

3). Column five gives the concentration of hydrogen ion, calculated from the figures in column four by means of the formula given by Rosenstein¹.

The results of these experiments are shown graphically in Fig. 1. The curves A and B show the variation, with the hydrogen ion concentration, of the un-ionized phenolphthalein and of the colored ion, respectively. The concentration of the doubly charged ion becomes the same as that of the un-ionized substance when the concentration of hydrogen ion is 5.8×10^{-10} mols per l.; and at about this concentration the curve C, which represents the fraction of phenolphthalein present as intermediate ion, reaches a maximum. These facts are in complete accord with the statements contained in equations five and six, and therefore corroborate the assumptions from which these equations are derived.

Summary.

1. The distribution ratio of phenolphthalein between benzene and water has been found colorimetrically to be 13.1, the concentration in benzene being the greater.

2. The fraction of un-ionized phenolphthalein in solutions of different hydrogen ion concentrations was determined by shaking out with benzene; the fraction of doubly charged ion in the same solutions was found from their colors.

3. The sum of the two fractions above mentioned was always much less than unity; the maximum observed difference from unity being 0.509 at a hydrogen ion concentration of 7.63×10^{-10} m. per l. This difference represents the fraction of phenolphthalein present as intermediate ion.

4. By means of the two constants for phenolphthalein previously determined, and by assuming that the divalent ion from phenolphthalein alone is colored, it was shown that in a solution containing a concentration of hydrogen ion of 5.71×10^{-10} mols per l. the concentration of intermediate ion should be a maximum and equal to 50.2 per cent. of the phenolphthalein present, 24.9 per cent. of the phenolphthalein should be present as divalent ion, and 24.9 per cent. as un-ionized phenolphthalein. It has been found graphically that at a concentration of hydrogen ion of 5.8×10^{-10} mols per l. the concentration of intermediate ion is a maximum and equal to 50.5 per cent. of the phenolphthalein present.

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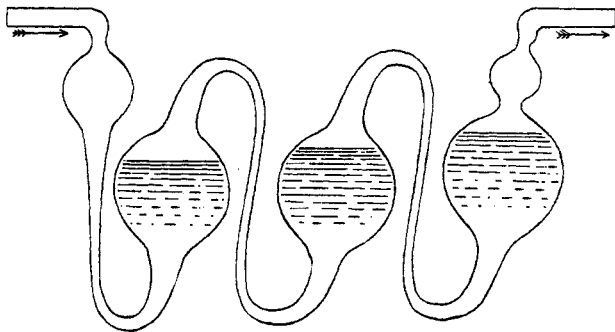
NOTES.

A Simple Form of Absorption Bulb.—The many forms of bulbs that have been devised for the absorption of certain constituents from gaseous mixtures are so constructed as to leave considerable air space above the surface of the absorbent. To displace thoroughly all of the sample of

¹ *Loc. cit.*

gas remaining in these spaces, after absorption is complete, takes time. In the form of bulb depicted in the accompanying sketch these spaces are reduced in volume and time is thereby saved. Another advantage is that the absorbent can be removed for titration if desired and the bulbs easily rinsed out after each determination.

The apparatus can be readily made in the laboratory, of any desired size or shape, after very little practice. Bulbs of the required size are blown at intervals of about two



inches in a rather thick-walled glass tube. The intervening space between two bulbs is then heated and drawn out to a length of some six inches and then bent as shown in the figure. The small bulb at the left serves to prevent possible loss from back pressure when the air current is stopped.

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An Improved Thermoregulator.—The sensibility of those thermoregulators, which involve an electric contact between mercury and a wire, depends in large measure upon the sharpness with which the contact is made and broken. It is suspected that the resort to toluol as the expansive fluid is in many cases only a makeshift effort to overcome the uncertainty of make and break at a fouled mercury meniscus.

A little consideration will show that if the mercury meniscus **retains** its proper form and if there is no "wetting" of the contact wire by the mercury, an extremely small rise or fall of the mercury thread will be sufficient to make or break the circuit.

The author¹ noticed in 1910 that the sensibility of a mercury thermoregulator is seriously affected by adherence of mercury to clean platinum. When this occurs, the breaking of the circuit takes place at an appreciably lower temperature than the "make." By substituting for platinum a nickel or "nichrome" wire, the making and breaking of the circuit may be made to occur at temperatures much closer to one another.

The preservation of a clean mercury surface at the contact is a much more difficult matter to manage. The elimination of oxidizable metals

¹ W. M. Clark, "A contribution to the investigation of the temperature coefficient of osmotic pressure," dissertation, Johns Hopkins University, p. 10, 1910.

from the mercury by Hulitt's method¹ is a great aid. More important is the prevention of sparking at the contact by the use of a small current and a condenser. But the most satisfactory results are to be accomplished by keeping oxygen away from the mercury. This principle has been frequently employed. The contact wire may be sealed in and the "head" of the regulator evacuated; adjustment is then still possible if the mercury thread can be broken at the proper point and the excess mercury stored in a cup sealed on at the side. Such a regulator is very hard to adjust to a definite and exact temperature. This may be more easily done if the bore of the capillary be kept fairly large, but the instrument then becomes one of relatively low sensibility unless an unwieldy amount of mercury is used. Such an instrument, while maintaining quite permanently a clean mercury meniscus, has the often serious disadvantage that a slight jar will break the thread.

By substituting hydrogen for mercury as the expansive fluid, Regaud and Fouilliand,² on the one hand, and Bousfield,³ on the other, have eliminated oxygen from the contact.

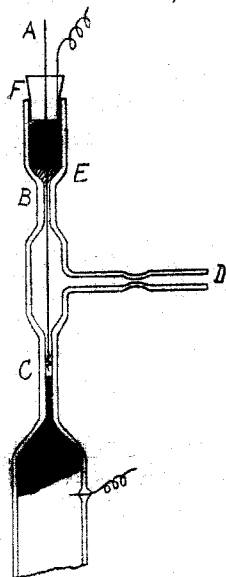
But the certainty with which hydrogen retained by a barometric column of mercury will change its volume with very slight fluctuations of temperature, unless the mercury column is tapped, is seriously doubted. Richards⁴ protects the mercury by means of hydrogen supplied by a small hydrogen generator.

A simpler device for protecting the mercury with hydrogen is described as follows:

The essential parts are shown in the figure.

The mercury in the regulator should first be carefully boiled to expel all air and moisture. Then the instrument is brought to the temperature at which it is to be used and the mercury in the capillary broken off at such a point that it will stand midway in the capillary at the working temperature. The nickel contact wire *A*, which should fit the capillary *B* quite snugly, and

should taper to a point at the contact *C*, is now put in place. Pure, dry hydrogen is next passed for a few hours in at *D*. It wastes through *B*. When it is believed that all air has been displaced, a bit of heavy lubricating wax is melted about the wire at *E*, with care that it does not flow far into the capillary *B*. Just as the wax solidifies the flow of hydrogen is stopped, a layer of mercury is poured on top of



¹ *Physic. Rev.*, 21, 388; 33, 307.

² *Z. Mikroskop.*, 20, 144 (1903).

³ *Chem. News*, 105, 13 (1912).

⁴ *Ibid.*, 107, 220 (1913).

the wax to insure a perfect seal, and the tube *D* is fused off at the constriction. The contact wire, though held rather firmly by the cork *F*, may now be adjusted by pushing it up or down, and with very little danger of allowing air to gain access to the mercury.

In order that the mercury thread shall not be parted, if through accidental overheating it should be pushed past the contact point, the wire should be sandpapered to a fine thread. Then by properly kinking the wire, the point can be kept centered on the mercury meniscus.

The regulation of an air chamber provides a severer test for the sensibility of a thermoregulator than does the regulation of a water bath. The air bath, for which the regulator described above was designed, will be described in a later publication, as will an account of the temperature records. The regulator has kept the temperature constant to within $0^{\circ}.002$, as read on a Beckmann thermometer, for periods of 8 hours. The daily variations have been considerably larger, but the most satisfactory feature has been the fact that, except for an occasional adjustment of the wire, the regulator has required no attention during three months continuous and uninterrupted use.

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AN ANOMALOUS REACTION OF RESORCINOL.

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It is stated in the literature that resorcinol may be titrated by means of caustic alkali, with Poirrier's blue, C₄B, as indicator, and that resorcinol, under these circumstances, acts as a dibasic acid.¹

As the result of many experiments I have been unable to verify this statement, although phenol and salicylic acid may be titrated readily with caustic alkalies, both being monobasic to the indicator.

If an aqueous resorcinol solution, of 0.1 to 0.5 molar concentration, be treated with one molecular proportion of caustic alkali of normal strength, it soon changes through yellow and greenish yellow shades of increasing depth to a deep brown color. Sodium carbonate effects the same change of color at a slower rate.

If such a resorcinol solution be titrated with standard caustic alkali as rapidly as possible, in the presence of sufficient of the indicator solution (1 : 500), the neutrality point will be reached when between 1 and $1\frac{1}{2}$ molecular proportions of the alkali have been added. The amount of alkali necessary for the neutral color change will vary, for the same concentration of the resorcinol solution, with the strength of the caustic

¹ Engel, *Compt. rend.*, 102, 214-17 (1886); *Chem. News*, 53, 87-88 (1886); also *Bull. soc. chim.*, 45, 321-28 (1886); Allen, *Com. Org. Anal.*, 4th Ed., 3, 337; Cohn, "Indicators and Test-Papers," 2nd. Ed., p. 136.