which do not show this, the monosubstituted salts and dipropyl- and diethylammonium chlorides, would be expected to have increasing conductance in more concentrated solutions. Additional measurements were made extending concentrations to higher values than those reported for dipropyl and diethylammonium chlorides but no increase in conductance with increasing molecular concentration was noticed with these two salts.

Acknowledgments.—The authors are indebted to Dr. W. G. Bickford for help and suggestions while constructing the conductance bridge and its auxiliaries. A substantial part of the experimental work was done in the Chemistry Laboratories of the University of Vermont.

V. Summary

The conductances of solutions of mono-, di-, tri- and tetrasubstituted methyl-, ethyl- and *n*-propylammonium chlorides in liquid hydrogen sulfide have been measured. These show that the molecular conductance increases both with the number and the size of the substituted groups, the number having a greater effect than the size.

The conductance concentration curves show a minimum which is characteristic of solutions of electrolytes in solvents of low dielectric constant.

AMES, IOWA RECEIVED AUGUST 16, 1939

[CONTRIBUTION FROM THE LABORATORY OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Chemical Activation by Isomeric Radioactive Transition; the Reaction of Br^{80} (18 min. half-life) with Carbon Tetrachloride

BY JOHN E. WILLARD

Investigations in this Laboratory utilizing radioactive bromine have shown that it undergoes a reaction with carbon tetrachloride. This reaction is not activated by either heat or light but must be accounted for on the basis of chemical activation resulting from the radioactive transition of Br^{80} (4.4 hr. half-life) to Br^{80} (18 min. half-life).

Freshly prepared radioactive bromine contains a mixture of Br^{80} (4.4 hr. half-life), Br^{80} (18 min. half-life) and Br^{82} (34 hr. half-life), all of which may be formed from the common isotopes Br^{79} and Br^{81} by neutron capture. Br^{80} (4.4 hr.) and Br^{80} (18 min.) are radioactive isomers[1,2,3,4] the first of which changes into the second as a result of a loss in nuclear energy. In somewhat less than 70% of the transitions[5] this energy appears as a gamma ray while in the remaining transitions it serves to eject a conversion electron from one of the electron shells of the atom.

It has been shown that the change from Br^{80} (4.4 hr.) to Br^{80} (18 min.) is capable of activating the hydrolysis of *t*-butyl bromide,[2] the rupture of bromate ion,[3] and the decomposition of ethylene dibromide.[6] These reactions result in the preferential splitting out of Br^{80} (18 min.) atoms from the parent molecule. The activation of these processes has been attributed to the recoil energy imparted to the Br^{80} (18 min.) by the ejection of a gamma ray or conversion electron, but in view of a subsequent determination[7] of the energy of the conversion electrons involved, this explanation is not tenable.

In agreement with the work cited above, it has been found that Br^{80} (18 min.) is the reactive bromine species in mixtures of bromine isotopes with carbon tetrachloride. Calculations discussed below indicate that only those transitions of Br^{80} (4.4 hr.) to Br^{80} (18 min.) which occur with the emission of a conversion electron result in reaction with the carbon tetrachloride. The electronic rearrangements which follow such emission afford ample energy to account for the activation.

The results which have been obtained emphasize the fact that special precautions must be exercised in the use of certain radioactive elements as isotopic tracers if erroneous conclusions are to be avoided. It is to be noted, however, that Br^{82} (34 hr.) may be used as an isotopic tracer without danger of ambiguity. This isotope may be obtained by allowing mixtures of isotopes to stand until the relatively short-lived Br^{80} isomers have decayed.

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[1] Snell, *Phys. Rev.*, **52**, 1007 (1937).

[2] Segre, Halford and Seaborg, *ibid.*, **55**, 321 (1939).

[3] DeVault and Libby, *ibid.*, **55**, 322 (1939).

[4] Roussinow and Yusephovich, *ibid.*, **55**, 979 (1939).

[5] Siday, *Nature*, **143**, 681 (1939).

[6] Le Roux, Lu and Sugden, *ibid.*, **143**, 518 (1939).

[7] (a) Valley and McCreary, *Phys. Rev.*, **55**, 666 (1939); (b) **55**, 863 (1939).

It might be expected that reactions caused by the beta rays in solutions of the type under consideration would mask reactions, such as those observed, which preferentially separate one period of activity. This, however, does not occur because the proportion of radioactive bromine to normal bromine is extremely small.

Experimental Procedure

Radioactive Bromine.—Radioactive bromine was produced by irradiating 3 liters of ethyl bromide with neutrons from a Ra (200 mg.)–Be source for twenty-four hours. Following irradiation the ethyl bromide was extracted with 150 cc. of water containing about 0.05 g. of sodium bromide. The water solution was then evaporated to about 0.5 cc. and pipetted into the reaction tube (A) of Fig. 1, together with a small amount of potassium bromate and sulfuric acid. The reagents were frozen with liquid air to prevent reaction until (A) had been sealed shut. The bromine which was liberated in (A) with gentle warming was condensed in (B) with an ice–salt mixture. The reaction tube (A) was then sealed off from the system, the gas-escape (D) was sealed, and the bromine was frozen with liquid air. The system was then evacuated through the tube (H) with the aid of a mercury vapor pump and the bromine was distilled onto phosphorus pentoxide in the trap (C), where it was kept until it was admitted to the carbon tetrachloride in the tubes (F).

Carbon Tetrachloride.—Mallinckrodt "Low Sulfur" carbon tetrachloride was strongly illuminated while saturated with chlorine and chlorine dioxide,[8] washed with sodium hydroxide and with water, and dried over phosphorus pentoxide. It was then distilled into an all-glass reservoir (G) equipped with glass taps which could be opened by a magnetically operated hammer. It was degassed by several repetitions of the process of freezing–evacuating–melting. Samples were taken from the reservoir as desired by distilling into evacuated reaction tubes (F). After a sample was obtained the reservoir was sealed off while the carbon tetrachloride was frozen. About 1 cc. was collected in each tube.

Reaction Mixture.—The bromine which was collected in the trap (C) was transferred to the tubes (F), containing the carbon tetrachloride, by cooling the latter with liquid air and opening the stopcock or glass tap at (E). (Stopcocks were greased with Apiezon grease.) The tubes (F) were then sealed from the system as a unit; their contents were melted, mixed and refrozen, and they were sealed off from one another. Their bromine concentration was about 0.05 *M*.

Analysis.—After the reaction tubes had been allowed to stand for the desired length of time, they were opened and the contents washed three times with 5-cc. portions of 20% potassium iodide to give a colorless carbon tetrachloride layer containing the reaction products. This layer showed no radioactivity if the extraction was made immediately after the bromine was added to the carbon tetrachloride.

The relative radioactivity of samples was determined by means of a Geiger–Müller counter tube the end of which consisted of a thin glass bulb which could be lowered into a cup of the solution to be tested. Counts were made on unextracted carbon tetrachloride–bromine solutions, carbon tetrachloride from which the bromine had been extracted, and on the extraction liquid. Frequent determinations of the background count showed it to be very constant at a value of 10 ± 2 per min. The activities which were measured ranged from several thousand counts per min. down to the value of the background.

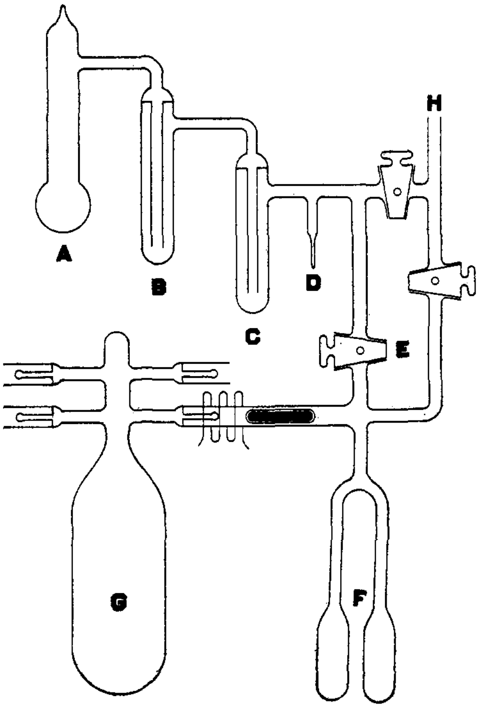

Fig. 1.

Results

Activity Entering Carbon Tetrachloride.—When bromine containing an equilibrium mixture of Br^{80} (4.4 hr.) and Br^{80} (18 min.), some Br^{82} (34 hr.), and a large proportion of non-radioactive bromine is allowed to stand for two hours or more with carbon tetrachloride, between 30 and 40% of the activity measured by the counter described above is found to enter the carbon tetrachloride. This activity is, within the limits of resolution of the apparatus, solely 18 min. activity. A typical decay curve for such a solution is shown in (A) of Fig. 2. The circles represent the experimental data; the line is a calculated curve for the decay of activity with an 18 min. half-life.

Growth of Activity in Carbon Tetrachloride.—If bromine enters the carbon tetrachloride molecule as a result of activation accompanying the transition of Br^{80} (4.4 hr.) to Br^{80} (18 min.) it

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(8) Dickinson and Jeffreys, THIS JOURNAL, **52**, 4289 (1930).

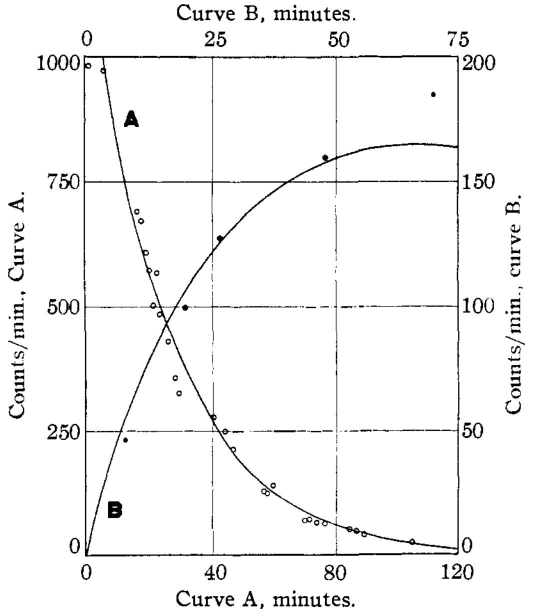

Fig. 2.—Curve A: circles show decay of radioactive bromine which has reacted with carbon tetrachloride. Solid line is calculated decay curve for species with 18 min. half-life. Curve B: points show growth of activity in carbon tetrachloride reacting with radioactive bromine. Solid line shows calculated growth of 18 min. activity from 4.4 hr. activity.

would be expected that a plot of activity entering the carbon tetrachloride against time of contact of the carbon tetrachloride with the bromine would show a growth curve typical of the build-up of 18 min. activity from a relatively long-lived parent. Such a curve is shown in Fig. 2(B). The points were obtained from counts on five samples of the same solution which had been allowed to react for different lengths of time before extraction. The counts have been corrected for the decay which occurred between the start of extraction and the time of taking the counts. The solid line is a theoretical growth curve for the production of 18 min. activity from 4.4 hr. activity.

Activity in Extraction Solution.—The circles of Fig. 3 show the experimentally determined values (less the 34 hr. activity) for the activity of bromine at different times after extraction from a carbon tetrachloride solution in which it had stood for two hours. The activity increases immediately after extraction, passes through a maximum, and finally falls off with a 4.4 hr. decay period. This behavior would be expected if the freshly extracted bromine contained less than the equilibrium amount of Br^{80} (18 min.), that is, if some of the latter had reacted with the carbon tetrachloride.

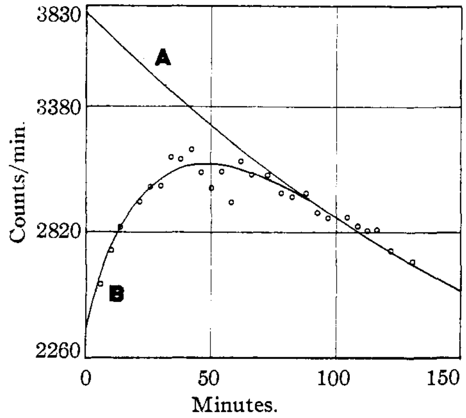

Fig. 3.—Circles show activity of radioactive bromine extracted from carbon tetrachloride solution after standing in the latter for two hours. Curve A: calculated decay of equilibrium mixture of Br^{80} (4.4 hr.) and Br^{80} (18 min.). Curve B: calculated change in radioactivity of extraction solution assuming that 37% of Br^{80} (18 min.) has been removed by reaction with carbon tetrachloride and that radiations from Br^{80} (4.4 hr.) do not register on the counter.

The intersection of the line (A) of Fig. 3 with the zero time ordinate gives the counts per min. which would have been obtained from the extraction solution at the time of extraction if none of the 18 min. activity had reacted with the carbon tetrachloride. It is calculated from the 4.4 hr. decay curve given by the experimental points for times after equilibrium was reëstablished.

Reaction Efficiency.—If the relative efficiency with which the radiations from Br^{80} (4.4 hr.) and Br^{80} (18 min.) affect the Geiger–Müller counter is known, the fraction of the Br^{80} (18 min.) atoms which react with carbon tetrachloride can be obtained readily from the value for the count in the extraction solution at the time of extraction and the value of the intercept of curve (A), Fig. 3, with the zero ordinate.

The 4.4 hr. radiations consist of conversion electrons with energies of 23.6, 35.5, and 47.2 kev., and gamma rays with energies of 48.9 and either 37.1 or 25.3 kev.[7] Calculations show that the fraction of such gamma rays which are absorbed by the counter used in this work is so slight that the number of counts which they produce is negligible. The conversion electrons are also ineffective in counting because they are almost completely absorbed by the walls of the counter tube before entering the counting chamber.

Therefore it may be concluded that the total count produced by mixtures of Br^{80} (4.4 hr.) and Br^{80} (18 min.) is due to the β rays ejected in the change from Br^{80} (18 min.) to Kr^{80}. These have been found to have a maximum energy of 2 mev.[9]

This conclusion is in agreement with the results of DeVault and Libby[3] and LeRoux, Lu and Sugden,[6] whose data indicate that less than 25 and 10%, respectively, and possibly no part of the total count from radioactive bromine in their counters is due to the 4.4 hr. isomer.

With the knowledge that the radiations from Br^{80} (4.4 hr.) do not affect the counter, it may be determined from the data of Fig. 3 that 0.37 of the Br^{80} (18 min.) atoms formed from Br^{80} 4.4 hr. react with the carbon tetrachloride. This value is in agreement with values of 0.3 to 0.4 obtained by measuring both the activity in the carbon tetrachloride layer and that in the extraction solution immediately after extraction of solutions of radioactive bromine in carbon tetrachloride.

Effect of Temperature and Phase.—If the energy which is made available to a bromine atom by the change from the 4.4 hr. to the 18 min. species is greatly in excess of the activation energy required for a given chemical reaction of the bromine, it is to be expected that the reaction will be independent of temperature. To test this point the maximum fraction of the activity which will enter the carbon tetrachloride has been determined at room temperature, at −10° where the reaction mixture is a liquid, at −50° where it is a solid, and at liquid air temperatures. The results are given in Table I. The values given in the table have been corrected for the background count and for the decay which occurred between the start of extraction and the time of taking the count.

TABLE I

T, °C.	Total counts/min.	CCl_4 counts/min.	% in CCl_4
25	1061	361	34
− 10	518	155	30
− 50	566	45	8
−190	1190	145	12

Different determinations at a single temperature varied as much as 20% from the average, probably due in a large part to the fact that the counter tube was not designed for exactly reproducible comparisons of different samples. The accuracy is adequate, however, to show qualitatively that temperature has little or no direct effect upon the reaction but that the reaction efficiency is reduced to about one-third of its liquid phase value when the reaction system is frozen.

It is to be noted in the table that the reaction does occur even in the solid phase at liquid air temperatures. The amount of reaction at −10° where the mixture is liquid is equivalent to that at 25°. The amount of reaction at −50° where the mixture is a solid is equivalent to that at −190°. The change in going from −10 to −50° evidently is due to the change in phase.

If the reaction were a chain reaction with secondary steps for which thermal activation energy was required, it would be dependent on temperature. However, this would not be apparent from the measurements made in this work since they show only the final disposition of Br^{80} (18 min.).

Mechanism of Activation.—It has been suggested[2] that chemical activation by the isomeric transition of Br^{80} is due to the recoil energy which the newly formed Br^{80} (18 min.) atoms acquire as the result of the ejection of a gamma ray or conversion electron when they are formed from Br^{80} (4.4 hr.). Since the publication of this suggestion Valley and McCreary[7] have determined the upper energy of the conversion electrons emitted in this transition to be 47.2 kev. and have concluded from their data that the upper energy of the gamma rays is 48.9 kev.

The recoil energy acquired by a bromine molecule as the result of the ejection of a 47.2 kev. electron is about 3.7 kcal. per mole and the recoil energy made available by the emission of a 48.9 kev. gamma ray is about 0.2 kcal. per mole. These energies are not adequate to account for the observed reaction of bromine and carbon tetrachloride, which are normally very inert to one another.

A larger source of activation energy is, however, available. In emitting a conversion electron a bromine atom initiates an electronic rearrangement of which evidence is given by X-rays[4] and Auger electrons.[5] Such a rearrangement readily can produce highly reactive states of the bromine molecule, atom or ion. A knowledge of the exact nature of the state which leads to the reaction of Br^{80} (18 min.) with carbon tetrachloride is not

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(9) Livingston and Bethe, *Rev. Mod. Phys.*, **9**, 245 (1937).

necessary for the purposes of this paper. However, a number of possibilities may be suggested. The molecular ion, formed when a conversion electron, followed by an X-ray, is emitted from a bromine molecule, may have an electronic configuration which makes it capable of reacting directly with a carbon tetrachloride molecule. Alternatively the electronic state may be such as to lead to the dissociation of the molecular ion into a neutral atom and an atomic ion. If this latter process occurs the fragments may part with sufficient kinetic energy to cause them to react with carbon tetrachloride molecules, or the reaction may be accounted for by the electronically excited state of the atomic ion formed. Another possibility is that the reaction is due to a reactive excited state produced when the ion regains an electron.

Whatever the exact mechanism of the activation is, it is necessary to conclude that only those isomeric transitions which occur with the emission of a conversion electron, and consequent electronic rearrangements, can produce reaction.

Siday[5] has found that the fraction of the Br^{80} (4.4 hr.)$\longrightarrow Br^{80}$ (18 min.) transitions which emit a conversion electron is slightly more than 0.3. This value sets an upper limit for the fraction of the Br^{80} (18 min.) atoms which can react with carbon tetrachloride, if reaction occurs only following the ejection of an electron. This upper limit is in close agreement with the experimentally determined reaction efficiency discussed above. Therefore it may be concluded that essentially all of those Br^{80} (18 min.) atoms which are formed with the emission of a conversion electron react.

Since the decomposition of radioactive bromate ion[3] and of radioactive ethylene dibromide[6] occur for at least 75 and 90%, respectively, of the Br^{80} (4.4 hr.)$\longrightarrow Br^{80}$ (18 min.) transitions and since, according to Siday, a much smaller fraction of these transitions involve the loss of a conversion electron, it appears that some explanation not dependent on the emission of a conversion electron must account for at least part of the observed reaction in these cases. The recoil energy from the transition gamma rays (0.2 kcal.) is insufficient to do so. Therefore, if the observed values for the reaction efficiencies, for the conversion coefficient, and for the energies of the conversion electrons, are valid, some explanation which is not yet apparent must be sought.

Reaction Due to Beta Rays.—Since each beta ray and conversion electron shot out from the radioactive atoms in solution probably disrupts or ionizes several thousand carbon tetrachloride molecules, there must be many reactive fragments capable of combining with bromine in the solution. If more than a very small fraction of the bromine were radioactive, experiments would therefore show a considerable proportion of the 4.4 hr. Br atoms as well as of the 18 min. atoms entering the carbon tetrachloride. However, the proportion of radioactive to non-radioactive bromine atoms in the solution is probably less then $1:1 \times 10^{12}$, so the effect in question is not observable in the measurements of activity.

Neutron–Bromine Reaction.—Incidental to the preparation of radioactive bromine, determinations were made of the rate of decay of the activity of ethyl bromide samples which had just been removed from the Ra–Be source after twenty-four hour exposures. In all cases plots of the logarithm of the activity against time showed the initial decay to have a half-life of the order of twenty minutes, which changed to a half-life of about four and one-half hours after the ethyl bromide had been away from the neutron source for a little over an hour. This indicates that Br^{80} (18 min.) may be formed directly by neutron bombardment, since if all of the 18 min. activity were produced as daughter activity of the 4.4 hr. isomer, the decay curves would be of the 4.4 hr. type from the start.

The author wishes to express his appreciation to Mr. William Van Horne and Mr. Hugh Hulburt for the loan of the counting apparatus used in the foregoing work, to Dr. Joseph O. Hirschfelder for helpful discussions, and to the Wisconsin Alumni Research Foundation for the use of the Ra–Be neutron source.

Summary

1. It has been found that the radioactive transition from Br^{80} (4.4 hr.) to Br^{80} (18 min.) activates bromine in such a way as to enable it to react with carbon tetrachloride.

2. Decay and growth curves of the activities involved give consistent proof of the existence of the reaction.

3. Experiments over a wide temperature range show the reaction to be independent of temperature and to have an efficiency about one-third as great in the solid phase as in the liquid phase.

4. The evidence indicates that only those

Br^{80} (18 min.) atoms react which are produced as the result of the emission of a conversion electron.

5. In the light of new data, the recoil energies previously thought to account for chemical activation by the isomeric radioactive transition of bromine, are found to be too small to do so.

MADISON, WIS. RECEIVED SEPTEMBER 2, 1939

[CONTRIBUTION FROM THE NEW YORK STATE AGRICULTURAL EXPERIMENT STATION, NO. 345]

Partial Vapor Pressures from Nicotine Solutions at 25°*

BY L. B. NORTON, C. R. BIGELOW AND W. B. VINCENT

Little information is available on the loss of nicotine by evaporation and the concentration of nicotine vapor which can be built up when a dilute solution of nicotine is applied to foliage as an insecticide. A knowledge of the partial vapor pressures of both water and nicotine through the complete range of their solutions is therefore of great practical importance from that standpoint, and of theoretical interest in showing the thermodynamic behavior of a highly non-ideal solution.

The published values of the vapor pressure of pure nicotine at ordinary temperatures are in very poor agreement. The values at 25° range from 0.02 mm., determined experimentally by Harlan and Hixon,[1] to 0.17 mm. calculated from the equation found by Gorbachev[2] to be valid from 100 to 250°. A similar equation obtained by Young and Nelson[3] gives 0.12 mm. as the vapor pressure at 25°. No data are available on the evaporation of nicotine from solutions, except some approximate determinations by McDonnell and Young[4] of the final concentration and the loss of nicotine from a dilute solution exposed to the air for a long period at room temperature.

Experimental

Materials.—The nicotine was prepared by purifying the commercial 95% alkaloid, furnished by the Tobacco By-products and Chemical Corporation of Louisville, Ky., according to the method of Ratz,[5] and distilling it *in vacuo*. The product boiled at 125° at 17 mm. pressure, was water-white, and had a specific rotation $[\alpha]^{20}\mathrm{D}$ $-168.90°$. Different samples which were purified at intervals during the investigation varied from this rotation not more than 0.2°. Ordinary distilled water was used as the other component.

Apparatus.—The dynamic gas-saturation method was used for the measurements because of the extremely low vapor pressure of the nicotine. The apparatus was arranged as in Fig. 1. Nitrogen, which was used instead of air to eliminate slow oxidation of the nicotine, was passed from the cylinder A over the mercury trap B, which served as a safety valve and pressure regulator, and into the vaporizers C and D. C was a series of three small bulbs charged with the solution to be measured, which saturated the gas partially, thus preventing appreciable changes in the concentration of the solution in the main vaporizer D by evaporation losses. D was the main vaporizer, consisting of a Friedrichs spiral gas-washing tower containing 200 cc. of the solution under investigation. The upper part of the tower was packed with glass wool saturated with the same solution to stop any spray and to ensure complete saturation of the nitrogen passing out. Both vaporizers were completely immersed in a water-bath maintained at 25 ± 0.02°. The outlet tube E was heated electrically by a winding of resistance wire to prevent condensation of vapor and was connected with a manometer. The nicotine was absorbed in the modified Turner absorption bulb F, which was filled with dilute sulfuric acid. The second absorption bulb G was filled with anhydrous magnesium perchlorate "Anhydrone" to absorb the water vapor coming from the vaporizer and the first absorber. The U-tube H also contained Anhydrone to absorb any water vapor coming back from the aspirator The aspirator bottle I had a capacity of 40 liters and was fitted with a manometer, thermometer, and siphon tube.

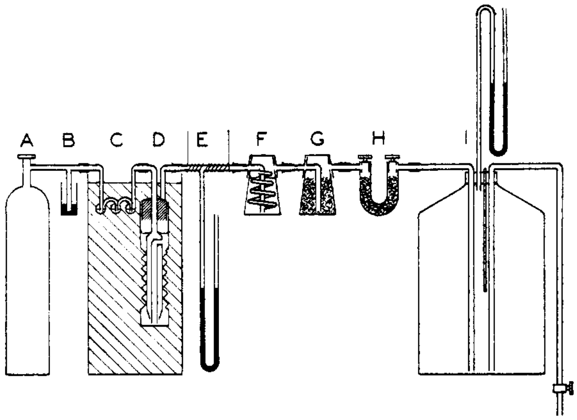

Fig. 1.—Apparatus for vapor pressure measurements.

(*) Approved by the Director of the New York State Agricultural Experiment Station for publication as Journal Paper No. 345, October 30, 1939.

(1) Harlan and Hixon, *Ind. Eng. Chem.*, **20**, 723 (1928).

(2) Gorbachev, *J. Applied Chem.* (*U. S. S. R.*), **7**, 388 (1934).

(3) Young and Nelson, *Ind. Eng. Chem.*, **21**, 321 (1929).

(4) McDonnell and Young, *U. S. Dept. Agr. Bull.*, No. 1312 (1925).

(5) Ratz, *Monatsh.*, **26**, 1241 (1905).