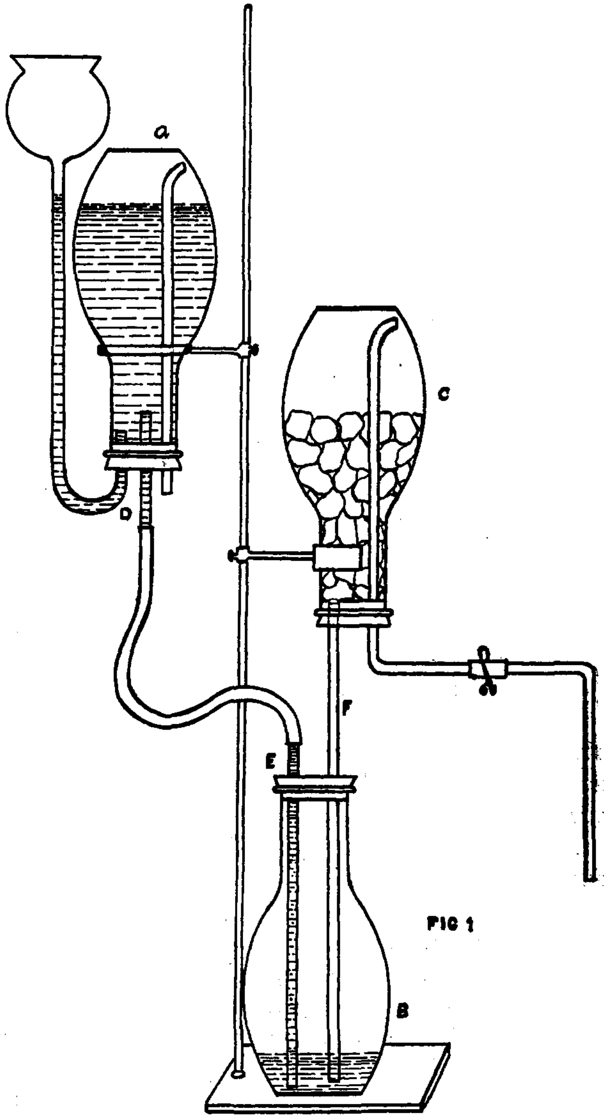


FIG 1

The stopper of bottle *c* is removed, carrying with it the stopper of bottle *b*. Bottle *c* is then filled with the necessary material and the stopper inserted. The other stopper is then inserted in bottle *b*. The clamp is then attached as shown.

The reservoir bottle is filled with the proper strength of acid by means of the thistle-tube. Opening the pinchcock forces acid up into the generating bottle, while closing the pinchcock drives acid automatically back into reservoir bottle. Since the upper end of tube *f* is level with the

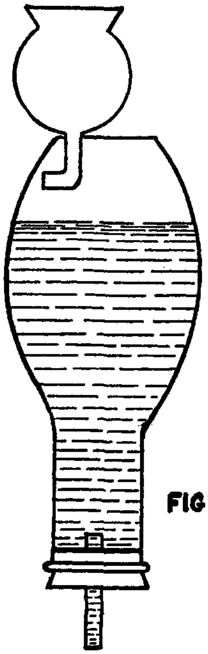


FIG 2

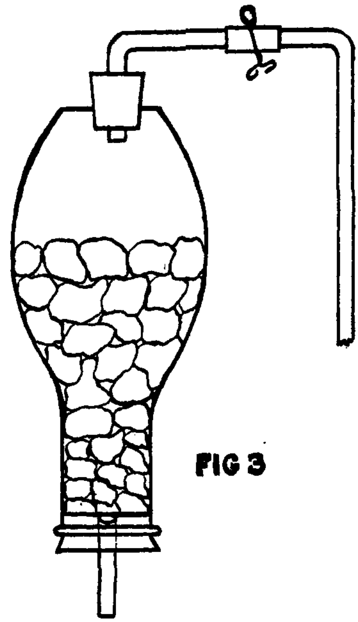


FIG 3

stopper, no acid remains in bottle *c*. To empty the generator of spent acid, detach bottle *b*, pour out the contents, replace the bottle and fill again.

Fig. 2 shows another type of reservoir bottle while Fig. 3 shows still another form. The use of gas bottles with openings in them can be substituted.

The unique advantages of this generator are:

1. Slight possibility of large pieces of material getting into the reservoir bottle and rapidly diluting the strength of the acid.

2. Rapid change as a generator for one gas to that of another by adding proper materials.

3. A regulating pressure device by sliding the reservoir bottle up and down the iron rod.

4. And finally, it is quickly constructed, portable, cheap and its capacity can be readily increased.

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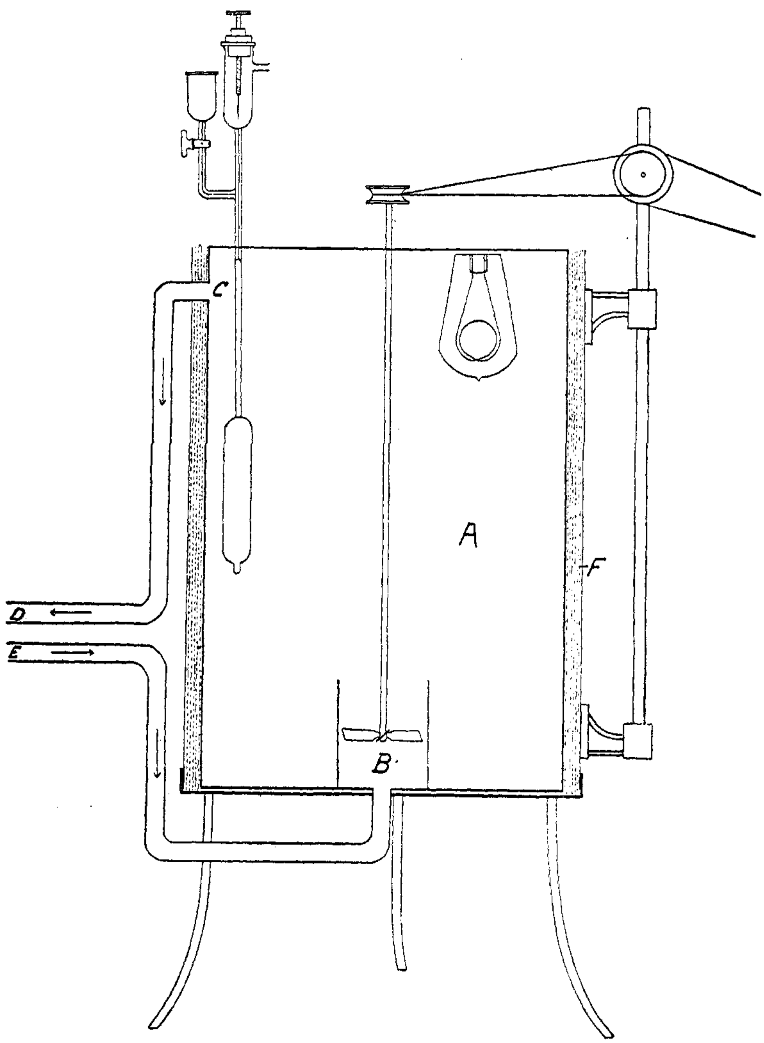
An Improved Heating Apparatus for Maintaining Constant Temperatures in Work with Polarimeters and Refractometers.—In the course of some work upon the effect of temperature upon the specific rotation of optically active substances in solution, it was found necessary to maintain constant temperatures over long periods of time. The conditions demanded that the heating apparatus be one which is simple and convenient and at the same time one which permits the easy reproduction of any given temperature.

Various forms of apparatus devised for this purpose are described in the literature. Some of these consist in principle of a coil for running



water heated either by a Bunsen flame, or an electric coil. Where such methods are used in large crowded chemical laboratories the results obtained are unsatisfactory owing to fluctuations both in the gas and water pressures. Several modifications of this form were tried and discarded. While satisfactory as regards the regulation of temperature, the heating apparatus devised by Landolt for polarimeters is nevertheless inconvenient.

After several attempts the apparatus sketched in the accompanying diagram was perfected and the results obtained far exceeded our expectations.

In the figure, *A* is a round cylindrical vessel 25 cm. in diameter and 40 cm. in depth. Directly in the center and at the bottom of *A* is soldered the small cylinder, *B*, 62 cm. in diameter by 75 cm. in depth. Within the small cylinder rotates a motor-driven stirrer of propeller form. At *C*, slightly below the water level, is soldered a 9 mm. galvanized iron tube. A similar tube opening directly into the center of *B* is soldered to the bottom of the bath. The two open ends, *D*, *E*, are attached directly to the jacketed observation tube by means of short pieces of rubber tubing. Surrounding the bath is a layer, *F*, of felt or asbestos paper.

For temperatures near that of the ordinary laboratory temperature, the bath is heated by means of an immersed incandescent lamp and the temperature electrically controlled by means of a contact toluene regulator in series with a telegraph relay and battery. For temperatures considerably above that of the room, a second lamp is connected in parallel with the first. By applying the heat from a Bunsen burner the bath may be quickly heated and adjusted to any desired higher temperature. Owing to the presence of the small cylinder, *B*, the bath is equally adapted for use with ice at 0°, while for temperatures between 0° and that of the room a cooling coil connected with the water supply may be introduced.

When the bath is connected with the observation tube and the stirrer is driven at the rate of 500 to 600 r. p. m., the water circulates through the tube with an exceedingly high velocity. To judge of the force driving the water, it may be stated that when the tubes, *D*, *E*, are open and the stirrer is revolving at the above rate, the lifting power of the stirrer is sufficient to support a column of water eight inches in height. The speed with which the water is driven under hydrostatic equilibrium is, therefore, obvious. Under these conditions it is possible to maintain any desired temperature constant to $\pm 0.01° - \pm 0.02°$ for any desired period of time.

Owing to the fact that the observation tube is of necessity at some distance from the bath, its temperature will be slightly lower and the difference will be greater, the higher the temperature to which the bath is heated. If the liquid in the observation tube must be at a definite temperature, the temperature of the bath can easily be adjusted so as to produce the desired temperature and the temperature of the tube regulated with the same degree of constancy. J. N. PEARCE.

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THE STATE UNIVERSITY OF IOWA.

Measurement of the Vapor Pressures of Solutions.—In the December number of THIS JOURNAL[1] there is an article by Frazer and Lovelace on the measurement of vapor pressures of solutions by means of the Rayleigh manometer. A very similar method will be found described by me in THIS JOURNAL in 1908,[2] except that I employed the form of manometer devised by Morley.[3] The principle of the two manometers is, however, the same, and the sensitiveness of one can be made fully equal to that of the other. O. F. TOWER.

CLEVELAND, O.

[CONTRIBUTIONS FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY, No. 243.]

THE ADDITION COMPOUNDS OF ALDEHYDES AND KETONES WITH ORGANIC ACIDS.

BY JAMES KENDALL AND WILLIS A. GIBBONS.

Received November 14, 1914.

In the first article of this series,[4] it has been shown that dimethylpyrone forms addition products with organic acids, and that these addition products are uniformly more stable the stronger the acid employed. The basic (unsaturated) properties of dimethylpyrone were regarded as due to the presence of the carbonyl group, $>C = O\underline{+}$, the compounds formed being oxonium salts. These views have been more fully developed in subsequent papers,[5] and found to be consistent with the experimental results throughout.

In the present investigation the same problem is taken up from the reverse direction. The *acid* component of the system is kept constant, while the *basic* component, containing the typical carbonyl group, is made to vary. For the acid component trichloroacetic acid was selected, since in the previous work it has been found, as the strongest of the simple organic acids, to give the most stable compounds with substances containing unsaturated oxygen. For the basic component two substances were chosen as starting points: benzaldehyde, the simplest aromatic aldehyde, and acetophenone, the simplest aromatic ketone.[6] The examination of the freezing-point curves of these substances with trichloroacetic

[1] **36**, 2439 (1914).
[2] THIS JOURNAL, **30**, 1219 (1908).
[3] *Am. J. Sci.*, **13**, 455 (1902).
[4] Kendall, THIS JOURNAL, **36**, 1222 (1914).
[5] Kendall, *Ibid.*, **36**, 1722 (1914); Kendall and Carpenter, *Ibid.*, **36**, 2498 (1914).
[6] Aliphatic aldehydes and ketones will be studied in a future communication.