

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

A Study of the Distribution of Arsine in Impregnated Charcoal by Means of Radioactive Tracers

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The object of the present work, which formed part of an investigation of the mechanism of arsine removal by impregnated charcoals, was to study the distribution of arsine in beds of charcoal using a radioactive tracer. The various experiments were carried out in the light of certain facts that had already been ascertained concerning arsine removal. Of chief interest were the effects of the time of exposure to the toxic gas, the water content both of the charcoal and of the air stream, the concentration of arsine in the air stream, and the nature of the absorbent. In conjunction with the arsine distribution, the distribution of water was also determined in an attempt to find some correlation with the effect of water in the removal process.

Experimental Details

Absorbent.—The absorbent, supplied by Edgewood Arsenal, was a 12–16 mesh (U. S. Standard Sieve Series), activated coconut shell charcoal which had been impregnated to contain cupric oxide. It was dried by heating for three hours at 150°. In some experiments the charcoal was previously equilibrated to a definite relative humidity.

Radioactive Arsine.—The radioactive arsenic employed was obtained by bombarding Ge⁷³ with deuterons in a cyclotron to give As⁷⁴ with a half-life of seventeen days.

Since the radioactive material was obtained from a germanium dioxide target, it was necessary to separate arsenic from germanium and also from copper from the bombardment chamber. Treatment of the radioactive material with aqua regia followed by a sodium carbonate fusion of the residue rendered the sample soluble. After addition of pure sodium arsenite as a carrier, a large part of the germanium was removed as volatile germanium chloride by evaporating the solution nearly to dryness twice with hydrochloric acid. Removal of copper was effected by precipitation with hydrogen sulfide and subsequent treatment with polysulfide reagent. After this separation the arsenic was fairly pure except for a small amount of germanium which might conceivably form germane during the reduction of the arsenic to arsine. The separation of the remaining germanium was carried out after the method of Abrahams and Müller,² using a double precipitation of arsenic sulfide to ensure complete removal of germanium. The pure radioactive arsenic sulfide was dissolved in aqua regia, evaporated with a small amount of sulfuric acid and diluted in a volumetric flask. Both procedures for the removal of germanium chloride by boiling and the separation of arsenic from germanium by precipitation of the sulfide were checked using samples of radio-arsenic and radio-germanium. It was found that practically all of the germanium was lost by boiling with a hydrochloric-nitric acid mixture while the arsenic stayed in the solution. Also, it was shown that no appreciable amount of germanium came down in the second precipitation of arsenic sulfide while the arsenic was obtained in good yield.

(1) From a thesis submitted in 1942 to the Graduate School of the University of Rochester in partial fulfillment of the requirements for the degree Doctor of Philosophy. Present address: Atlantic Refining Co., Philadelphia, Pennsylvania.

(2) Abrahams and Müller, *This Journal*, **54**, 86 (1932).

Radio-arsine was prepared by reaction of metallic zinc with a solution of dilute sulfuric acid and sodium arsenate to which some of the radio-arsenic solution had been added. The arsine and hydrogen evolved were passed through anhydrous calcium sulfate and a dry ice-ether trap to remove water vapor. Thence the gases were led through two liquid air traps to freeze out arsine and the non-condensable gases removed with a Hyvac pump. The pure arsine was later allowed to expand into a storage bottle.

Absorption Apparatus.—The set-up used to expose the absorbent bed consisted essentially of an apparatus for obtaining an air-arsine stream of known concentration, temperature and humidity, at a constant flow rate of 500 cm. per minute through the empty absorption tube. The main air stream was split into two streams, one of which flowed through two bottles of distilled water and a glass wool trap and thence to a mixing chamber while the second passed through concentrated sulfuric acid, a glass wool trap and into the wet air stream. Any desired relative humidity could be obtained by varying the ratio of the two streams. The entire humidifying system was placed in a thermostat at 25.0° to insure constant humidity. The humidified air passed on through a calibrated wet and dry bulb psychrometer enclosed in an insulated box, the pressure being kept constant by a small overflow in a hydrostatic regulator. The air stream was then mixed with arsine in a mixing chamber.

Arsine was forced out of the storage vessel at a constant rate by allowing sodium chloride solution to run slowly into the vessel under a constant head. The amount introduced into the air stream was determined by passing the arsine through a flowmeter before entering the mixing vessel. The flowmeter was calibrated by actual chemical analysis of the air-arsine stream and the proper flowmeter setting checked by analysis at the beginning of each run. From the mixing vessel the air-arsine stream passed through a second flowmeter, kept constant to insure a constant arsine concentration, and into the manifold. A small excess flow was allowed to escape through a stopcock into the hood.

Attached to the manifold were six absorption tubes, each preceded by its own flowmeter and constant temperature coil. Water jackets, through which a rapid flow of water at 25° was maintained, surrounded both the coil and the absorption tube. A three-way stopcock inserted after the flowmeter permitted diversion of the flow either to a waste line or an analysis train. The analysis for arsine was carried out by allowing a known flow, as measured by the tube flowmeter, to pass for a measured length of time, through two bubbler tubes containing a mercuric chloride-gum arabic solution. The latter quantitatively absorbs arsine, which was then determined by the method of Cassil.³

The absorption tube, shown in detail in Fig. 1, was a uniform Pyrex tube of internal diameter 19.0 ± 0.1 mm. with a semi-ball joint at each end. In order that the absorption tube might be attached and detached without using rubber connections, a U-tube with a ground glass joint at each end was placed between the bottom of the absorption tube and the rest of the system. About half way up the absorption tube on the inside and held by a ring seal was a glass ring with a ground surface. This ring served as a seat for a perforated porcelain disk which in turn was the support for the charcoal bed. The disk (of the type used as small filtering plates) had about sixty-three regularly spaced holes, and its diameter was such that it could be just slipped in and out of the tube. The

(3) Cassil, *J. Assoc. Official Agr. Chem.*, **24**, 196 (1941).

sealed-in ring support decreased channeling of the gas stream at the periphery of the disk. This design of the absorption tube was necessary so that the entire bed (5.0 ± 0.1 cm. in depth and introduced by the standard Chemical Corps procedure) could be pushed up the tube as a unit after exposure to arsine. The absorbent could then be progressively removed in layers of known size at the top of the tube. To carry this out, the tube was removed from the system, the joints carefully cleaned with ether to remove the grease and the tube mounted vertically. The bed was raised up the tube by means of a rod pressing against the bottom of the supporting porcelain disk. This rod was moved by a screw shown at the bottom in the diagram. When the top of the bed was exactly level with the top of the tube, a millimeter scale attached to the rod was read. The rod was then moved up gradually for a measured distance (usually 3 mm.). The absorbent thus forced up beyond the top of the tube was removed, collected in a rubber mat surrounding the tube and placed in a small corked tube. The procedure was repeated until the entire bed had been sectioned. No mixing or appreciable contraction of the bed was ever noticed in using this method of layer separation. This was checked by coloring some of the charcoal particles.

The breakpoint indicator apparatus followed the absorption tube. A three-way stopcock was used in order that the flow might be changed instantly to either of two bubbler tubes. The absorbent was considered "broken" to arsine when a faint brown color appeared in a 2% silver nitrate solution in three minutes. This corresponds to 0.02% transmission of arsine by the absorbent for an initial arsine concentration of 4.15 mg. per liter.

Geiger Counter Assembly.—The separated layers of charcoal were weighed and, in most cases, dried to determine their moisture content after the run. It was found experimentally that the drying procedure had no effect on the counting rate of the sample. Then a 0.350-g. portion of each layer was placed evenly in a circular brass counting cup and covered with thin aluminum foil. This size sample proved satisfactory for the absorbent used and for the counter tube.

The Geiger-Müller tube, the quenching circuit and the assembly for holding the counting cup in place were enclosed in a grounded brass housing. The counting cup was placed in a fixed position on a support that could be moved up and down directly beneath the window of the counting tube. With the cup raised to a fixed distance from the window the average counting rate of the sample was determined. One sample was kept and counted from time to time during a set of experiments in order to measure the rate of decay of the radioactivity. Using the decay data, the counting rates of the various samples were calculated back to the time of starting the experiments.

The counting tube, with a thin mica window sealed on the bottom, was filled to a pressure of 8 cm. with a mixture of 90% argon and 10% ethanol and had a background of about thirty counts per minute. The counter itself consisted of a Neher-Harper type quenching circuit, a high voltage supply, a counting rate meter circuit capable of counting up to 20,000 counts per minute and a Cenco mechanical counter for low counting rates. The counting rate meter circuit was calibrated frequently by means of a standard pulse generator. In actual operation the rate meter was used for all the samples except those with counting rates less than 100 counts per minute.

Calculations.—The counting rates measured were for a 0.350-g. (or 0.300-g. in some cases) portion of the layer. The total counting rate per layer was found by simple weight proportion. It was observed by actual experiment that the counting rate was proportional to the weight of a given sample over the range used. Since the layers of absorbent obtained by the sectioning method were small and sometimes different in size, the data were expressed as weight of arsine absorbed per gram of dry absorbent at a given depth. It was assumed that the dried layers contained only the dried absorbent and arsenic trioxide. The latter has been found⁴ present by

(4) H. F. Johnstone, NDRC Informal Report, 1941.

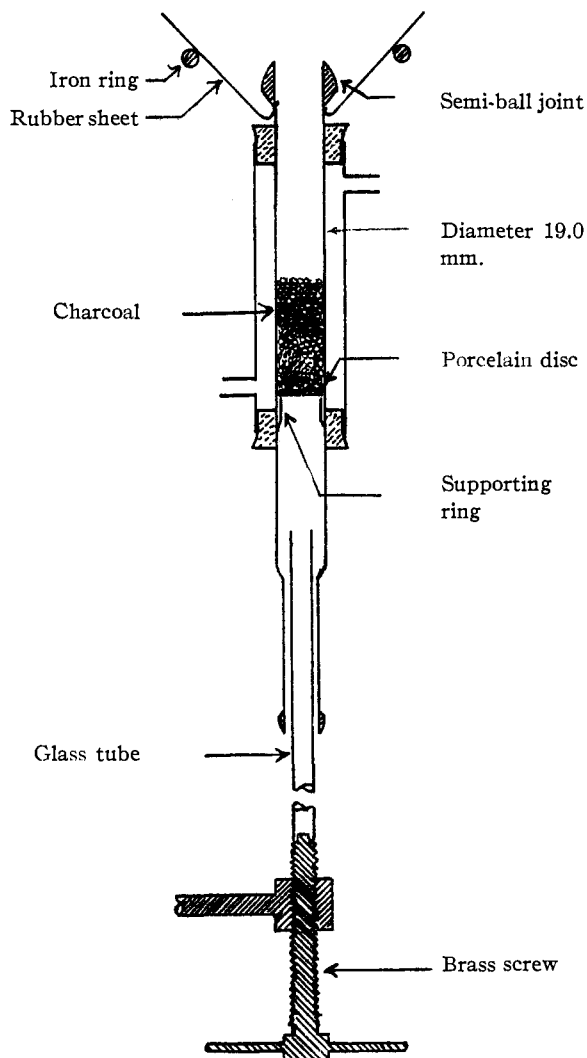


Fig. 1.—Apparatus for sectioning.

X-ray analysis of similar absorbents exposed to a dry air-arsine stream. Also, Pierce⁵ observed in some experiments on the change in weight of the same type of absorbents on exposure to arsine that this oxide was a strong possibility.

In order to obtain the amount of arsine absorbed in any layer, it was necessary to know the counting rate per unit weight of arsenic trioxide. The total number of counts in an entire bed was found by adding together the counting rates of all the layers. This total count divided by the weight of arsenic trioxide in the whole bed, calculated from the known amount of arsine absorbed during the run, gave the desired ratio. In actual practice the value used was an average for all the samples exposed to the same batch of radioactive arsine and not run beyond the breakpoint. Using this factor, the weight of arsenic oxide in each layer was obtained. The amount of dry absorbent in each layer was found by subtracting the weight of arsenic trioxide from the total weight of the dried layer. This method of finding the amount of absorbent in each layer was verified by adding together the weights of all the layers of a given sample and comparing with the weight of absorbent as calculated from the apparent density and the volume of the char used. These two values agreed to within 1–4%, including several samples

(5) W. C. Pierce, NDRC Formal Report, 1941.

that had absorbed almost 2 g. of arsine. Finally, the weight of arsine originally absorbed per gram of dry absorbent in each layer was calculated and plotted against the bed depth (the distance from the influent end to the center of the layer).

As a matter of allied interest, the weight of water (equal to the loss in weight on drying) per unit weight of dry absorbent was calculated for the various layers and plotted as a function of bed depth.

Results and Discussion

A study of the distribution curves in Figs. 2-6 shows the marked influence of water on arsine removal. With dry absorbent as much arsine is removed by the very first layers in ninety-three

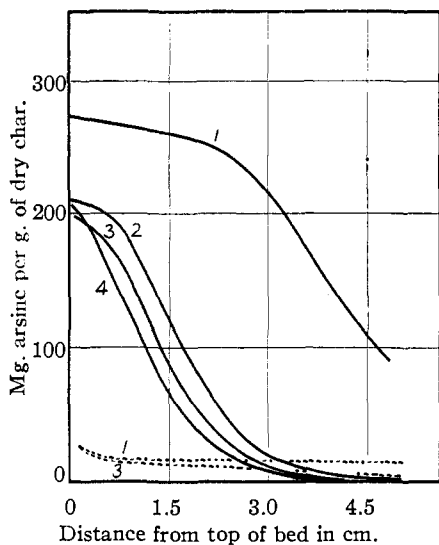


Fig. 2.—Variation of the distribution of arsine with time using dry char and dry air. 1-300 min., 2-100 min., 3-78 min., 4-60 min. Dotted curves represent water distribution.

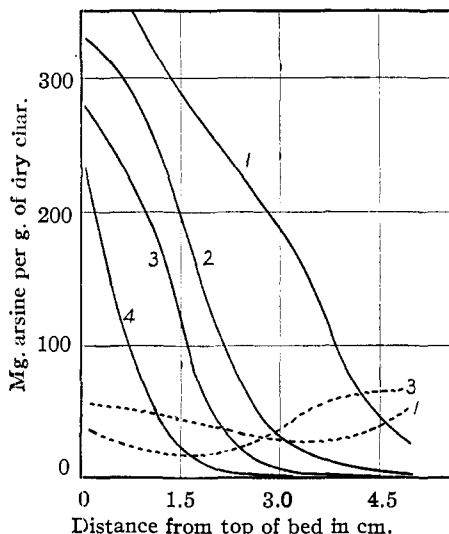


Fig. 3.—Variation of arsine distribution with time using dry char and air at 50% relative humidity. 1-300 min., 2-150 min., 3-93 min., 4-40 min. Dotted curves represent water distribution.

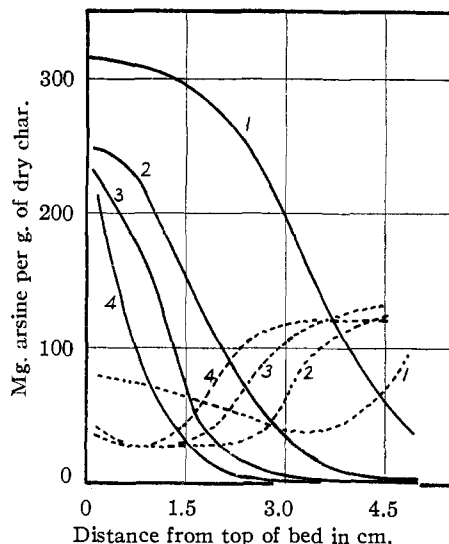


Fig. 4.—Variation of arsine distribution with time using char equilibrated to 50% relative humidity and air at 50% relative humidity. 1-300 min., 2-130 min., 3-80 min., 4-48 min. Dotted curves represent water distribution. Original water content about 100 mg. per g. of dry char.

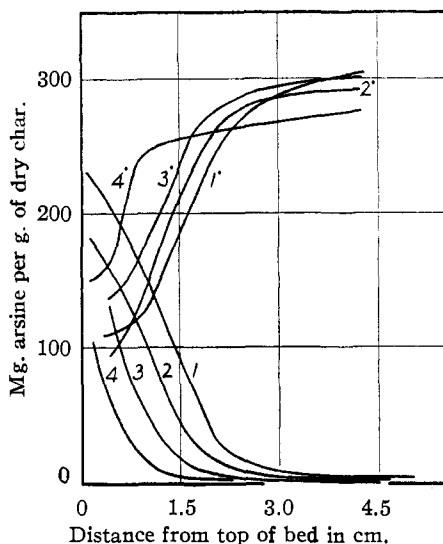


Fig. 5.—Variation of arsine distribution with time using char equilibrated to 70% relative humidity and air at 70% relative humidity. 1-80 min., 2-60 min., 3-40 min., 4-20 min. Upper primed curves represent water distribution. Original water content = 325 mg. per g. of dry char.

minutes from 50% relative humidity air as is taken up in three hundred minutes from dry air. Water vapor in the air stream is obviously accelerating the removal. In the former case, however, the amount of arsine drops sharply through the bed whereas with dry air it falls more slowly. This indicates that water also inhibits the removal of arsine. Water vapor, which is incompletely absorbed by charcoal, moves ahead of the arsine wave and poisons the more active centers.

This inhibiting effect of water is seen in comparing Figs. 3, 4 and 5. Using 50% relative humidity air more arsine is removed at the influent end in ninety-three minutes by dry char than is absorbed in one hundred thirty minutes by char equilibrated to 50% relative humidity. The inhibiting effect is very marked in experiments with air at 70% relative humidity and absorbent equilibrated to this humidity. In the latter case the amount of arsine removed at the influent end still remains greater than for dry char and dry air, as may be seen in Fig. 6. The rate of removal of arsine at lower concentrations as it passes through the bed is evidently less for the equilibrated char as indicated by the appreciable amount at the effluent end.

From the longest runs it appears that the arsine saturation value depends upon the amount of water present in the gas stream and on the charcoal. The highest value obtained for the dry absorbent using dry air was about 270 mg. of arsine per gram of char while values of over 400 mg. were found using dry charcoal and air at 50% relative humidity. The highest value for the absorbent equilibrated to 50% relative humidity and run at this humidity was intermediate at about 315 mg. of arsine per gram of dry charcoal. Since the apparent density of the absorbent was 0.50, the value obtained with dry air corresponds to 135 mg. of arsine per cc. of charcoal. This latter value agrees quite well with values of about 130 mg. per cc. reported by Pierce⁵ from the results of his experiments on the change in weight of the same absorbent on absorption of arsine. Yost,⁶ using a different base charcoal impregnated with copper oxide, found 120 mg. of arsine absorbed per cc. of absorbent by a radioactive method similar to the one used here. The difference in the saturation values with dry absorbent using in one case dry air and in the other air at 50% relative humidity may be correlated with the observation⁷ that the breaktime for arsine using dry absorbent varies with the relative humidity of the air stream, gradually rising to a maximum at about 30% humidity and then falling off to low values at very high humidities.

The rate of approach toward a saturation value in the first layers of a bed varies considerably with conditions and presumably with the gas being absorbed. In the case of the inorganic gas cited by Klotz⁸ (which was done in this Laboratory) the approach toward a saturation value proceeds at a slowly decreasing rate. The behavior of arsine with 70% relative humidity char and air stream (Fig. 5) or with dry char and 50% relative humidity air (Fig. 3) is somewhat similar. With 50% relative humidity char and air stream (Fig. 4) or dry char and dry air (Fig. 2), however, practically the same large amount of arsine is removed

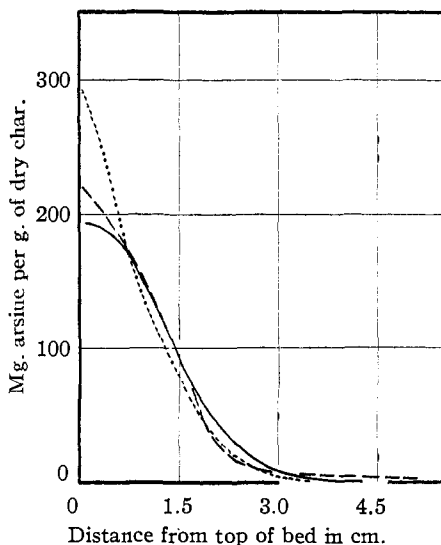


Fig. 6.—Arsinedistribution under different humidity conditions with the same total amount of arsine passed through the char (80 min.). Dotted curve --- is dry char, 50% relative humidity air. Dashed curve -- is char equilibrated to 70% relative humidity, air 70% relative humidity. Full curve — is dry char, dry air.

by the influent end of the bed for exposures of fifty to one hundred thirty minutes and then the amount removed increases very slowly.

The reaction of arsine with oxygen is known to be highly exothermic (arsine is endothermic to the extent of 43.5 kcal.). The effect of the heat liberated can be readily traced by a study of the water distribution curves in Figs. 2-5. As arsine is removed at the influent end, the heat generated results in local desorption of water and an increase further down the bed. There is a distinct minimum in the water curves in most cases at a point corresponding roughly to the steep part of the arsine distribution curve where most of the adsorption was taking place. On continued exposure as the rate of accumulation of arsine at the influent end and the heat effects decrease, the amount of water present increases again. Experiments with and without water jackets on the absorption tube (Fig. 7) show that this heat also results in a displacement of the arsine distribution. As the air stream is warmed by the heat of reaction at the influent end evidently the rate of removal (oxidation of arsine) is increased a short distance down the bed.

Three runs with dry char and dry air at different concentrations of arsine for such lengths of time that the total amount of arsine passed through was the same in each case gave distribution curves similar to those in Fig. 2. The distributions at 4.15 and 7.18 mg. of arsine per liter were identical within experimental error, but at 1.67 mg. per liter the arsine was spread more throughout the bed. These observations can be correlated with the product of the breaktime and

(6) D. M. Yost, NDRC Formal Report, 1941.

(7) Scoville and Wiig, forthcoming publication.

(8) Klotz, *Chem. Rev.*, **39**, 241-268 (1946).

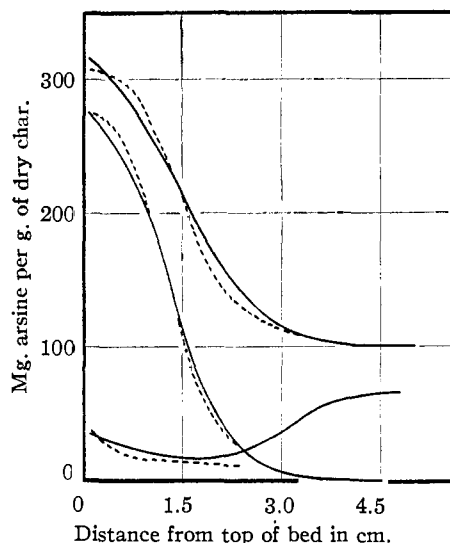


Fig. 7.—Effect on the arsine distribution of water cooling the absorption tube. Full curves — shows water jacket. Dotted curves ... have no water jacket. Top two curves with dry char and dry air have been displaced upward 100 mg. Other four curves are for dry char and 50% relative humidity air. Lowest two curves represent corresponding water distribution.

initial concentration (C_0T) that have been found at these concentrations:

C_0 (mg./liter)	1.67	4.15	7.18
C_0T	2.82	3.28	3.38

It would seem that only the more active catalyst centers are effective at low concentrations, and of course this is also shown by the tailing off of all the distribution curves. It suggests that if this charcoal were exposed to a very low concentration of arsine for some time to use up the more active centers throughout the bed, the breaktime toward a higher concentration would be much less than expected.

No attempt was made in this investigation to make a complete study of the distribution of arsine in various absorbents. One experiment was performed with an activated, zinc chloride-treated, wood charcoal impregnated with cupric oxide. This absorbent had a breaktime of fifty minutes as compared to ninety minutes for the other, using dry char and air at 50% relative humidity. A comparison of the two absorbents run for the same time at the same concentration (Fig. 8) shows that the coconut char apparently had a higher saturation value. The water distributions were similar except that the amount absorbed by the wood char was greater, in agreement with the observation that the latter also absorbed more water, 13% compared to 10%, when equilibrated to 50% relative humidity.

The actual mechanism of arsine removal cannot be assumed on the basis of this investigation, but it does involve the oxidation of arsine mainly to

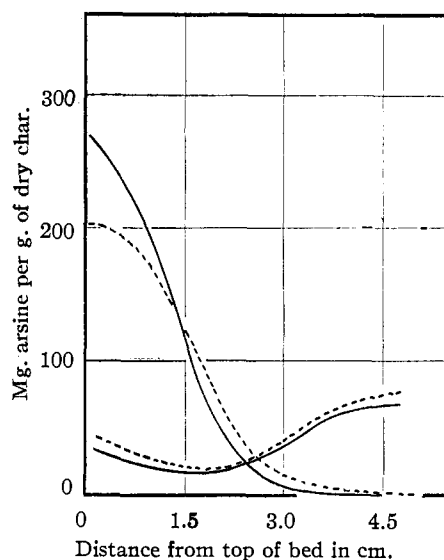


Fig. 8.—Arsine distribution in two different base chars impregnated with copper oxide using dry char and 50% relative humidity air. Full curve — shows coconut shell char. Dotted curve ... is $ZnCl_2$ activated wood char. Two lower curves represent corresponding water distribution.

arsenic trioxide and water with copper oxide as a catalyst. It is necessary to have both charcoal and copper oxide present since copper oxide alone will not remove arsine, and unimpregnated charcoal removes it for only a very short time. Furthermore, it is evident from the highest values obtained for the amount of arsine accumulated in the top layer that arsine is not removed by reacting directly with copper oxide since there is only 58 mg. of copper present per gram of absorbent. It seems quite probable that the first step in the removal is adsorption of arsine followed by the oxidation reaction. The role that small amounts of water play is not at all certain, but it might be mentioned that even in the gas phase arsine and oxygen undergo practically no reaction in the absence of water.⁹ The presence of large amounts of water on the charcoal and covering the copper oxide may decrease the initial adsorption of arsine to such an extent that little arsine is removed until some of this water is driven off by the heat of a small amount of reaction.

Acknowledgment.—The authors wish to express their thanks to the National Defense Research Committee of the OSRD who sponsored this research, to the Edgewood Arsenal Laboratories for their cooperation and to Drs. John H. Raley and Herbert Scoville, Jr., for their assistance with some of the experimental work.

Summary

The distribution of arsine on a charcoal bed has been followed as a function of the humidity of the air stream and the absorbent, concentration of ar-

(9) W. C. Johnson, private communication.

sine, time of exposure and cooling, by the use of radioactive arsenic. The distribution curves show a marked accelerating effect of small amounts of water and an inhibiting effect of larger

amounts. A constant saturation value for arsine at the influent end of the bed is apparently not reached even after long exposure.

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[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

Determination of the Product of the Constants for the Overlapping Dissociation of Weak Acids by Electromotive Force Methods

BY ROGER G. BATES

The exact determination of the thermodynamic dissociation constants of many weak dibasic and tribasic acids is complicated by the "overlapping" of the successive ionization steps. When the ratio of the thermodynamic constants for the primary and secondary steps, K_1/K_2 , is less than 500 to 1000, as it is for most of the common aliphatic dicarboxylic acids¹ and many substituted benzoic acids,² the ionic and molecular concentrations cannot be established with sufficient accuracy by consideration of a single equilibrium. Hence, a determination of the constants often requires laborious arithmetical approximations.^{3,4,5,6}

The constant for the second overlapping step in the dissociation of a dibasic acid can often be determined by the thermodynamic method of Harned and Ehlers⁷ from measurements of cells without liquid junction. The determination is facilitated through choice of buffer solutions on the alkaline side of the midpoint of the neutralization curve for the second group, with a decrease in the correction for the first dissociation equilibrium. A buffer ratio of 5:1 appears not to be excessive.⁸ However, the advantage of a similar procedure is sometimes offset in the evaluation of the first constant by the enhanced correction for hydrogen ion, the concentration of which must be established by successive approximations or, at a sacrifice of accuracy, derived from a pH measurement.⁹

When conditions cannot readily be chosen to isolate each of the individual equilibria in turn, solutions of the acid salt, where overlapping of the two equilibria is at a maximum, can be used to

advantage in establishing the product of the constants for two overlapping equilibria. A thermodynamic method for the determination of this product from measurements of the electromotive force of cells without liquid junction is described. If one dissociation constant of an overlapping pair is known, this procedure usually permits the other to be determined accurately.

Method

The electromotive force, E , of the cell



where M represents an alkali metal and the acid salt is of one of the three types: MHA, MH_2A , or M_2HA , is given by

$$\frac{F(E - E^0)}{2.3026 RT} + \log m_{\text{Cl}} = -\log (f_{\text{H}} f_{\text{Cl}} m_{\text{H}}) \equiv pH \quad (1)$$

For convenience, this experimental quantity will be termed p_wH . In equation (1), f is an activity coefficient on the scale of molality (m), F is the faraday, and the other symbols have their usual significance. The hydrogen-ion concentration, m_{H} , is readily expressed in terms of dissociation constants, molalities, and activity coefficients. The product of the thermodynamic constants for the two overlapping steps is obtained by extrapolation of an appropriate function of E , with the aid of the Debye-Hückel formula,¹⁰ to infinite dilution, where the estimated activity coefficients are exact. To simplify the treatment, the following discussion is restricted to solutions of acid salts with $pH < 8$, in which the concentration of hydroxyl ion can be ignored.

Case I. Acid Salt of a Dibasic Acid, $K_1/K_2 < 500$.—The molecular and ionic species participating in the equilibria are H^+ , H_2A , HA^- , and A^{2-} . The concentration of hydrogen ion, m_{H} , in solutions of the acid salt is given by

$$m_{\text{H}}^2 = \frac{K_1 K_2 m_{\text{H}_2\text{A}}}{m_{\text{A}}} \times \frac{f_{\text{H}_2\text{A}}}{f_{\text{H}}^2 f_{\text{A}}} \quad (2)$$

Inasmuch as

$$m_{\text{A}} = m_{\text{H}_2\text{A}} + m_{\text{H}} \quad (3)$$

we obtain, by combination of equations (1) and (2)

$$(10) \text{ P. Debye and E. Hückel, } \textit{Physik. Z.}, \textbf{24}, 185 (1923).$$

(1) R. Gane and C. K. Ingold, *J. Chem. Soc.*, 2153 (1931).

(2) W. R. Maxwell and J. R. Partington, *Trans. Faraday Soc.*, **33**, 670 (1937).

(3) F. Auerbach and E. Smolczyk, *Z. physik. Chem.*, **110**, 65 (1924); H. T. S. Britton, *J. Chem. Soc.*, 1896 (1925); N. Bjerrum and A. Unmack, *Kgl. Danske Videnskab. Selskab., Math.-fys. Medd.*, **9**, No. 1 (1929).

(4) H. S. Simms, *THIS JOURNAL*, **48**, 1239 (1926).

(5) W. J. Hamer and S. F. Acree, *J. Research Natl. Bur. Standards*, **35**, 381 (1945).

(6) W. J. Hamer, G. D. Pinching and S. F. Acree, *ibid.*, **35**, 539 (1945).

(7) H. S. Harned and R. W. Ehlers, *THIS JOURNAL*, **54**, 1350 (1932).

(8) G. D. Pinching and R. G. Bates, *J. Research Natl. Bur. Standards*, in press (data for oxalic acid).

(9) The simultaneous evaluation of overlapping K_1 and K_2 from pH -titration data obtained from cells with liquid junction has been described by J. C. Speakman, *J. Chem. Soc.*, 855 (1940).