the abnormal absorption effects due to crystal perfection are shown to be negligible in the case of iodine.

5. The atoms are found to be grouped in molecules of I_2. The distance between centers of the two atoms in one molecule is found to be 2.70 Å. Distances of closest approach of centers of 3.54 and 4.35 Å. exist in the crystal. Either of these may correspond to the ion radius of iodine.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY AND FROM THE WEST VIRGINIA GEOLOGICAL SURVEY]

A NEW EQUILIBRATOR: A DEVICE FOR THE DETERMINATION OF THE DISTRIBUTION RATIO OF A VOLATILE SOLUTE BETWEEN TWO MISCIBLE SOLVENTS

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In the course of an investigation on the normal potential of the iodine electrode to be described in a subsequent paper it became necessary to determine the free iodine present in a solution containing potassium iodide, iodine and tri-iodide. For this purpose we invented a device which we call an equilibrator, which permits the determination of the distribution ratio of a volatile solute between two miscible solvents. Since it is planned to use this device in several other researches in this Laboratory it seems desirable to describe it in a separate paper.

The equilibrator is a closed glass apparatus without mechanical valves and contains no liquids to produce seals except the two separated solutions under investigation and yet by mere rotation it causes a continuous circulation of gas or vapor so that it bubbles through the two solutions in turn for as long as the rotation continues. This ensures equality of vapor pressure of the common volatile constituent from the two separated liquid phases if the rotation is continued long enough. After equilibrium has been established the two solutions are separately available for analysis and for any other use that may be desired.

The design and mounting of the equilibrator will be clear from the figure, which shows the plan or top view, end elevation, side elevation and mounting in the thermostat. The essential features are two tubes (A) and (B) which make an angle of about 14 circular degrees with each other in a vertical direction and which are connected at each end by glass tubes (C) and (D) each provided with a ground glass stopper (I) and (J). The stoppers may be replaced at the end of the run by delivery tubes of the type (L) shown in the figure which are ground to fit the same openings. The connecting tubes permit free circulation of the vapor but prevent mixing of the solutions. They are bent inward and upward as shown so that

centrifugal force and gravity will help to prevent spattering. It was repeatedly demonstrated by methods which are so obvious as not to require detailed explanation that these connecting tubes are effective in preventing mixing of the two separated solutions by spattering. However, if the equilibrator is started or stopped too suddenly the momentum of the liquids may carry the liquids over the peak of the connecting tubes. In our apparatus tubes (A) and (B) each have a capacity of about 300 cc.

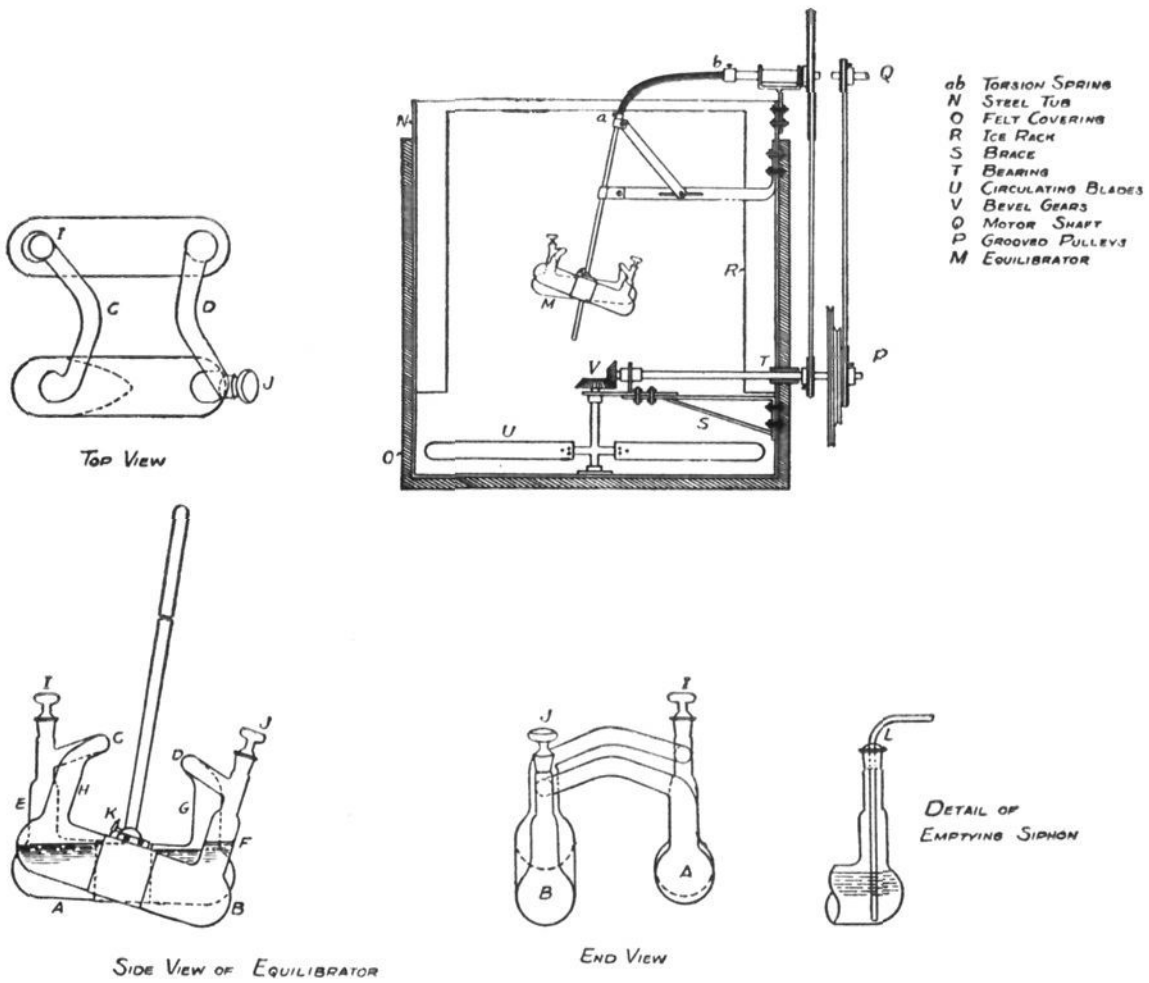

Fig. 1.

The equilibrator is mounted in a brass bracket (K) (not shown in the top view or in the end view) on a shaft so that the shaft bisects the angle between the two glass tubes (A) and (B). This shaft is then mounted so that it can revolve in a bearing at an angle with the vertical which is adjustable. The angle with the vertical should be greater than one-half the angle between the two glass tubes. Our apparatus which had an angle of 14 degrees between the two glass tubes is most effective as an automatic circulating pump when the shaft is mounted so that the angle between the shaft and the vertical is 11 degrees. The shaft is then connected to a horizontal driving shaft by means of a flexible coiled phosphor bronze torsion spring or by a universal joint. A suitable speed is sixteen

rotations of the equilibrator per minute. Instead of rotating the equilibrator it may be rocked back and forth on a horizontal axis at right angles to the tubes (A) and (B) and will then function equally well as a circulating pump.

For use at 0° a cylindrical rack (R) made of coarse mesh wire screen is placed inside of and concentric with the tub. By filling this rack with ice and stirring vigorously the entire tub can be kept at 0°. A cover with heat insulation not shown in the figure is used.

In our use of the apparatus the common volatile solute was iodine while one solvent was water and the other a solution of potassium iodide in water. After equilibrium had been attained the vapor pressure of iodine from the potassium iodide solution must be the same as from the water. Therefore, in spite of abundant formation of tri-iodides, the activity of the free iodine in the potassium solution must be the same as the activity of the free iodine in water. Since the latter is a very dilute solution of a non-electrolyte, its activity is sensibly the same as its concentration, which may be readily determined by titration. From the analysis of the solution containing potassium iodide the equilibrium constant of the iodine–iodide–tri-iodide reaction can be computed. This solution of known iodine activity and composition was used in galvanic cells with a platinum electrode for the measurement of the normal potential of the iodine electrode and for measurements of the free energy of formation of silver iodide. These data, which give a proof of the usefulness and reliability of the equilibrator, will be published in the near future.

The time required to attain equilibrium depends on the vapor pressure of the volatile solute, the size and dimensions of the equilibrator and speed of rotation and must therefore be determined in each case. In our apparatus it was proved that pure water can be completely saturated with iodine through the vapor phase in twenty-two hours at 25° and in fifty hours at 0° with 16 rotations per minute. This is a maximum time for iodine, as less time will be required with unsaturated solutions. Moreover, it is possible to add in advance the approximate amount of iodine required to give within 10% of the concentration expected at equilibrium and thus shorten the time necessary to attain equilibrium.

The new equilibrator makes it possible to determine the distribution ratio of any volatile solute between two miscible solvents, whereas the usual method of determining distribution ratios is applicable only to solvents which are immiscible or incompletely miscible. Partial mutual solubility, however, complicates the interpretation of the data. If the solvents are sufficiently non-volatile the new equilibrator avoids this difficulty. Emulsification of the two solvents may make a sharp separation difficult or impossible and thus cause errors in the old method but this difficulty is avoided with the equilibrator.

An even more important field of usefulness, or at least one of greater interest to us, is for the determination of the distribution ratio of a volatile solute between a pure solvent (not necessarily non-volatile) and a solution of a non-volatile solute in the same solvent. The distribution of iodine between pure water and a solution of potassium iodide is of this type. Of course in this case there will be some distillation of water into the potassium iodide solution, thereby diluting it slightly, but this distillation is very slow and if in any particular case the distillation is rapid enough to be significant this merely makes it necessary to analyze the solution for the non-volatile solute at the end of the run instead of depending on the known composition of the original solution.

A similar study of the distribution of bromine between water and aqueous solutions of potassium bromide is now in progress in this Laboratory. The apparatus seems suitable for the study of the distribution of carbon dioxide between water and any salt of carbonic acid from which conclusions as to the concentration or more strictly of the activity of the free acid in the solutions of its salt may be drawn and hence the dissociation constants of the acid can be computed. Similarly the distribution of sulfur dioxide between water and solutions of its salt can be studied. The hydrolysis of sulfides can be determined with distribution experiments with hydrogen sulfide. The amount of free ammonia formed by hydrolysis of any of its salts can be found and hence the dissociation constant of the acid determined or the equilibrium between ammonia and its complex compounds of the type $Ag(NH_3)_2^+$ can be determined.

Summary

A description is given of a new device, called an equilibrator, which by mere rotation acts as an automatic circulating pump, forcing a gas or vapor to bubble continuously and in turn through two separated liquids.

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