which gas chemisorbed at −78° could be released from the surface into a vacuum they found desorption occurring in two steps sharply separated from one another. Some 14% of the gas readily was liberated below 0° while the remainder required temperatures above 50° for release into a vacuum. The authors deduce from their data a marked distribution of centers of activity over their total surface. Evidence already available to us indicates that such data with metallic nickel catalysts are to be obtained in even more definite degree with copper catalysts. Dr. P. H. Emmett has called our attention to the fact that the earlier work of Emmett and Brunauer[15] on the chemisorption of hydrogen on iron synthetic ammonia catalysts also reveals the same phenomenon of increased adsorption on decreasing the temperature which we have noted above as characterizing the chemisorption of zinc oxide and revealing the heterogeneity of the catalyst surface.

The data obtained in the present research are in best agreement with the earlier data by E. A. Smith and Taylor[16] on the interaction of deuterium and hydrogen on zinc oxide catalysts. In that research it was shown that the catalyst operated in the range 143–491°K. with activation energies which increased from 0.6 kcal. in the temperature range 143–178°K. through a region 195–373°K. with an activation energy of 7 kcal. to a high temperature region with an activation energy of 12 kcal. In this latter there was a temperature range 405–430°K. where the apparent activation energy was zero. This abnormality was explained on the basis of a decrease in the active surface covered with increase of temperature. The exchange reaction was shown to occur from 50 to 800 times faster than the net rate of adsorption as measured by Strother at atmospheric pressure. The adsorption process effective in the exchange reaction was identified with the fast initial adsorption of gas observed by Strother with zinc oxide and, in the case of chromium oxide, by Burwell and Taylor already cited. The argument developed by E. A. Smith and Taylor was dependent on the postulate that the slow step in the exchange reaction was the desorption of chemisorbed hydrogen deuteride, HD, from the surface. This postulate has been challenged by others[17,18] as a result of parallel studies of the same exchange on other surfaces. Hence, the argument for heterogeneity of the zinc oxide surface thus advanced by E. A. Smith and Taylor could always be discounted. The present research which reveals this same heterogeneity by methods entirely free from any postulate as to reaction mechanism fortifies the earlier conclusions and, at the same time, exhibits an experimental technique whereby the heterogeneity of a catalyst surface can be rigorously revealed.

## Summary

A new experimental technique for determining isobars of adsorption on zinc oxide at various temperatures has been developed.

The technique reveals desorption of chemisorbed hydrogen from a surface on raising the temperature through certain temperature ranges at constant pressure; the desorption is then followed by further chemisorption of the gas.

Chemisorption of hydrogen, in addition to van der Waals adsorption, is indicated at a temperature of 80°K. on the zinc oxide preparations studied.

The data indicate a marked heterogeneity of the surface in the chemisorption of hydrogen.

Analysis of earlier literature reveals the generality of the phenomenon; its consequences in the determination of activation energies of chemisorption and its significance in catalysis at surfaces has been emphasized.

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[15] Ref. 5, see Tables IV, X and XIII.

[16] E. A. Smith and Taylor, THIS JOURNAL, **60**, 362 (1938).

[17] Eley and Rideal, *Nature*, **146**, 401 (1940); Eley, *Proc. Roy. Soc.* (London), **A178**, 452 (1941).

[18] Farkas and Farkas, THIS JOURNAL, **64**, 1594 (1942).

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[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY, LEHIGH UNIVERSITY]

# Active Magnesia. II. Adsorption of Fluoride from Aqueous Solution

BY ALBERT C. ZETTLEMOYER, EARL A. ZETTLEMOYER[1] AND WILLIAM C. WALKER

Observations have shown that the fluoride content of drinking water is a very important factor in dental health. Small amounts cause the teeth to be exceptionally healthy, but in high concentrations fluoride causes severe mottling. In several areas of the United States the fluoride content of drinking water exceeds the limit of safety. For this reason many substances have been studied as adsorbents for the reduction of fluoride concentration of drinking water. As a result of these studies Elvove[1a] has recommended active magnesia as the least expensive and most efficient adsorbent for the purpose. This author has reported a study of fluoride adsorption by active magnesia, but only for one grade at concentrations below 0.5 millimole per liter (10 p. p. m.).

The present paper is the second in a series[2] describing the properties of active magnesia. It is devoted to the presentation of fluoride adsorp-

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[1] Earl A. Zettlemoyer was a Roy C. Horner Fellow; present address: Budd Manufacturing Company, Philadelphia, Pennsylvania.

[1a] E. Elvove, *Public Health Reports*, **52**, 1308 (1937).

[2] Zettlemoyer and Walker, *Ind. Eng. Chem.*, **39**, 69 (1947).

tion isotherms to initial concentrations of 10 mmole./liter (200 p. p. m.) for six varieties of active magnesia and for one inactive variety. The rates of hydration and of fluoride adsorption were also measured, and other tests were made to elucidate the mechanism of fluoride adsorption on active magnesia.

## Experimental

**Materials.**—The magnesia samples were donated by the Westvaco Chlorine Products Corporation. The samples are referred to here by their Westvaco grade numbers 2641, 2642, 2652, $2661^{1}/_{2}$, 2665 and XP1. The analyses and methods of preparation have been described in the first paper of this series.[2] Sample XP1 is similar to magnesia XP of that paper except that it has a lower surface area. Both of these samples were prepared by calcination of magnesium carbonate trihydrate produced by the carbonation of magnesium hydroxide sludge precipitated from sea-water bitterns as previously described.[2]

**Procedures.**—For the determination of the adsorption isotherms, 25-mg. samples of magnesias were rotated with 100-ml. portions of sodium fluoride solutions for two hundred hours. Except for Magnesias $2661^{1}/_{2}$ and XP1, no appreciable change in fluoride concentration occurred after seventy-two hours. The initial concentrations ranged from 0.5 to 10 mmole./liter, and the samples were rotated at room temperature (23.5 ± 1.0°) at 50 r. p. m. in wax-lined 450-ml. bottles. Preliminary experiments indicated no change in fluoride concentration when solutions were rotated in the waxed bottles. The equilibrated solutions were centrifuged to provide clear samples for analysis. Filtration had to be avoided because of serious errors due to negative adsorption by the paper.

Adsorption isotherms were determined from freshly boiled distilled water, ordinary distilled water (*p*H 5.2) and from 0.001 *N* sodium hydroxide. All fluoride analyses were made by the volumetric thorium nitrate method according to Rowley and Churchill.[3] Sodium concentrations, before and after adsorption, were determined gravimetrically by the uranyl zinc acetate method.

The rates of adsorption of fluoride on the seven magnesias were studied, under the same conditions as described above. Negligible fluoride removal took place during the centrifuging. The initial concentration was approximately 6.0 mmole./liter in all cases.

For the determination of the rates of hydration 1-g. samples were rotated with 100 ml. of water at room temperature for various lengths of time. After filtration on an asbestos filter, the samples were dried under vacuum in the presence of phosphorus pentoxide for forty-eight hours to remove the occluded water. This treatment was followed by ignition at 1000° for one hour which effectively removed the chemically combined water. The amounts of hydration occurring during fluoride adsorption were measured in the same manner.

## Results and Discussion

The isotherms for fluoride removal from freshly boiled, distilled water on the seven varieties of magnesia are given in Fig. 1. These adsorption curves are neither Freundlich nor Langmuir isotherms. They do illustrate, however, that these magnesias differ very markedly in their fluoride adsorption capacities.

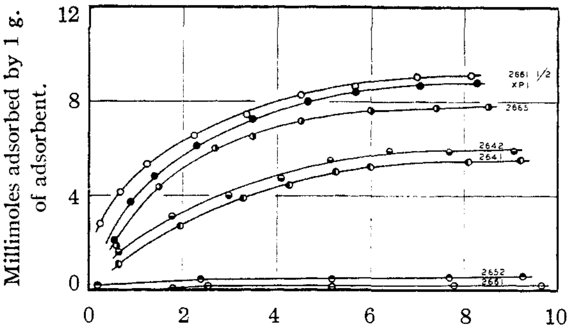

Fig. 1.—Fluoride adsorption isotherms on active magnesias.

In Fig. 2 are shown the rates of fluoride adsorption for the series of magnesias from a solution containing 6.0 mmoles of fluoride per liter. Since the per cent. of the amount of fluoride adsorbed at equilibrium is plotted against time, the heights of the curves are indicative of the rapidity with which equilibrium is attained by the various grades of magnesia. The data are not amenable to mathematical analysis by any of the usual kinetic approaches. In Table I the rate and capacity characteristics of the magnesias in fluoride adsorption are compared with their surface areas as determined by nitrogen adsorption.[2] It must be remembered that these areas are the initial areas of the samples. During the adsorption hydration takes place, changing the nature and extent of the surface.

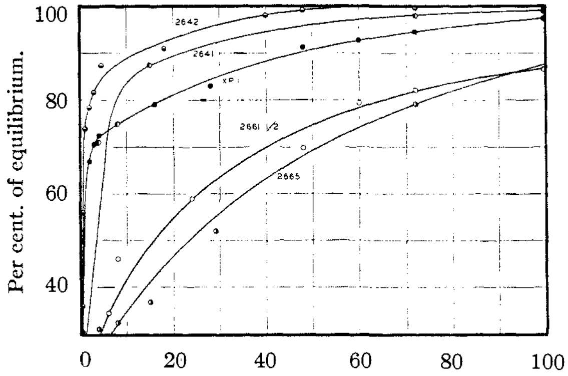

Fig. 2.—Rates of fluoride adsorption on active magnesias.

TABLE I

CHARACTERISTICS OF THE MAGNESIAS

| Magnesia | Surface area (BET) | Fluoride capacity[a] | Rate of fluoride ads.[b] | Rate of hydration[b] |
|---|---|---|---|---|
| 2642 | 154 m.$^2$/g. | 6.0 mmole/g. | 98 | 97 |
| 2652 | 125 | 0.5 | . . | 83 |
| 2641 | 71 | 5.5 | 95 | 96 |
| XP1 | 48 | 8.8 | 88 | 94 |
| $2661^{1}/_{2}$ | 33 | 9.1 | 68 | 68 |
| 2665 | 31 | 7.8 | 60 | 57 |
| 2661 | 0.8 | 0.2 | . . | 3 |

[a] Amount adsorbed in equilibrium with a solution containing 8 mmole/liter. [b] Per cent. of equilibrium reached in forty hours.

An examination of Table I shows clearly that there is no apparent relationship between the

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(3) Rowley and Churchill, *Ind. Eng. Chem., Anal. Ed.*, **9**, 551 (1937).

surface area and the fluoride adsorption capacity of a magnesia. There is a very striking relationship between surface area and rate of fluoride adsorption, however. The granular magnesia, 2652, and the inactive magnesia 2661, adsorbed so little fluoride ion that their rates of adsorption could not be determined with any degree of precision. It is believed that the granular magnesia adsorbed only a small amount of fluoride ion because much of its area is remotely situated at the ends of long capillaries which are quickly clogged by the hydration of the magnesia. The capillaries of this grade are much longer than those of the other grades because the particles are 1–3 mm. in diameter as compared with 2-5 microns for the other varieties.

Rates of hydration were also determined for these magnesias, and the results are presented in Fig. 3. The percentages in this figure do not include the initial water. The last column of Table I gives the relative heights of these rate curves for comparison with other properties. It is seen that the rates of hydration parallel the surface areas and the rates of fluoride adsorption.

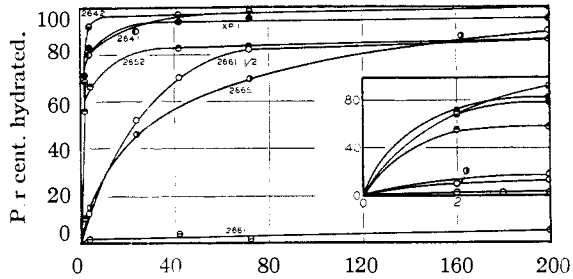

Fig. 3.—Rates of hydration of active magnesias.

Since the removal of fluoride from aqueous solution was studied at concentrations below the solubility limit of magnesium fluoride, fluoride removal by active magnesia must be attributed to an adsorption process. The lack of agreement between the amounts of fluoride and nitrogen adsorbed, and the existence of agreement between the rates of hydration and of fluoride adsorption suggested that the process is not a simple physical adsorption but has a more complex mechanism involving at least one chemical change. In order to reveal the nature of this mechanism, a number of additional measurements were made.

Several analyses were made of the sodium ion content of solutions before and after adsorption. In a typical case the sodium ion concentration dropped only from 5.37 to 5.24 (±0.02) mmole/liter during adsorption while the fluoride ion concentration dropped from 5.37 to 1.95 mmole/liter. Since approximately twenty-six times as many fluoride ions as sodium ions were removed from the solution during adsorption, fluoride is not adsorbed as sodium fluoride. Therefore, the fluoride must be removed either as the ion or in some other compound.

The second point to be established was the release of hydroxyl ions into the solution during adsorption. Measurements were made electrometrically of the *p*H changes taking place during adsorption and during the shaking of magnesia with distilled water. Average data from three determinations are given in Table II.

TABLE II

*p*H CHANGE DURING FLUORIDE ADSORPTION

| | | *p*H |
|---|---|---|
| Distilled water | Before rotation with MgO | 5.24 |
| | After rotation | 10.47 (±0.08) |
| Fluoride solution | Before adsorption | 5.30 |
| | After adsorption | 10.73 (±0.03) |

The *p*H's of solutions from which fluoride had been adsorbed were definitely higher than the *p*H's of distilled water samples rotated with magnesia in the same proportions.

The release of hydroxyl ions into the solution during adsorption was further substantiated by the following observations. In Fig. 4 are shown the isotherms for fluoride adsorption from solutions made up with distilled water containing carbon dioxide (*p*H 5.2) with freshly boiled distilled water, and with a 0.001 *N* sodium hydroxide solution. As the basicity of the solution was increased, the amount of fluoride adsorbed decreased. This behavior is to be expected for a process in which hydroxyl ions are produced, according to Le Chatelier's principle.

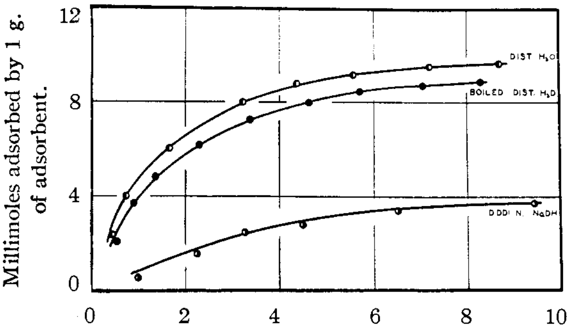

Fig. 4.—Fluoride adsorption isotherms from solutions of different initial *p*H.

It was found that the adsorption process was only slightly reversed by washing of magnesia with distilled water, but by using a sodium hydroxide solution, a large part of the adsorbed fluoride could be removed from the magnesia. In one instance, for example, 1-g. samples of Magnesia XP1 containing 0.97 millimole of adsorbed fluoride were rotated with 100 ml. of sodium hydroxide solutions of various strengths. These results are shown in Table III.

No fluoride removal ability was displayed by solutions of sodium chloride, bromide, iodide, sulfate or phosphate. This striking reversal of the fluoride adsorption by sodium hydroxide confirms the idea that hydroxyl ion is one of the products of fluoride adsorption on magnesia.

TABLE III

REVERSAL OF FLUORIDE ADSORPTION WITH SODIUM HYDROXIDE

| Sample | Normality of NaOH soln. | Fluoride removed, % |
|---|---|---|
| 1 | 0.0000 | 5 |
| 2 | .0532 | 38 |
| 3 | .269 | 57 |
| 4 | .494 | 80 |

The production of hydroxyl ion in the solution and the non-participation of the sodium ions during fluoride adsorption suggest that the adsorption mechanism starts with the reactions

$$MgO + H_2O \longrightarrow Mg(OH)_2$$

$$2NaF + Mg(OH)_2 \longrightarrow MgF_2 + 2NaOH$$

with subsequent adsorption of the magnesium fluoride. The hydration of the magnesia is by far the slower of the two reactions and is therefore the rate-controlling process. This conclusion is in accord with the agreement between rates of hydration and rates of fluoride adsorption as presented above.

The next stage in the adsorption process is clarified by the fact that magnesium hydroxide (J. T. Baker Medicinal, surface area = 30 m.$^2$/g.) was found to have no measurable ability to adsorb fluoride. It should be able to undergo metathesis with sodium fluoride to produce magnesium fluoride, yet no measurable adsorption took place. The only obvious difference between the two cases is the possibility for the magnesium fluoride to become attached to a magnesium oxide surface in the case of the magnesia.

The surface areas of the magnesias as listed in Table I were determined by nitrogen adsorption by the BET method and are, in most instances, insufficient to accommodate the observed amounts of adsorbed fluoride in a monomolecular layer. The possibility that the magnesium fluoride may be adsorbed in multimolecular layers is rendered unlikely by studies made of the extent of hydration which accompanies fluoride adsorption.

For this determination 1-g. samples of the various magnesias were rotated with 100 ml. of a solution containing 21 mmoles of fluoride. Ignition loss and fluoride adsorption were determined as before. Per cent. hydrations were calculated on the basis that all fluoride was lost upon ignition at 1000° according to the equation[4]

$$Mg(OH)_2 + MgF_2 \longrightarrow 2MgO + 2HF$$

The remainder of the ignition loss was attributed to dehydration of magnesium hydroxide as above. Table IV presents the results for Magnesias 2642, $2661^1/_2$ and XP1 at forty-eight and seventy-two hours in comparison with results for hydration alone from Fig. 3.

The data presented in Table IV show that a very considerable amount of hydration accompanies fluoride adsorption. If the adsorbed magnesium fluoride formed a multimolecular layer on the magnesia surface, it would be expected to provide considerable protection against hydration. Magnesia $2661^1/_2$ is an excellent example. After forty-eight hours it had adsorbed five millimoles of fluoride per gram which would make a layer seven molecules deep, assuming that a magnesium fluoride molecule occupies the same area as a nitrogen molecule. This layer should be ample protection against hydration, but in the next twenty-four hours the extent of hydration increased from 48.6 to 70.7%, showing that the adsorbed fluoride provided little protection against hydration and that the adsorbed magnesium fluoride probably does not coat the magnesia particles with a multimolecular layer.

TABLE IV

HYDRATION ACCOMPANYING FLUORIDE ADSORPTION

| Magnesia | Fluoride ads., mmole/g. | Hydration, % | Hydration alone, % |
|---|---|---|---|
| | 48 hours | | |
| 2642 | 5.13 | 88.8 | 97.2 |
| $2661^1/_2$ | 4.98 | 48.6 | 74.5 |
| XPI | 7.17 | 75.8 | 94.2 |
| | 72 hours | | |
| 2642 | 5.24 | 92.7 | 97.9 |
| $2661^1/_2$ | 7.84 | 70.7 | 82.0 |
| XP1 | 7.91 | 80.3 | 95.5 |

Although this and succeeding steps in the process are not well understood, it seems plausible that the magnesium fluoride forms a stable complex with the magnesium oxide surface resembling an oxyfluoride. This complex, like the magnesium hydroxide resulting from hydration of the magnesia, does not adhere to the surface but leaves it available for further adsorption and hydration. This use of nascent magnesium oxide surface would account for the ability of active magnesia to adsorb much more fluoride than nitrogen.

## Summary

The isotherms for the adsorption of fluoride ion from sodium fluoride solution on a series of active magnesias have been measured. An attempt was made to correlate the rates of hydration and the amounts and rates of fluoride adsorption with the surface areas of the magnesias as determined by nitrogen adsorption. No correlation was found between the surface areas and the amounts of fluoride adsorbed. The rates of hydration and of fluoride adsorption, however, were found to increase with increasing surface area for powdered magnesias.

The following steps in the mechanism of fluoride adsorption on magnesia have been shown to conform with the experimental data: (1) partial hydration of the magnesia; (2) metathesis between sodium fluoride and magnesium hydroxide to give magnesium fluoride and sodium hydroxide; (3) attachment of magnesium fluoride to magnesium oxide.

BETHLEHEM, PENNA. RECEIVED NOVEMBER 23, 1946

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(4) Domange, *Compt. rend.*, **200**, 239 (1935); **202**, 1276 (1936).