Structures of the type comparable to those proposed[8] as intermediates in the acid-catalyzed isomerization of maleic to fumaric acid seem inappropriate since no evidence for isomerization of maleic acid as catalyzed by cuprous chloride was obtained. Also the equilibrium for formation of a cuprous complex appears to be independent of the nature of anions (X^-) present in the medium.[9]

(8) Nozaki and Ogg, THIS JOURNAL, **63**, 2583 (1941).

(9) Preliminary studies of certain other olefins indicate that the solubility of cuprous chloride in aqueous solutions of the unsaturates is influenced by chloride ion concentration. Further studies of maleic and fumaric acids are planned in the light of this observation.

Summary

Solubility measurements have been used to study the equilibria for formation of water soluble complexes of cuprous chloride with maleic and fumaric acids. The results indicate that with fumaric acid a 1–1 complex of the type $H_2F \cdot CuCl$ is formed. In the case of maleic acid evidence for the formation of not only $H_2M \cdot CuCl$ but also of $HM \cdot CuCl^-$ was obtained even in solutions of reasonably high hydrogen ion concentration. Supporting evidence for these conclusions was obtained by studies of the absorption spectra of the complexes.

DAVIS, CALIFORNIA RECEIVED APRIL 6, 1948

[CONTRIBUTION FROM THE FLORIDIN COMPANY]

Low Temperature Nitrogen Adsorption Studies on Attapulgite (Floridin)

BY W. T. GRANQUIST AND R. C. AMERO*

Introduction

Recently Marshall and Caldwell[1] have presented an excellent survey of the colloid chemistry of attapulgite (floridin, fullers earth); their data on clay films exhibit an interesting variation in mean refractive index with temperature of preheating. A differential thermal curve presented by Grim and Rowland[2] and included in this paper indicates definite changes in this mineral with temperature. Finally, in adsorption problems involving the percolation of a fluid through a bed of granular fullers earth, it has long been known in the trade that there are various heat activation optima for the adsorbent depending on the nature of the adsorbate. Little information of this type has been published; however, FitzSimons, Amero and Capell[3] report data correlating the yield of decolorized bright stock solution with the activation temperature of the clay, which exhibit an optimum between 590 and 650°.

On the basis of this past work, it seemed to be of interest to conduct an investigation into the variation of the properties of the adsorbent with activation temperature. This paper presents the results of a low-temperature nitrogen isotherm study; later, data will be presented in an attempt to correlate optimum activation temperature with molecular weight of adsorbate in a number of adsorbate–solvent systems. This study has been extended to include a sample of extruded fullers earth, since high pressure extrusion results in a marked increase in oil decolorizing ability.[4,5]

* The present address of R. C. Amero is Johns-Manville Research Center, Manville, New Jersey.

(1) C. E. Marshall and O. G. Caldwell, *J. Phys. Colloid. Chem.*, **51**, 311 (1947).

(2) R. E. Grim and R. A. Rowland, *Am. Mineral.*, **27**, 746–761, 801–818 (1942).

(3) O. FitzSimons, R. C. Amero and R. G. Capell, Ref. Tech. Ed., *Nat. Petroleum News*, Oct., 1941.

(4) F. W. K. Hartshorne, U. S. Patent 2,079,854, May 11, 1937.

(5) R. C. Amero and R. G. Capell, *Pet. Ref.*, **22**, 22–26 (1943).

Experimental

Preparation of Samples.—Crude clay was ground in an attrition mill and screened to 30/60 mesh for low temperature nitrogen adsorption. For extrusion, the crude was pulverized in the laboratory Raymond mill, kneaded with sufficient water to give a free moisture content of 50%, and extruded through a Chambers Bros. Type 3B auger-type extrusion machine equipped with a die 2 cm. thick, containing 8 holes 1 cm. in diameter. The rods were air-dried, ground and screened to 30/60 mesh. The crude samples were activated at 218, 316, 427, 538, 649, 704 and 816° (425, 600, 800, 1000, 1200, 1300, 1500° F.), and the extruded sample at 649°. This activation was carried out in a laboratory muffle furnace equipped with a Leeds and Northrup Micromax controller. Heating was continued for one hour after activation temperature had been reached; the samples were then placed in a drying oven at 110° and allowed to cool before sealing in small sample bottles.

Low-Temperature Nitrogen Adsorption.—Adsorption–desorption isotherms were determined with the apparatus described by Emmett and Brunauer[6] and by Emmett.[7] The pressure arm of the manometer was equipped with a zero-indicating device to assist in maintaining the volume of the free space essentially constant—a condition necessary for precision in a given series of measurements. The liquid nitrogen-bath was agitated with a stream of gaseous nitrogen to prevent temperature stratification and to decrease the rate of condensation of atmospheric oxygen into the bath.

The nitrogen used as the adsorbate was a special high purity nitrogen supplied by the Linde Air Products Co., and this was further purified while filling the nitrogen reservoir by batch distillation from a trap cooled in liquid nitrogen. The helium utilized for measuring the free space in the samples was obtained from the Ohio Chem. and Mfg. Co. and its purity was enhanced by passing the gas during filling through active carbon cooled to liquid nitrogen temperatures.

Between 0.5 and 1.0 g. of the sample in question was weighed into the sample tube, and was then outgassed at 200° and *ca.* 10^{-5} mm. for one hour. The various points on the isotherm were determined in the usual way. To determine the final points at or very near saturation the volume of the system was decreased and the pressure observed; as soon as the pressure fell below P_0, the volume

(6) P. H. Emmett and S. Brunauer, THIS JOURNAL, **56**, 35 (1934).

(7) "Advances in Colloid Science," Vol. I, Interscience Pub. Co., New York, N. Y., 1942.

TABLE I

Act. temp., °C	Area sq. m/g. BET	V_m, cc. gas in mono-layer/g. adsorbent	V_s, gas adsorbed at P_0 cc./g.	Highest[a] P/P_0 reached in detg. isotherm	V_s/V_m no. of layers at P_0	Pore vol. V_s, cc. liq. N_2	$R_{av.}$ (Å)[b] $\frac{2V_s(liq.)}{A}$	R_d – Å[c]
218	132	30.2	301	0.994	9.95	0.463	71	69
316	138	31.4	340	.999	10.8	.524	76	96
427	134	30.5	250	999	8.2	.384	58	<20
538	127	29.1	253	.998	8.7	.390	62	33
649	120	27.4	292	.996	10.6	.450	76	74
704	97.5	22.2	281	.998	12.7	.433	88	90
816	49.1	11.2	180	.992	16.1	.278	113	103
649 (Ext.)	128	29.4	352	.996	12.0	.541	85	120

[a] These values are listed as an indication of the accuracy of the corresponding V_s. [b] "Geometrical" average pore radius—*i. e.*, 2 × pore vol./surface area. [c] Pore radius taken from maxima displayed by differential curves.

was again decreased. This was continued until values near saturation were obtained; the system was then allowed to come to equilibrium, requiring periods of two to five hours. The oxygen thermometer used for determining the P_0 value for the adsorbate at a given pressure reading was continually immersed in the bath and readings for P_{O_2} were taken for each point on the isotherm.

Results

The results of this study are shown in Figs. 1–8, and in Table I.

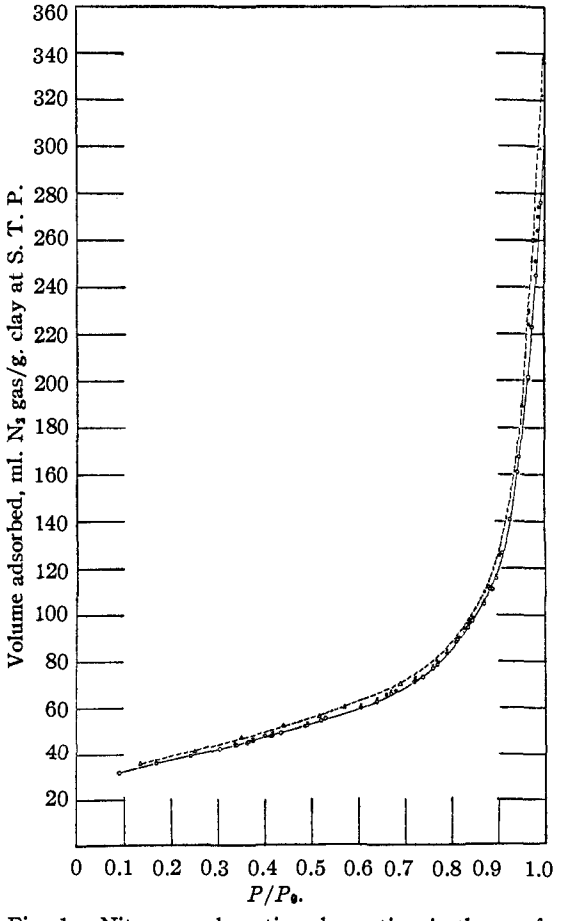


Fig. 1.—Nitrogen adsorption–desorption isotherms for clay activated at 218 and 316°: O, ô, 218°; △, 316°; solid points are for desorption at T, 77.3°K.

Figures 1–4 are the isotherms and are self-explanatory. In those cases where the results of only one determination have been used in drawing the isotherm, accurate positioning has been obtained by assuming rough parallelism with the neighboring isotherm on the curve sheet. In the calculation of the volume–pressure values at each point on the isotherm, correction was made for the deviation of nitrogen from the perfect gas laws. The data used were those presented by Emmett and Brunauer[8] and later by Emmett.[7] The deviation was assumed to vary linearly with pressure and a graph was prepared relating the deviation to the pressure of the system. In this way, a correction

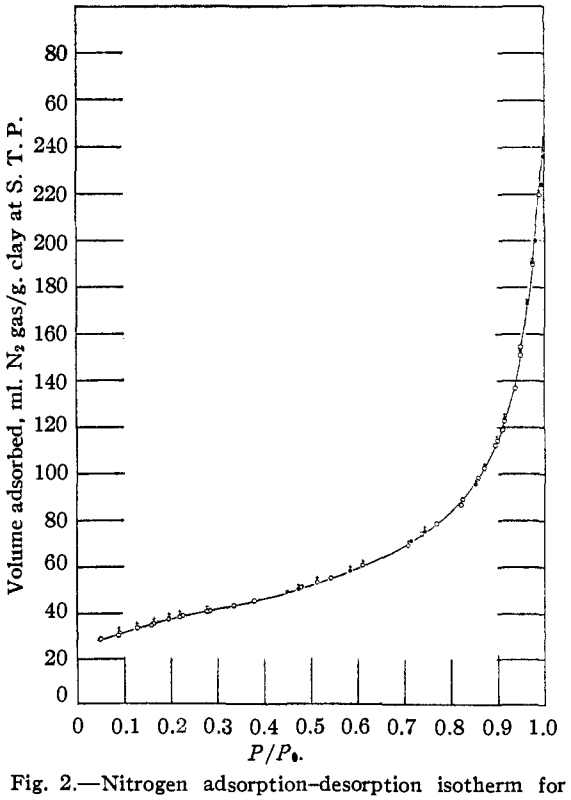


Fig. 2.—Nitrogen adsorption–desorption isotherm for clay activated at 427°: solid points are for desorption at T, 77.3°K.

(8) Emmett and Brunauer, THIS JOURNAL, 59, 1553 (1937).

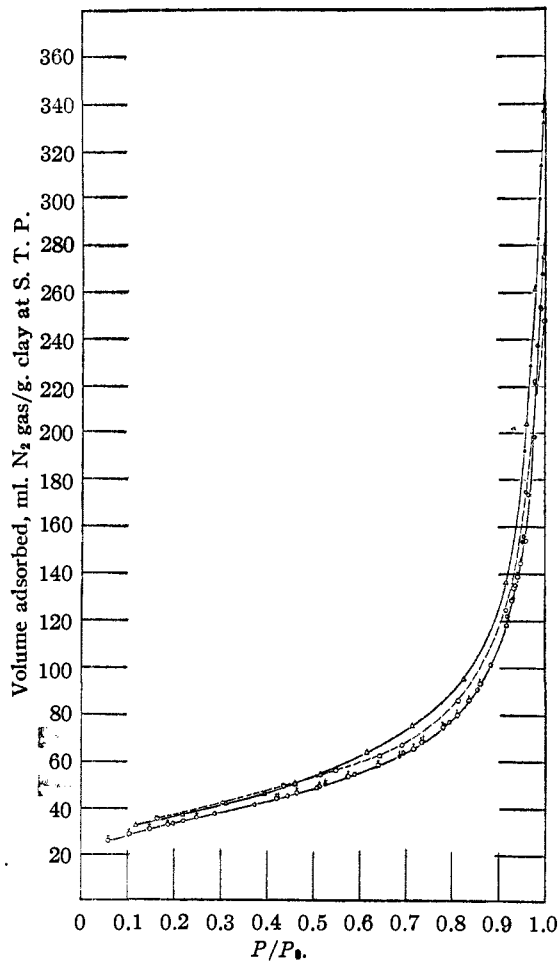


Fig. 3.—Nitrogen adsorption–desorption isotherms for clay activated at 538, 649 and 649°, extruded: O, 538°; ◐,◑, ♁, 649°; △, 649° extruded; solid points are for desorption at T, 77.3°K.

could be applied at each equilibrium pressure used in the determination. In Type II isotherms[9] such as these, the large increase in adsorption near saturation makes it difficult to estimate with certainty the value of the saturation volume. However, due to the long equilibration times and the technique of approaching saturation, the values listed in Table I are certainly close approximations of the true values, and, more important, the true values vary in the order shown. It is important to note that hysteresis effects were not observed.

By means of the Kelvin equation, the isotherm data were converted to structure curves relating volume adsorbed to pore radius. These curves were then graphically differentiated giving plots of $\Delta V/\Delta R$ *vs.* R, as shown in Figs. 5 and 6. This procedure and the validity of the resultant curve will be discussed more thoroughly in the following section.

(9) S. Brunauer, "The Adsorption of Gases and Vapors," Vol. I. Princeton University Press, Princeton, N. J., 1943.

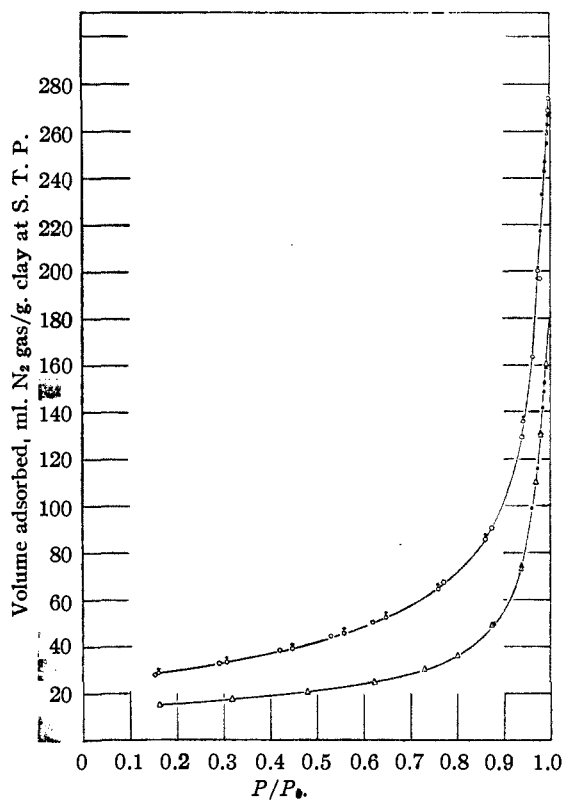


Fig. 4.—Nitrogen adsorption–desorption isotherms for clay activated at 704 and 816°: O, ♁, 704°; △, 816°; solid points are for desorption at T, 77.3°K.

In Fig. 7, the variation of saturation volume (pore vol.) and surface area with activation temperature is demonstrated. The area values given were calculated by the method of Brunauer, Emmett and Teller[10]; the plots necessary to the calculation were linear over the P/P_0 range employed. Figure 8 shows the variation of $R_{av.}$ $(2V_s/A)$ and R_d (taken from the maxima of the differential curves) in Å., with the activation temperature. All values plotted are listed in Table I. The data for the extruded material activated at 649° are included at the end of Table I to show the change in properties of the clay upon extrusion.

Discussion of Results

The lack of hysteresis in the isotherms and the large values of $n(V_s/V_m)$ at all activation temperatures are characteristic of a non-porous solid. Bradley[11] has presented a detailed X-ray study of the structure of attapulgite; the ideal cell formula established by the study for the magnesium end member of this series is $(OH_2)_4(OH)_2Mg_5Si_8O_{20}\cdot 4H_2O$ (actually there is extensive replacement of Mg by Al). As a consequence of the arrangement of the crystallite, channels having a free cross-section of *ca*, 3.7 Å. by 6.0 Å. run parallel to the fiber

(10) S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, 60 309 (1938).

(11) W. F. Bradley, *Am. Mineral.*, 25, 405 (1940).

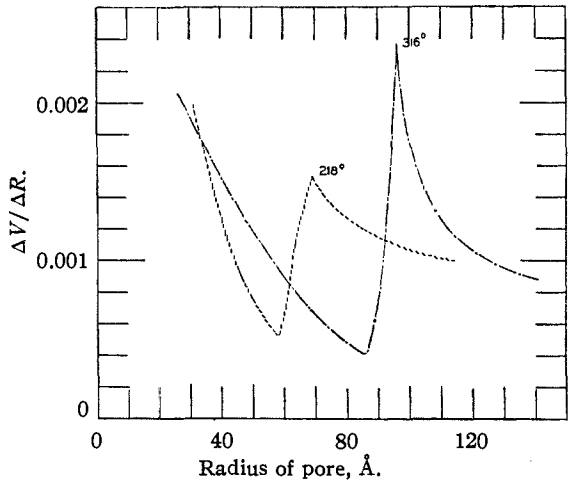


Fig. 5.—Distribution of pore volume for samples 218 and 316°.

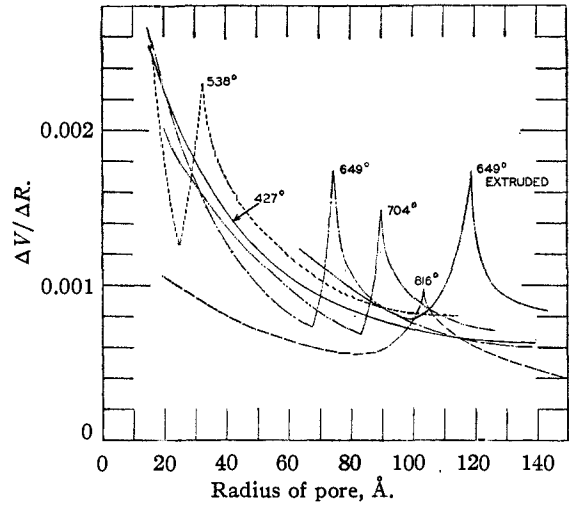


Fig. 6.—Distribution of pore volume for remaining samples.

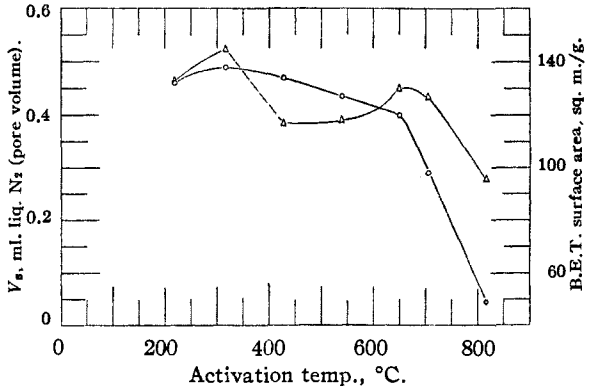


Fig. 7.—Variation of pore volume (△) and surface area (○) with activation temperature.

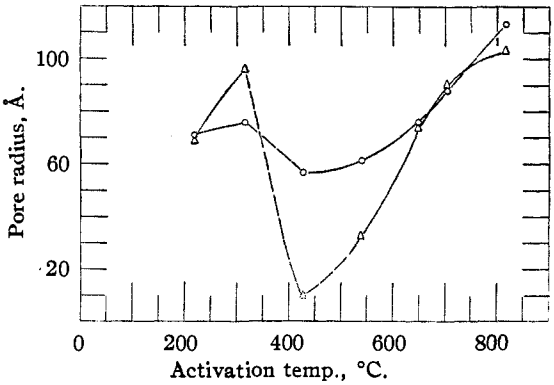


Fig. 8.—Variation of R_{av}(○) and R_d(△) with activation temperature.

axis; however, the availability of these channels for adsorption is questionable, due to their small size (diam. of N_2 mol. = 3.15 Å. from viscosity data and from the van der Waals equation, 3.53 Å. from heat conductivity data, and 4.58 Å. from the cross-sectional area value used in the calculation of area values by the B–E–T equation). Reference to published electron microscopy studies[12] and the discussion by Marshall and Caldwell[1] shows the fundamental particle to be lath-like in character; agglomerates of these particles would then make up the larger particles such as those used in this study. Thus a particle of attapulgite can be considered as a pile of these lath-like fragments. A "pore" would then be part of the void space of this heap of ultimate particles, and therefore would possess widely variable cross-sectional size and shape. Such a structure would not seem to fill the requirements of the "bottle-neck" explanation of hysteresis advanced by Kraemer and McBain. It is also extremely probable that a given "pore" would possess portions as narrow or narrower than 4 molecular diameters, or possess a closed end, or could be considered as space between parallel walls, or as wedge-shaped capillaries, conditions which, according to Cohan, would account for the lack of hysteresis. Tentatively, therefore, the lack of hysteresis and the large values of n can be attributed to the extreme cross-sectional heterogeneity of the void space in the sample,

This postulated structure would also explain the changes in properties due to extrusion. It can be assumed that, in the crude material, these lath-like units are arranged in some order, and that extrusion disrupts this order, resulting in a more random arrangement of the units, which in turn would yield an increase in pore volume, with a small accompanying increase in surface area. The use of the Raymond pulverizer in preparing the sample for extrusion introduces a factor that might have an effect on the properties of the extruded sample. However, it has been found many times in the course of routine preparation of extruded fullers earth adsorbents both in the laboratory and in the plant that the type of grinding has little effect on the pick-up of decolorizing ef-

(12) C. E. Marshall, R. P. Humbert, B. T. Shaw and O. G. Caldwell, *Soil Science*, **54**, 149 (1942).

ficiency resulting from the extrusion step. In early work on a less efficient crude a direct comparison of surface areas on crude and extruded materials is available, the latter being prepared from crude that was ground only to approximately minus 10 mesh on an attrition mill; the two surface areas were 119 sq. m./g. and 127 sq. m./g., respectively. This is the same order of increase in surface area as was observed in this case.

The lack of hysteresis and the large values of n would indicate that adsorption in this case is probably more closely related to multi-molecular layer adsorption on a plane surface than to adsorption on the walls of a capillary. The treatment of such data by the Kelvin equation is therefore unorthodox and not justified from a theoretical viewpoint. It is interesting to note, however, that the differential curves indicate the expected variation in distribution of pore volume over a wide range of pore sizes, with maxima at successively higher values of R. The values of $R_{av.}$, despite the inherent inaccuracy of V_s, correspond rather closely with the R_d values in most cases. This would seem to indicate that both methods measure a change of some property of the clay with activation temperature; this might be expressed as a change in the availability of the adsorbent surface with temperature.

Several anomalies appear in these data, *i. e.*, the absence of a maximum in the curve at 427°, and the difference between R_d and $R_{av.}$ for the extruded sample. This absence of a maximum over the range of R indicated is difficult to explain, but seems logical since it falls in the orderly sequence of the maxima. It may be that a maximum does occur, but that the adsorption data did not extend to sufficiently low values of P/P_0 (and thus of R) to establish this point; the R_d value in this case is reported therefore as <20 Å. The variation between the values for R_d and $R_{av.}$ in the case of the 649° extruded sample seems contradictory; however, both values indicate a definite increase in the availability of the surface over that of the 649° crude sample.

The variation in properties with activation temperature and the discontinuity between 316 and 427° can be related to the differential thermal curve, Fig. 9. The first endothermic reaction up to about 200° represents the loss of free and loosely adsorbed water. Between 230 and 340° another endothermic reaction occurs which results in greater pore volume, surface area and pore size (Figs. 7 and 8). Between 340 and 400° a slight but significant exothermic reaction occurs. In this range, the discontinuities appear in Figs. 7 and 8, the clay develops maximum resistance to disintegration in water, and it changes from grayish-white in color to a light tan. This can tentatively be attributed to a change in the nature of the bond between the fundamental units of attapulgite, resulting from the complete removal of interstitial water. However, it is conceded that the discontinuities may represent alteration of the 218 and 316° samples by the outgassing conditions necessary to the determination of the isotherms. In this event, the discontinuities would not represent a real effect.

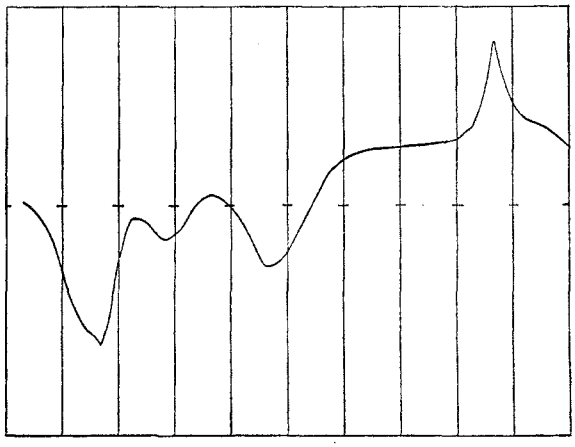


Fig. 9.—Differential thermal analysis of attapulgite (floridin) (courtesy Dr. R. E. Grim).

The endothermic reaction from 400 to 550 or 600° is definitely considered as loss of (OH) lattice water, with a consequent tendency for increased surface area. This is accompanied by crystal growth or shrinkage of the lattice which becomes the sole or predominating phenomenon between 600 and 800°. This is reflected in decreased surface area and increasing pore size. The exothermic peak at 870° is a phase change related to sintering or fusion, but is well beyond the range in which adsorbent characteristics are important.

In general, it can be stated that structure calculations based on low temperature nitrogen isotherms indicate variations in structural characteristics with activation temperature, and that these variations are supported by the inferences drawn from the differential thermal curve.

Acknowledgment.—The authors wish to acknowledge the assistance of Mr. A. Rock in constructing the Emmett and Brunauer apparatus. Acknowledgment is also gratefully extended to Dr. E. P. Barrett and Mr. R. G. Capell of Mellon Institute for their interest and advice in the early phase of this work, and to Dr. R. E. Grim of the Illinois State Geological Survey for furnishing the differential thermal curve.

Summary

1. The results of a low-temperature nitrogen adsorption study of attapulgite are presented, indicating, in general, gradual decrease of surface area and increase of pore volume with activation temperature from *ca.* 400° up to *ca.* 700°, followed by abrupt decrease of both of these properties with higher temperatures. Below 400°, anomalous results were obtained.

2. Structure calculations, based on the Kelvin equation, result in curves showing the distribution of pore volume over a large range of pore radii. Radius values taken from the maxima of these curves show increase with activation temperature, and are of the same magnitude and vary in the same order as the "geometrical" average pore radius based on the relationship 2 × pore vol./surface area.

3. A relationship between the differential thermal curve and the behavior of the adsorbent upon activation is presented, and the conclusions are supported by the experimental data. The relationship also serves to explain tentatively the discontinuity in properties noted between 340 and 400°,

WARREN, PA. RECEIVED FEBRUARY 28, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Stability of Chelate Compounds. IV. Effect of the Metal Ion[1]

BY MELVIN CALVIN AND NORTEN C. MELCHIOR[2]

In the first paper[3] of this series it was shown that there are at least two components of the forces which bind cupric ion in chelate molecules. One component is of the same character as for hydrogen ion; the other is dependent upon the nature of the ion of the organic portion, and is different for cupric ion and for hydrogen ion. This second component was ascribed to homopolar binding of copper, which allowed the resonance in the ion to extend to copper, thus making the stability of the chelate sensitive to changes in the resonance of the ion.

It was therefore of interest to compare the stabilities of chelates formed from a given organic ion and a series of metal ions. The ions cobaltous, nickelous, cupric and zinc were selected for comparison, and the dinegative ion of 5-salicylaldehydesulfonic acid[4] was chosen as the organic portion. This selection gave water soluble chelates, thus eliminating difficulties due to low solubility as well as any question about the interpretation of the readings of the glass electrode.[3] To determine the relative stability of these chelates the titration method of Calvin and Wilson[3] was used, with a modification intended to avoid difficulties which might be caused by the presence of small amounts of impurities.

Experimental

Materials.—Sodium 5-salicylaldehydesulfonate was prepared essentially as described by Blau[4] and recrystallized ten times from water. The metal salts used in titrations were reagent grade nitrates. The sodium hydroxide solution was carbonate-free, carefully standardized. The nitric acid was standardized against the sodium hydroxide solution used.

Titrations.—All titrations were made under purified nitrogen gas in a glass vessel immersed in a thermostat controlled to ±0.01°. The vessel was provided with openings for the electrodes, a stirrer, the buret and the nitrogen gas. Standard sodium hydroxide was added from a buret which could be read to 0.002 ml. *p*H readings were made using a Beckman model "G" *p*H meter equipped with extension electrodes. To eliminate any effect of traces of impurities the following procedure was adopted: 50 ml. of a water solution of sodium 5-salicylaldehydesulfonate (0.2 or 0.02 *M*) was pipetted into the titration vessel, the solution purged with nitrogen, and the electrodes inserted. When the *p*H reading became constant, 5 ml. of 0.01 *M* nitric acid which was 0.002 to 0.005 *M* in the desired metal ion was added by pipet, and the titration begun. The control titrations were carried out using 0.01 *M* nitric acid containing no metal ion. Careful comparison titrations showed exactly the same results with either solution in the absence of a chelating agent up to *p*H 6, whereas all comparisons were made at *p*H's less than 6. Typical titration curves are shown in Fig. 1.

Preparation of Chelate Compounds: Nickelous, Cobaltous, Cupric.—To 30 ml. of a water solution containing 0.02 mole of sodium 5-salicylaldehydesulfonate, 19 ml. of 1.0 *M* sodium hydroxide and 10 ml. of 1.0 *M* metal chloride solutions were added in succession. The solution, protected from air, was heated on the steam-bath for three hours, then allowed to cool overnight. The solid was filtered on a Büchner funnel, washed with two 10-ml. portions of 50% alcohol and dried over fused calcium chloride *in vacuo*.

$(C_7H_4O_5SNa)_2Ni\cdot 2H_2O$, light green. Calcd.: C, 31.1; H, 2.24; H_2O, 6.7. Found[5]: C, 30.5; H, 2.62; residue, 41.3; H_2O,[6] 6.7. $(C_7H_4O_5SNa)_2Co\cdot 2.5H_2O$, light orange. Calcd.: C, 30.6; H, 2.38; H_2O, 8.2. Found: C, 30.7; H, 2.63; residue, 47.4; H_2O, 7.6. $(C_7H_4O_5SNa)_2Cu\cdot 3H_2O$, pea green. Calcd.: C, 29.8; H, 2.50; H_2O, 9.6. Found: C, 29.7; H, 2.64; residue, 43.2; H_2O, 9.6.

Zinc.—The preparation method described above gave only a small amount of solid, but by decreasing the total amount of water slightly (from 59 to 43 ml.) a yellow crystalline solid was obtained which was washed and dried as before. Calcd. for $(C_7H_4O_5SNa)_2Zn$: C, 32.7; H, 1.57. Found: C, 31.8; H, 1.95; residue, 48.3; H_2O, *nil*.

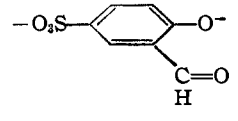
Results

If we write the reaction of chelate formation as two successive reactions

$$Me^{++} + Ke^{-} \rightleftarrows MeKe \quad (1)$$

$$MeKe + Ke^{-} \rightleftarrows MeKe_2^{-} \quad (2)$$

Me represents the metal being considered and Ke^{-} refers to the ion



(1) Abstracted from the thesis of N. C. Melchior, submitted in partial fulfillment of the requirements for the Ph.D. degree, at the University of California, Berkeley, California, September, 1946.

(2) Shell Research Fellow in Chemistry, 1945–1946; present address: Northwestern University, Evanston, Illinois.

(3) M. Calvin and K. W. Wilson, THIS JOURNAL, 67, 2003 (1945).

(4) F. Blau, *Monatsh.*, 18, 123 (1897).

(5) Microanalyses by Charles Koch.

(6) H_2O = weight loss at 140°. 0.001 mm.