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THE ADSORPTION OF ARSENIOUS ACID BY HYDROUS FERRIC OXIDE

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Almost a century ago Bunsen and Berthold[1] observed that freshly precipitated ferric oxide had the power of removing arsenious acid from solution and considered the action as due to the formation of a basic ferric arsenite. A similar view was later held by Reychler.[2] On the other hand, Biltz[3] and Boswell and Dickson[4] considered the action as due to adsorption and expressed their results approximately by the adsorption equation $X = kC^{1/n}$, where X is concentration of arsenious oxide on the ferric oxide, C is concentration of arsenious oxide at equilibrium, and k and n are constants. Lockemann[5] and his co-workers have studied the conditions under which arsenious acid is *completely* removed from solution and they varied the amounts of both adsorbent and arsenic, as well as the temperature. Moreover, each adsorption was measured at the temperature at which the adsorbent was formed.

Since the adsorption power is altered by various factors such as (1) temperature at which the hydrous oxide is formed, (2) the temperature at which adsorption takes place, (3) rate of formation of the adsorbent, etc., it seemed desirable to study the adsorption under a definite set of conditions. In general, the experimental conditions and procedure were the same as those employed in a similar investigation of the adsorption of arsenious acid by hydrous aluminum oxide.[6]

Experimental Part

Rate of Adsorption.—A series of adsorptions was carried out at 25° using hydrous ferric oxide formed at the same temperature, and the adsorption period was varied from a few minutes to forty-two hours. The results are recorded graphically in Fig. 1, where the millimoles of arsenious oxide adsorbed by a given amount of hydrous ferric oxide (corresponding to 0.250 g. of Fe_2O_3) have been plotted as ordinates, and the total times in hours as abscissas.

Adsorption of Arsenious Acid by Hydrous Ferric Oxide Formed at Various Tem-

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[1] Bunsen and Berthold, "Das Eisenoxydhydrat, ein Gegengift der arsenigen Säure," Göttingen, **1834**; *cf.* Guibourt, *Arch. Pharm.*, [2] **23,** 69 (1840).

[2] Reychler, *J. chim. phys.*, **7,** 362 (1909); **8,** 10 (1910); *cf.* Oryng, *Kolloid-Z.*, **22,** 149 (1918).

[3] Biltz, *Ber.*, **37,** 3138 (1904); *J. chim. phys.*, **7,** 570 (1909); *cf. Kolloid-Z.*, **26,** 179 (1920).

[4] Boswell and Dickson, THIS JOURNAL, **40,** 1793 (1918).

[5] Lockemann and Paucke, *Kolloid-Z.*, **8,** 273 (1911); Lockemann and Lucius, *Z. physik. Chem.*, **83,** 735 (1913).

[6] Yoe, THIS JOURNAL, **46,** 2390 (1924).

peratures.—Two series of measurements were made using oxides precipitated at 0, 25, 50, 75 and 100°, respectively. The concentration of the arsenious acid in each series varied from about 0.9 to 4.5 millimoles of As_2O_3 per 250 cc. All adsorptions were carried out at 25°. One series was run at an adsorption period of forty-two hours and another at a thirty-day period. The rate of adsorption previously determined had shown that an approximate equilibrium point is reached at the end of twelve hours and that adsorption at the end of forty-two hours was identical (within the limits of accuracy) with the twelve-hour period. The results are shown graphically in Figs. 2 and 3, where millimoles of arsenic trioxide adsorbed by a given amount of hydrous ferric oxide (corresponding to 0.250 g. of Fe_2O_3) are plotted as ordinates, and the temperatures at which the oxides were formed as abscissas.

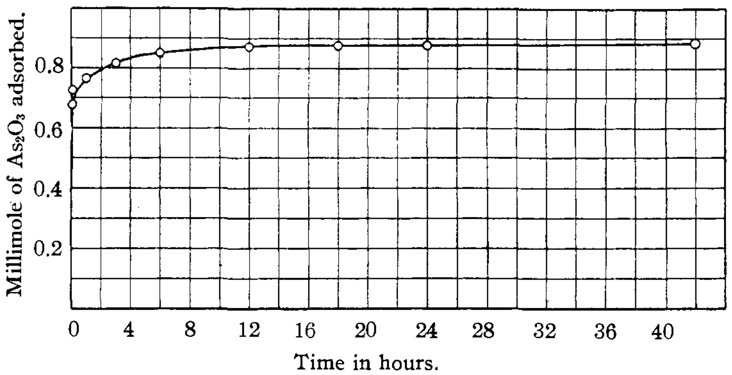

Fig. 1.—Rate of adsorption of arsenious acid by hydrous ferric oxide at 25°.

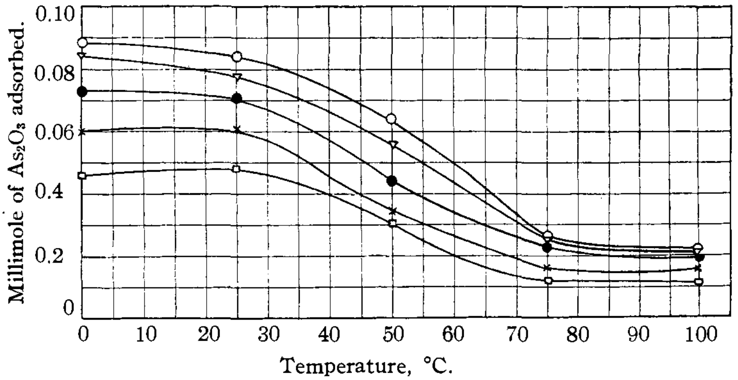

Fig. 2.—Adsorption of arsenious acid by hydrous ferric oxide formed at various temperatures (adsorption time, 42 hours).

Adsorption Isotherms.—Adsorption isotherms were obtained for hydrous ferric oxides formed at temperatures of 0, 25, 50, 75 and 100°, respectively, and for the oxide formed at 100° and boiled for twenty-four hours under a reflux condenser. One series of isotherms was run at an adsorption period of forty-two hours and another at a thirty-day period. All measurements were made at 25°. The data are given in Figs. 4 and 5, where the ordinates show the millimoles of arsenious oxide adsorbed by a given amount of hydrous ferric oxide (corresponding to 0.250 g. of Fe_2O_3), and the abscissas the millimoles of arsenious oxide unadsorbed. The corresponding logarithmic plots are given in Figs. 6 and 7.

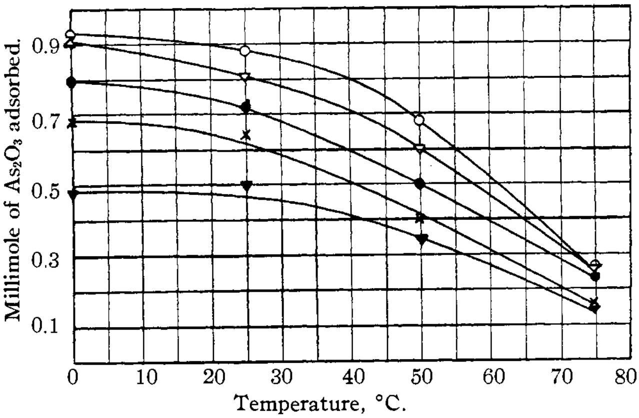

Fig. 3.—Adsorption of arsenious acid by hydrous ferric oxide formed at various temperatures (adsorption time, 30 days).

Discussion of Experimental Data

Rate of Adsorption.—As seen in Fig. 1, the rate of adsorption is quite rapid, about 75% of the total adsorption taking place within the first five minutes. At the end of twelve hours 0.871 millimole of arsenious oxide had been adsorbed and 0.885 millimole at the end of forty-two hours.

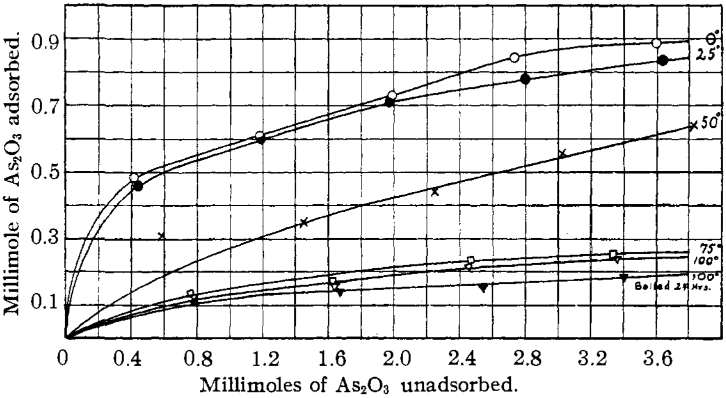

Fig. 4.—Adsorption isotherms of arsenious acid on hydrous ferric oxide at 25° (adsorption time, 42 hours).

The run was discontinued at the end of forty-two hours since it was evident that at least an approximate equilibrium had been reached. That there is a very slight continued adsorption was observed later when determining the adsorption isotherms. For instance, one run with the hydrous ferric oxide formed at 25° gave an adsorption value of 0.84 millimole at the end of forty-two hours and 0.88 millimole at the end of thirty days, an increase of only 0.04 millimole. This slight increase in adsorption of the thirty-day period over the forty-two-hour period was shown in all cases, regardless of the temperature (0 to 100°) at which the hydrous ferric oxide was formed and the concentration (0.9 to 4.5 millimoles per 250 cc.)

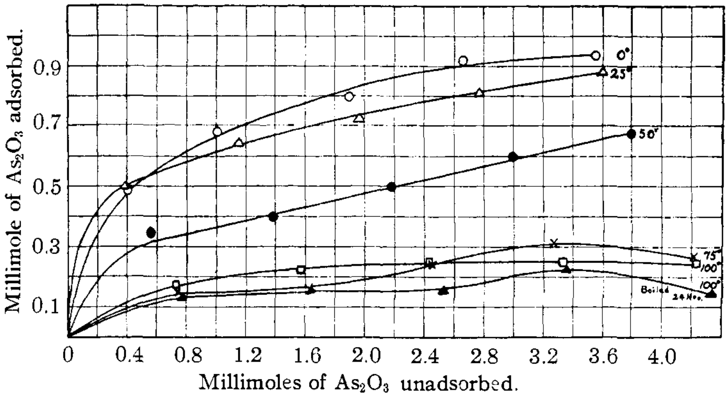

Fig. 5.—Adsorption isotherms of arsenious acid on hydrous ferric oxide at 25° (adsorption time, 30 days).

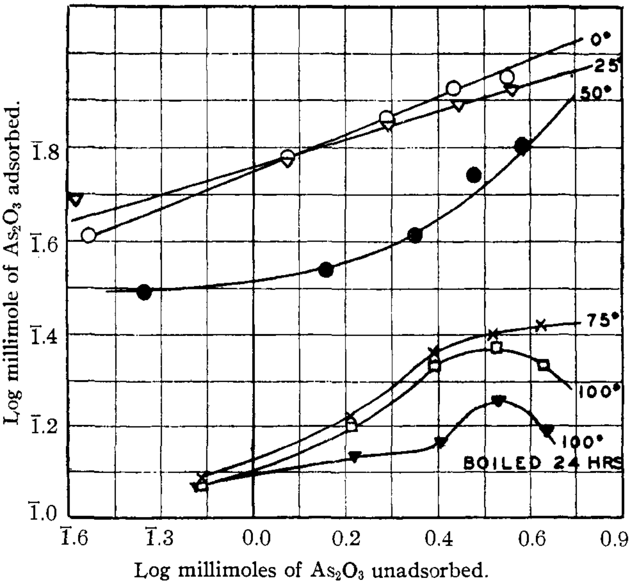

Fig. 6.—Logarithmic plot of curves in Fig. 4.

of the arsenious acid. The increase in adsorption varied from about 0.01 to 0.08 millimole, but was usually about 0.04 millimole. Hydrous aluminum oxide shows a similar slow increase in adsorption. Several explanations have been suggested.[6]

Adsorption of Arsenious Acid by Hydrous Ferric Oxide Formed at Various Temperatures.—The adsorption power of the hydrous ferric oxide decreases, the higher the temperature at which it is formed. The effect is much greater over the range from 0 to 75° than from 75 to 100°. The marked effect of boiling on the adsorption power of the hydrous oxide is shown by the fact that precipitating at 100° and then boiling under a reflux condenser for twenty-four hours cut down the adsorption power more than 30% of that precipitated at 100° but not boiled. Adsorption by the hydrous oxide precipitated at 0° is about 4.2 times greater than by that formed at 100° and about 5.8 times greater than that of the hydrous oxide precipitated at 100° and refluxed for twenty-four hours. The effect of raising the temperature of formation, therefore, is to decrease the adsorption power of the hydrous oxide, which is in agreement with results previously obtained with hydrous aluminum oxide.[6]

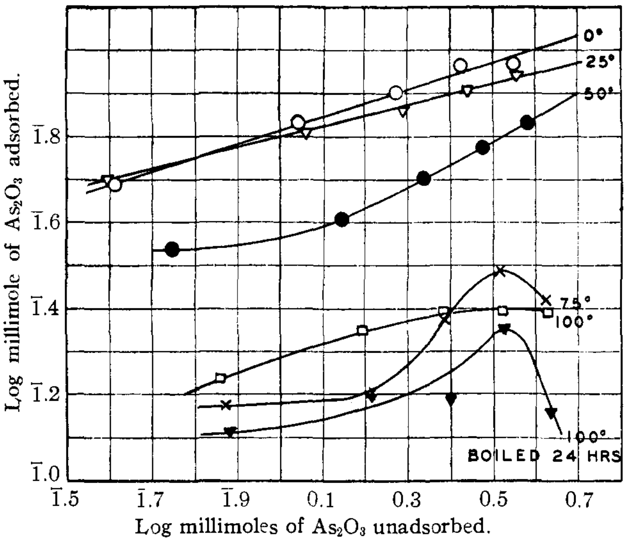

Fig. 7.—Logarithmic plot of curves in Fig. 5.

Adsorption Isotherms.—Since the rate curve had shown that between twelve and forty-two hours adsorption is constant or at least very nearly so, a concentration function or adsorption isotherm was obtained for a forty-two-hour period for each lot of hydrous ferric oxide formed at the various temperatures ranging from 0 to 100°. Corresponding isotherms were also measured for a thirty-day period. As noted in Figs. 4 and 5, the points fall on smooth curves, each curve lying below the preceding one—the one for 0° formation being the highest and that for precipitation at 100° and boiling for twenty-four hours being the lowest and almost flat. When logarithmic plots are made (see Figs. 6 and 7) some striking results are noted. The hydrous oxides formed at 0 and at 25° give straight lines, and hence the adsorption may be expressed by the adsorption equation $X = kC^{1/n}$. The curves for the hydrous oxide formed at 50° deviate from a straight line and are convex to the x-axis, while those for the oxides formed at higher temperatures are concave to the x-axis. It is obvious that the phenomenon of adsorption by these oxides cannot be expressed by the simple adsorption equation. The data also show considerable deviation from Langmuir's equation.

Summary

1. The rate of adsorption at 25° of arsenious acid by hydrous ferric oxide is very rapid, 75% or more of the adsorption taking place within the first few minutes. An apparent or approximate equilibrium was reached in about twelve hours but at the end of thirty days a very slight further adsorption had taken place.

2. Hydrous ferric oxides have been formed under a definite set of conditions and at 0, 25, 50, 75 and 100°, respectively, and at 100° and boiled gently under a reflux condenser for twenty-four hours. Adsorption isotherms at 25° have been obtained for each of these oxides with arsenious acid. Those formed at 0 and at 25° follow the simple adsorption equation, $X = kC^{1/n}$. The hydrous oxides formed at higher temperatures show considerable deviation from the simple adsorption equation, as well as from Langmuir's equation.

3. The adsorption power of hydrous ferric oxide for arsenious acid decreases the higher the temperature at which it is formed. Gentle boiling under a reflux condenser for twenty-four hours greatly reduces the adsorption capacity. These results are in good agreement with similar ones obtained with hydrous aluminum oxide.

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