

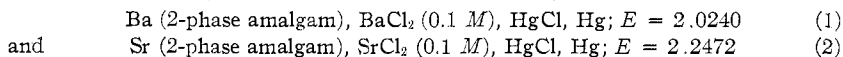
surface of contact between the amalgam and the solution, are recorded in Table II. All measurements were made at 25°.

TABLE II

ELECTROMOTIVE FORCE OF TWO-PHASE AMALGAM AGAINST CALOMEL IN 0.1 *M* CHLORIDE

Cell	1	2	3	4	5	6	7	Av.
Barium	2.0240	2.0241	2.0236	2.0240	2.0240	2.0241	2.0238	2.0240
Strontium	2.2474	2.2471	2.2472	2.2472

Taking the average values from Table II we may write,



It is of interest to note that the magnitude of these electromotive forces with respect to each other is in agreement with the idea that the bond between the very electropositive barium and the mercury in their compound is a much firmer one than that between the less electropositive strontium and mercury and is thus further evidence of the salt-like character of the mercurides.

Summary

Design of an electrode vessel for use with two-phase alkali and alkaline earth amalgams is discussed.

Details of construction and operation of three such vessels are given.

Measurements of the potential of the two-phase barium and strontium amalgams against calomel are recorded.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

THE ADSORPTION OF ARSENIOS ACID BY HYDROUS ALUMINUM OXIDE

BY JOHN H. YOE

RECEIVED JUNE 2, 1924

PUBLISHED NOVEMBER 5, 1924

Introduction

According to Lockemann and Paucke¹ arsenic, in the form of arsenite or arsenate, is completely removed from a dilute solution by aluminum hydroxide at the temperature of the water-bath (80–90°), but not at room temperature. The reverse, however, was found to be true in the case of ferric hydroxide. The authors explain this difference in adsorption as being due to the alumina precipitating incompletely in the cold but completely and in a flocculent condition from a hot solution, and hence offering a larger surface. The ferric hydroxide precipitates even from an ice-cold solution in a flocculent condition, and hence offers the combined ad-

¹ Lockemann and Paucke, *Z. Kolloidchem.*, **8**, 273 (1911).

vantages of larger surface and better adsorption due to the colder solution. This explanation may be correct, but it should be pointed out that Lockemann and Paucke used alums for their stock solutions of aluminum and iron and hence there was always present a relatively high concentration of electrolytes. Had the stock solutions been made from the nitrates or chlorides the effect of electrolytes on the character of the precipitates would have been much less. For example, a dilute solution of aluminum nitrate (corresponding to 0.5 g. of aluminum oxide per liter) at 50°, or above, will give a water-clear sol when 0.1 *N* ammonium hydroxide is added in the calculated amount, whereas a solution of the same aluminum content but made from alum gives a flocculent precipitate under similar conditions. Lockemann and Paucke were especially interested in *completely* removing arsenic from solutions and they varied the amounts of both adsorbent and arsenic, as well as the temperature. More recently Lockemann and Lucius² have studied the total adsorption of arsenic by ferric hydroxide and found that the amount adsorbed decreases with rising temperature.

The adsorption experiments of Lockemann and his co-workers were made with iron and aluminum hydroxides precipitated in the presence of arsenious acid at various temperatures and each adsorption was measured at the temperature at which the precipitation was made. Since the adsorptive power is probably altered both by the temperature at which adsorption takes place and by the temperature at which the adsorbent is formed, as well as other factors, it seemed to us desirable to study the adsorption under a definite set of conditions, namely: (a) temperature at which the hydrous oxide is formed, (b) temperature at which adsorption takes place, (c) concentration of the solution of the aluminum salt and of the ammonium hydroxide, (d) kind of aluminum salt, (e) rate of stirring and type of stirrer, (f) rate of formation of the hydrous oxide, (g) order of mixing the solutions, and (h) type of mixing device in the adsorption thermostat.

Experimental Conditions

All pipets, burets and flasks were precision instruments, and the usual temperature corrections were made.

The hydrous aluminum oxide was formed in a Pyrex beaker which was held in a water-bath at 0.0 ± 0.5°, 25 ± 0.1°, 50 ± 0.5°, 75 ± 0.5° and 99.5–100°, respectively, unless otherwise stated. The mixtures were stirred at the rate of 500 revolutions per minute, care being taken to adjust the stirrer to the same position each run.

All adsorptions were carried out in a thermostat containing a rotating wheel to which were attached ground glass-stoppered bottles filled with the adsorption mixtures. The temperature was maintained at 25 ± 0.05°. The thermometer was checked against a thermometer recently calibrated by the Bureau of Standards.

² Lockemann and Lucius, *Z. physik. Chem.*, **83**, 735 (1913).

Solutions.—The hydrous aluminum oxide was prepared by mixing dilute solutions of aluminum nitrate and ammonium hydroxide in equivalent quantities. The aluminum nitrate solution contained 41.3 g. of crystallized aluminum nitrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, per liter. The content of aluminum oxide equivalent was 0.080 g. per 15 cc., determined gravimetrically by adding ammonium hydroxide in slight excess (in the presence of ammonium nitrate), coagulating by boiling, filtering and igniting the precipitate to constant weight. The ammonium hydroxide was 0.100 *N*.

The arsenious acid solutions were made up directly from 100% pure arsenious oxide used as an iodimetric standard. The iodine solutions were made from resublimed iodine and were standardized against weighed portions of pure arsenious oxide, using starch suspension as an indicator.

Procedure.—Unless otherwise stated, the following procedure was observed in the formation of the hydrous aluminum oxide. Fifteen cc. of the standard aluminum nitrate solution and 145 cc. of distilled water in a Pyrex beaker, fitted with a stirrer regulated to 500 r. p. m., were brought to the desired temperature. Then 50.6 cc. of 0.1 *N* ammonium hydroxide was added, drop by drop, from a buret, the total time for the delivery being 15 minutes. The exact amount of the ammonium hydroxide required to precipitate the aluminum (0.080 g. of oxide) had been previously determined. At the end of the precipitation, the mixture was brought to room temperature (in case the precipitation was at 0°, 50°, 75° or 100°), transferred to a ground glass-stoppered bottle of about 270cc. capacity, diluted with sufficient water to make the final volume of the mixture exactly 265 cc., and a measured amount of the standard arsenious acid solution added. The bottles were tightly stoppered and placed at once in the thermostat at 25°. They were continuously and uniformly rotated on a motor-driven wheel. The time at which the arsenious acid solution was added was taken as the start. Before a sample was withdrawn for analysis, the bottles were allowed to stand (for 15 minutes) in the thermostat in an upright position to allow the hydrous aluminum oxide to settle. A 50cc. portion of the clear supernatant liquid was then withdrawn (care being taken not to disturb the precipitate), diluted with about 50 cc. of water and titrated against standard iodine solution, using starch suspension as an indicator.

Experimental Data

Rate of Adsorption.—A series of adsorptions was carried out at 25° using hydrous oxide formed at the same temperature, and the adsorption period was varied from a few minutes to several hundred hours. The results are recorded graphically in Fig. 1, where the millimoles of arsenious oxide adsorbed by a given amount of hydrous aluminum oxide (corresponding to 0.080 g. of aluminum oxide) have been plotted as ordinates, and the total times in hours as abscissas.

Adsorption Isotherms.—Several adsorption isotherms were determined for different adsorption periods and at various concentrations of

arsenious acid. The data are given in Fig. 2. The curves were obtained by plotting as ordinates the millimoles of arsenious oxide adsorbed by a given amount of hydrous aluminum oxide, and as abscissas the millimoles of arsenious oxide unadsorbed. The corresponding logarithmic plots are given in Fig. 3.

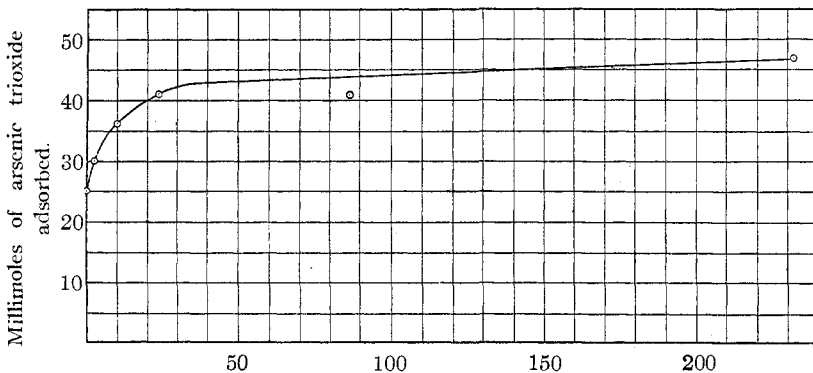


Fig. 1.—Rate of adsorption of arsenious acid on hydrous aluminum oxide at 25°.

Adsorption of Arsenious Acid by Hydrous Aluminum Oxide Precipitated at Various Temperatures.—In order to determine the effect of the temperature at which the hydrous alumina is formed upon its adsorptive power, a series of runs was made using alumina precipitated at

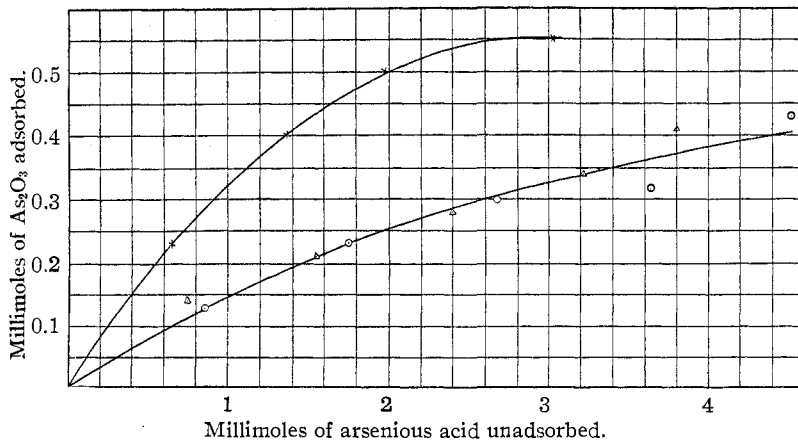


Fig. 2.—Adsorption isotherms of arsenious acid on hydrous aluminum oxide at 25°.

0°, 25°, 50°, 75° and 100°, respectively. All adsorptions were carried out at 25°. The results are shown graphically in Fig. 4, where millimoles of arsenic trioxide adsorbed by a given amount of hydrous alumina (corresponding to 0.080 g. of aluminum oxide) are plotted as ordinates, and the temperatures at which the alumina was formed as abscissas.

It was observed in the above experiment that the hydrous alumina did not precipitate when formed at 50° and above, but remained as a water-clear sol. Upon adding the arsenious acid coagulation took place at once.

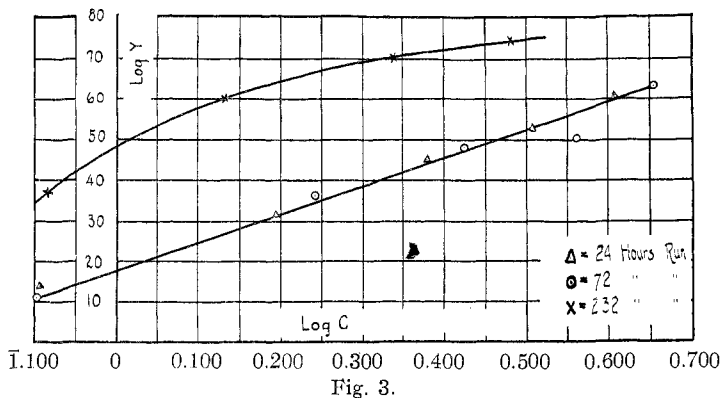


Fig. 3.

It is probable that even at 25° and at 0° the alumina is partly in the colloidal state. That agglomeration takes place upon the addition of the acid is easily seen. The above data show that adsorption decreases, the higher the temperature of formation of hydrous alumina. Unfortunately,

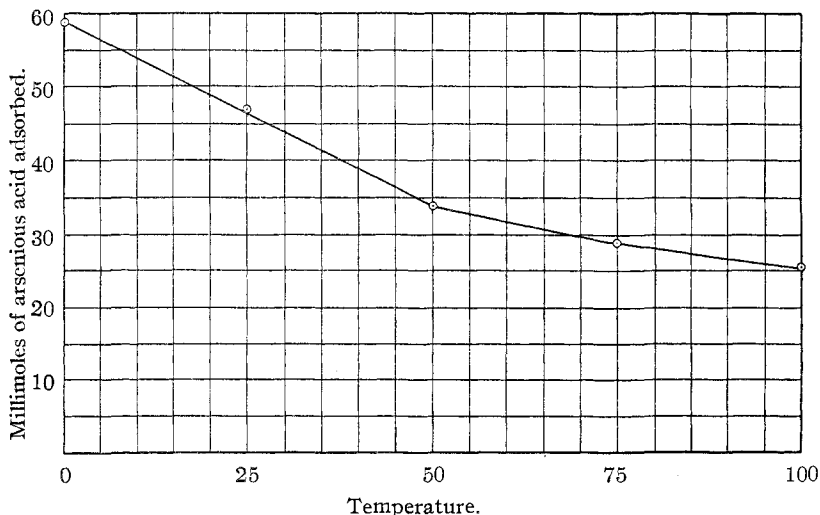


Fig. 4.—Adsorption at 25° of arsenious acid on hydrous aluminum oxide formed at various temperatures.

however, the hydrous oxide was in the precipitated state at the start of some of the experiments, in the colloidal state in others, and in both states in still others. Under these conditions the results are not strictly compar-

able. In general they agree well with the observations of Mecklenburg³ with hydrous stannic oxide.

Discussion of Experimental Data

Rate of Adsorption.—As seen in Fig. 1, the rate of adsorption is quite rapid, about 50% of the total adsorption taking place within the first five minutes. At the end of 24 hours 0.41 millimole of arsenious oxide had been adsorbed and no increase in adsorption was detected at the end of 86.5 hours. However, the adsorption at the end of 232 hours had increased to 0.47 millimole of arsenious oxide. Several explanations of this slow increase in adsorption are possible. It may be that it is due to (1) a slow diffusion of the solution into the pores of the hydrous oxide with further adsorption on the surface of the latter; (2) to a chemical reaction (neutralization) following adsorption; (3) to a change in the physical condition of the adsorbent and, therefore, its specific surface; for example, some of it may become peptized and thereby give an increase in the surface; or (4) any two or more of these processes may account for the slow increase in adsorption. It is possible that an equilibrium is reached in 24 hours and maintained for 60 hours or longer, and that the increase in adsorption at the end of 232 hours is due to some secondary cause; or, the equilibrium may be only apparent, the 86.5 hour point being a little too low due to experimental error. However, adsorption from a slightly more concentrated arsenious acid solution gave an adsorption value of 0.43 millimole of arsenious acid at the end of 72 hours, a value in good agreement with the 0.41 millimole found at the 86.5 hour point for the weaker solution.

Adsorption Isotherms.—Since the rate curve had shown that between 24 and 86 hours adsorption is constant or at least very nearly so, two concentration functions or so-called "adsorption isotherms" were measured for 24- and 72-hour runs, respectively. That the adsorption equation holds excellently over this wide range is clearly shown by the lower logarithmic curve in Fig. 3. The 24- and 72-hour points have to be represented by a single curve, although the arsenious acid solutions were a little more concentrated in the 72-hour run. This indicates that equilibrium is reached in about 24 hours, as is also shown in the rate curve (Fig. 1). The points obtained in the 232-hour run fall on a smooth curve but do not give a straight line for the logarithmic plot. This would seem to indicate that here we are not dealing with a simple case of adsorption, a result in agreement with the rate curve (Fig. 1).

Adsorption by Hydrous Aluminum Oxide Precipitated at Various Temperatures.—The adsorptive power of the alumina decreases, the higher the temperature at which it is precipitated. The effect is much

³ Mecklenburg, *Z. anorg. Chem.*, **74**, 215 (1912). Compare Weiser, *J. Phys. Chem.*, **26**, 654 (1922).

greater over the range from 0° to 50° than from 50° to 100° . Each of the points on the curve in Fig. 4 represents an average value of two or three measurements which were in close agreement. The 0° , 25° and 50° points lie on a straight line. Beyond the 50° point the curve is much less steep and is slightly concave towards the X-axis. The marked effect of boiling on the adsorptive power of the hydrous oxide is shown by the fact that precipitating at 100° and then boiling under a reflux condenser for 24 hours cut down the adsorptive power more than 50% of that precipitated at 100° but not boiled. Adsorption by the hydrous oxide precipitated at 0° is about 2.5 times greater than that formed at 100° and about 5.5 times greater than the hydrous oxide precipitated at 100° and refluxed for 24 hours. The effect of temperature of formation, therefore, is to decrease the adsorptive power of the hydrous oxide. The explanation may be that with increasing temperature at which precipitation is carried out the alumina is less flocculent and more compact and, hence, has a smaller surface when formed at higher temperatures. Boiling would give a still more compact precipitate. Moreover, since the solubility of the smaller particles is greater than that of the larger ones, the latter will grow at the expense of the former and the total surface of the adsorbent be correspondingly decreased. It is also possible that the porosity of the hydrous oxide decreases with increase in temperature.

Mechanism of the Adsorption Process.—Reychler⁴ has made a critical examination of the experimental data of Biltz⁵ on the adsorption of arsenious acid by ferric hydroxide and believes that the arsenious hydroxide is removed by compound formation and not by *adsorption* as claimed by Biltz. He says that one, two or three hydrogens are replaced by iron, three hydrogens being replaced when ferric hydroxide is present in large excess. Biltz⁶ criticizes Reychler's "chemical theory" on the ground that the mass law cannot be applied to heterogeneous systems. Moreover, the "chemical theory" predicts a large temperature coefficient for the adsorption. Actually the temperature coefficient is very small. With hydrous aluminum oxide it seems that the arsenious acid is removed by adsorption and not by compound formation as suggested by Reychler in the case of hydrous ferric oxide. That the adsorption can be expressed by the so-called adsorption-isotherm equation is seen in Figs. 2 and 3. However, after several hundred hours in contact with the acid it seems likely that some secondary process sets in. The data obtained for a 232-hour run cannot be represented by the simple adsorption isotherm (see Figs. 2 and 3).

I desire to express my appreciation to Dr. Harry B. Weiser who kindly reviewed this paper and made several helpful suggestions.

⁴ Reychler, *J. chim. phys.*, **7**, 362 (1909).

⁵ Biltz, *Ber.*, **37**, 3138 (1904).

⁶ Biltz, *J. chim. phys.*, **7**, 570 (1909).

Summary

1. The rate of adsorption at 25° of arsenious acid by hydrous aluminum oxide is quite rapid, 50% or more of the adsorption taking place within the first few minutes. An apparent equilibrium was reached in about 24 hours but at the end of 232 hours further adsorption had taken place. Several causes have been suggested to account for this slow continued adsorption.

2. Concentration functions at 25°, and for 24- and 72-hour adsorption periods gave results which may be expressed by the simple adsorption-isotherm equation. In the case of a 232-hour run the ideal isotherm is not followed.

3. Adsorption at 25° by hydrous aluminum oxide precipitated at 0° is about 2.5 times greater than that formed at 100° and about 5.5 times greater than that precipitated at 100°, and boiled under a reflux condenser for 24 hours. Causes of this difference in adsorptive power have been suggested and the mechanism of the adsorption process has been discussed.

UNIVERSITY, VIRGINIA

[CONTRIBUTION FROM THE COBB-CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

THE POSITION OF EQUILIBRIUM IN THE ALCOHOL-ETHER REACTION AT 130° AND 275°

BY ROBERT N. PEASE AND CHI CHAO YUNG

RECEIVED JUNE 4, 1924

PUBLISHED NOVEMBER 5, 1924

From the kinetic measurements of the catalytic dehydration of pure ethyl alcohol¹ at 275° and 300°, it was shown that the total percentage conversion of alcohol reaches a constant value which is unchanged as the time of run is increased. This, we concluded, was due to the fact that the reaction, $2C_2H_5OH \rightleftharpoons (C_2H_5)_2O + H_2O$, approaches a state of equilibrium at about 60-70% conversion. Accordingly, two series of measurements were made with the hope that this equilibrium point might be determined quantitatively, the first using alumina at 275° and the second using a mixture of concd. sulfuric acid and alcohol at 130° as the catalytic agent.

As a preliminary step, we definitely established the reversibility of the reaction by carrying out a run in which 154.5 cc. of ether and 24.2 cc. of water were introduced from separate burets. This mixture was passed over the alumina catalyst at 275°. The product was then fractionated and the following results were obtained. About 132.4 cc. distilled between 35° and 70°, 6.1 cc. between 70° and 78°, 4.2 cc. at 78°, and 9.5 cc. between 78° and 85°. The portion that distilled at 78° was undoubtedly mainly alcohol. A similar run was carried out later in the course of the

¹ THIS JOURNAL, 46, 390 (1924).