

MECHANISM OF NH₃ ADSORPTION BY MONTMORILLONITE AND KAOLINITE*

by

D. W. JAMES and M. E. HARWARD†

Oregon State University, Corvallis, Oregon

ABSTRACT

Dry, homoionic systems of two montmorillonites and a kaolinite were treated with NH₃ and then evacuated exhaustively to eliminate any physically adsorbed ammonia. It was concluded that the NH₃ retained by the minerals was associated with the exchangeable cations. The mechanism of this adsorption process is the same as that which leads to the formation of inorganic amines, namely, the mutual attraction between unshared electrons in the NH₃ molecules and ionic centers of positive charge. This sorption process is reversible at elevated temperatures and is described by the equation, $n\text{NH}_3 + \text{CX} \rightleftharpoons (n\text{NH}_3 \cdot \text{C})\text{X}$, where n is the number of NH₃ molecules associated with each exchangeable cation, C, on exchange complex X. Accordingly, n is a coordination number and has the following values for the cations indicated: NH₄, 0; K, 0; H, 1; Ca, 2; Mg, 2; Al_{in}, 3; Al_{ex}, 6. Here *in* and *ex* refer to interior and exterior exchange sites respectively. The retention of NH₃ by cations which saturate the exchange complex of clays was shown to be analogous to the formation of ammoniates by reaction of NH₃ with inorganic salts.

A reduced retention of NH₃ by the Mg and Al 1:1 systems was ascribed to the possibility that exchangeable Mg and Al on kaolinite occur as hydroxy complexes.

A significant amount of NH₃ was adsorbed to the weak acid hydroxyl groups on the broken clay edges. Relative to exchange capacities this phenomenon was greater in magnitude on the 1:1 than on the 2:1 clays.

Energies of NH₃ adsorption on CaCl₂, Ca-bentonite and NH₄-bentonite were determined. Values of ΔH as a function of temperature were shown to be different for the Ca and NH₄-clay systems. The data indicated stronger energies of retention of NH₃ by the Ca-clay than for the NH₄ clay. The thermodynamic data thus support the mechanisms proposed here.

INTRODUCTION

Sorption isotherms of gases on finely divided solids are frequently used as an aid in the characterization of colloidal media. In general, the processes that

* Technical paper no. 1604, Oregon Agricultural Experiment Station, Corvallis, Oregon. This paper includes portions of a thesis submitted by the senior author in partial fulfillment of the requirements for the Doctor of Philosophy degree at Oregon State University. Appreciation is expressed to J. L. Young U.S.D.A., A.R.S., Corvallis, for helpful discussions and exchange of ideas during the conduct of these studies.

† Formerly Instructor, Oregon State University, now Assistant Soil Scientist, Washington State University, Irrigation Experiment Station, Prosser, Washington, and Associate Professor of Soils, Oregon State University, Corvallis, Oregon, respectively.

bring about adsorption are reversible and are classified as physical reactions with regard to the energies involved. NH_3 is often used as the sorbate in such investigations and is particularly useful in the study of 2:1 expanding type clay minerals. This arises from the polar character of NH_3 and hence its ability to vigorously solvate the minerals, exploiting both the exterior and interior surface areas. However, ammonia that is retained against evacuation is sorbed by forces which logically fall into the realm of chemical reactions. Ammonia retention and ammonia chemisorption will thus be used synonymously in this report. Sorption isotherms are ordinarily run at temperatures which are low enough to permit the condensation of a liquid film about the solid medium. In the case of NH_3 , this requires temperatures somewhat below 0°C . Ammonia retained against strong vacuum at such temperatures is actually reversibly adsorbed at elevated temperatures.

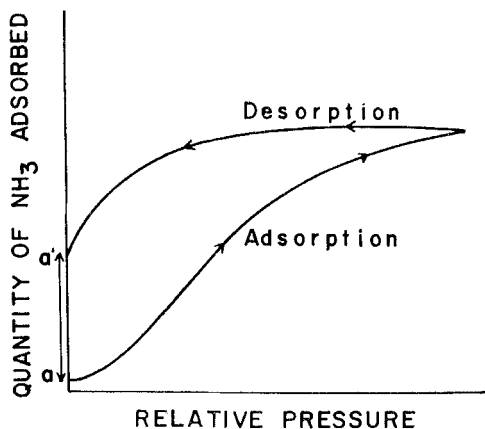


FIGURE 1.—Typical sorption isotherms of NH_3 on clay minerals.

It has been noted by several workers (Barrer and MacLeod, 1954; Brown and Bartholomew, 1962; Cornet, 1943; and Mortland, 1955) that there is wide hysteresis and a certain irreversibility in the adsorption-desorption cycle of NH_3 on clay minerals. These phenomena are illustrated in Fig. 1; the curves marked adsorption and desorption indicate the hysteresis loop and line aa' indicates the "irreversibly" adsorbed gas. The latter is somewhat exaggerated and serves to emphasize that it is this part of the sorption process, the amount of ammonia retained against evacuation, that we are concerned with in this paper.

Investigations into the mechanism of ammonia adsorption by clay minerals have been fruitful. The literature reveals that a number of different mechanisms have been proposed. Some of the proposals differ mostly in degree and for convenience may be grouped into several types.

The type of mechanism which has received the greatest attention involves association with a proton and the formation of ammonium. The proton could

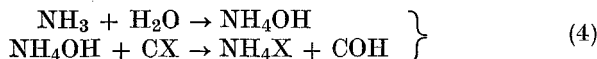
come from several sources. Reaction with acid clays has been proposed by Buswell and Dudenbostel (1941), Cornet (1943), Jenny *et al.* (1945) and Slabaugh and Siegel (1956). The reaction may be typified by



where X is the exchange complex. It has also been suggested (Cornet, 1943; Mortland, 1955) that hydroxyl groups may be involved in ammonia retention as illustrated by the reaction



Perhaps one of the more common viewpoints involves reaction with sorbed water. This has been discussed by Cornet (1943) Jackson and Chang (1947) and Mortland (1955). The postulates may be expressed as



where C is the exchangeable cation. Brown and Bartholomew (1962) in an investigation of NH₃ sorption by dry clays attributed chemisorption of ammonia to the mechanism give by equations (4); the source of the water for the reaction was given as the water of hydration about the exchangeable cations.

The second general type of proposed mechanism involves physical trapping of the NH₃. Barrer and MacLeod (1954) interpreted the hysteresis in terms of the energy required to force clay platelets apart initially upon ammoniation and then to collapse them as successive decrements of ammonia were removed. This suggests



where XNH₃X signifies physical trapping.

Another type of proposed mechanism involves formation of inorganic ammine type complexes. Barrer and MacLeod (1954) postulated that the hysteresis effect with ammonia may be a result of "irreversible nucleation phenomena." That is, the exchangeable cations in the montmorillonite system might act as nuclei about which the ammonia would condense in the adsorption process. Slabaugh and Siegel (1956), in an analysis of NH₃ adsorption by homoionic Wyoming bentonite proposed that the ammonia retained on the Ca system resulted from coordination of the NH₃ about the exchangeable Ca ion. In a review of the physico-chemical sorption characteristics of ammonia on clay minerals Mortland (1958) referred to the possibility of forming "ammoniates" with the exchangeable cations which are analogous to those known to occur with certain salts such as CaCl₂·2NH₃. This type of mechanism may be illustrated by



Another type of mechanism involved in ammonia retention concerns the hydrogen bond. In studies on homoionic systems of H, Ca, and Na montmorillonite, Mortland (1955) attributed most of the adsorption to a strong bond of the van der Waals' type since it is reversible, but this process, he indicated, was characterized by a fairly high heat of adsorption. He suggested that ammonia is associated with oxygen atoms in a hydrogen bond similar to the mechanism of water adsorption. This could be represented as



where O signifies the oxygens in the surface of the crystal lattice.

It is apparent that several mechanisms may be involved in the retention of NH_3 by clays, depending on conditions. In a study of sorption of NH_3 by clays, evidence was obtained which indicated the formation of ammoniates in some of the clay systems under investigation.* The purpose of this paper is to present some of these data and to suggest that this mechanism may be more important and extensive than has been generally realized.

MATERIALS AND METHODS

Three clay minerals were selected for this study. Two reference clays, kaolinite #7 and montmorillonite #11 were from Ward's Natural Science Establishment, Inc. The third mineral was a size fraction from Utah bentonite; it has been shown that this is predominantly montmorillonite. For convenience, the commonly recognized term Utah bentonite will be used in the rest of this paper. Anhydrous ammonia used in the experiments was supplied by the Pennsalt Chemical Corp. The impurities in this product were listed as 0.005 per cent by volume and no attempts were made to further purify the gas.

Starting with $< 2\mu$ size fractions of kaolinite and montmorillonite and $< 105\mu$ Utah bentonite which had been treated with HCl to remove the free carbonates, essentially homoionic systems containing Ca, Mg, Al, K and NH_4 were prepared by washing samples of the three clays with 1 N chloride solutions of the respective cations. Excess salt was eliminated by washing with 50 percent ethanol until a negative test for chloride ion was obtained. The clays were then dried at about 60°C and re-ground in a mortar.

The cation exchange capacities for the respective clays were estimated by measuring the exchangeable NH_4 on samples of the ammonium saturated systems. The values obtained were 119.5, 99.9 and 4.3 meq per 100 g on montmorillonite #7, Utah bentonite and kaolinite #11 respectively.

Measuring Ammonia Retention

A Napco vacuum oven provided the temperature control ($\pm 1^\circ\text{C}$ over the range $25\text{--}200^\circ\text{C}$) and also served as the ammoniating chamber. The oven was

* James, David Winston. 1962. Sorption of NH_3 in a dry system in relation to the chemical properties of clays and soils. Ph.D Thesis. Oregon State University, Corvallis.

attached to a manifold through a leak-proof ball and socket joint. Manometers and vacuum sources were also attached to the manifold. The inlet port of the oven was fitted with a three-way stopcock which allowed ammonia or dry air to be introduced into the system by a simple adjustment of the stopcock. The air was dried by passing it through concentrated sulfuric acid.

The general procedure for measuring ammonia retention was as follows. About 0.2 g of clay was placed in a 30 ml weighing bottle and dried for about 12 hr at 105°C at atmospheric pressure. After cooling in a desiccator the sample was weighed, placed in the ammoniating chamber and evacuated to less than 1 mm Hg pressure and temperature equilibrated for 45 min. The vacuum pump was then disconnected from the system by means of a stopcock and the system was flooded for 45 min at the desired pressure with ammonia. At the end of the ammoniating period the system was evacuated with the aid of a water aspirator to eliminate the excess gas. Dry air was allowed to sweep through the system to help flush out the ammonia. After about half-an-hour the aspirator was turned off, the high vacuum pump turned on, and the flow of dry air was reduced to the point where the final pressure was less than 1 mm Hg. At the end of 3.5 hr, the pump was turned off and atmospheric pressure was restored to the system. The sample was removed from the oven, stoppered and held for ammonia determination.

Ammonia retention was measured by means of a micro-Kjeldahl procedure and the results are reported as meq/100 g of clay. Retention values could be readily reproduced to 0.1 meq/100 g.

Factors which were found to influence ammonia retention are time of exposure to NH₃ and time of degassing. Preliminary experiments showed that a considerable rise in temperature of the clay on initial exposure to the gas would partially reverse the adsorption process but when sufficient time was allowed for the temperature of the clay to return to that of the ammoniating chamber then sorption became constant with time. The effect of time of degassing was very marked up to half-an-hour but after 2 hr the loss of NH₃ was very gradual.

Measuring NH₃ Sorption Energies

A 10 to 15 g sample of material was predried with heat and vacuum and then ammoniated at room temperature and 700 mm pressure of ammonia gas. The system was partially degassed at elevated temperature and was then reammoniated at room temperature. The sample was transferred to a specially constructed sample holder and manometer system and was immersed into a constant temperature bath which consisted of glycerol in a wide-mouth Dewar flask. Temperature control was maintained with a thermo-regulator and relay which controlled the temperature to within $\pm 0.01^\circ\text{C}$ at the desired level. The heater used was a low heat lag, knife type, 500 watt unit. The bath was kept in constant agitation with a mechanical stirrer. The sample was evacuated with a two-stage, high vacuum pump to zero pressure as read from the mercury manometer. The temperature of the bath was raised to 30°C and

evolution of sorbed gas forced out any remaining air. The system was then disconnected from the vacuum source and the temperature was raised, usually in 10° increments, and the pressure read when it attained a constant value. Time to attain equilibrium varied from a few hours to several days depending on the type of sample and the temperature level being maintained.

RESULTS AND DISCUSSION

The effects of temperature and pressure on the chemisorption of NH₃ are illustrated in Figs. 2 through 7. The scale for the ordinates in Figs. 4 and 7 are expanded compared with the other figures to bring out the details for the

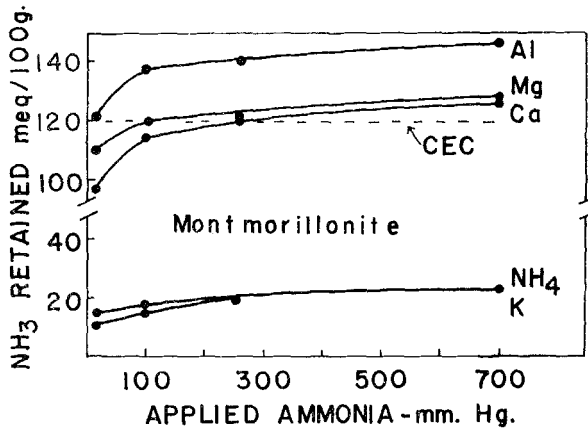


FIGURE 2.—Influence of saturating cation and exposure pressure on ammonia retention by montmorillonite #11 (25°C).

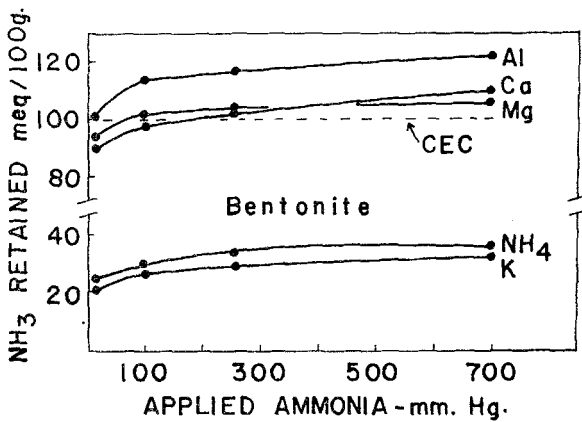


FIGURE 3.—Influence of saturating cation and exposure pressure on ammonia retention by Utah bentonite (25°C).

kaolinite systems. The data for NH₃ retention by the various NH₄-saturated clays were adjusted to a net value by subtracting the amount of ammonium initially present from the total ammonia measured in the micro-Kjeldahl procedure. At the higher temperatures the values for the NH₄-clays became negative due to decomposition of exchangeable ammonium and are so indicated in the figures.

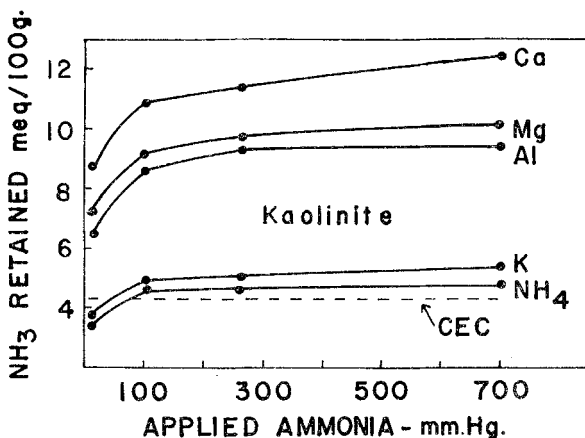


FIGURE 4.—Influence of saturating cation and exposure pressure on ammonia retention by kaolinite #7 (25°C).

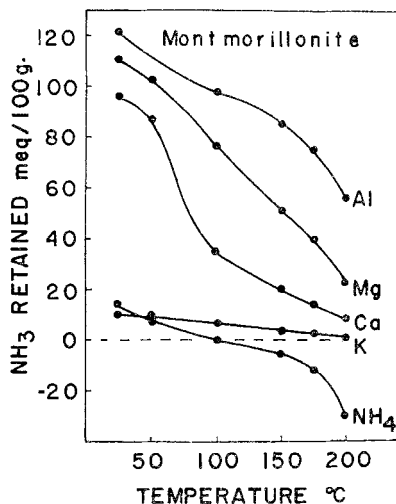


FIGURE 5.—Influence of saturating cation and temperature on ammonia retention by montmorillonite #11 (all samples exposed to NH₃ at 15 mm Hg).

It is clear from the data given in Figs. 2 through 7 that ammonia retention by the three reference clays was determined primarily by the species of the exchangeable cation. The order of retentivity for the 2:1 clays was $Al > Mg \geq Ca \gg K = NH_4$. Results on an "H" bentonite showed that the meq of NH_3 retained was essentially the same as for the Mg and Ca systems. The order of retentivity for the 1:1 clay was $Ca > Mg \geq Al > K = NH_4$.

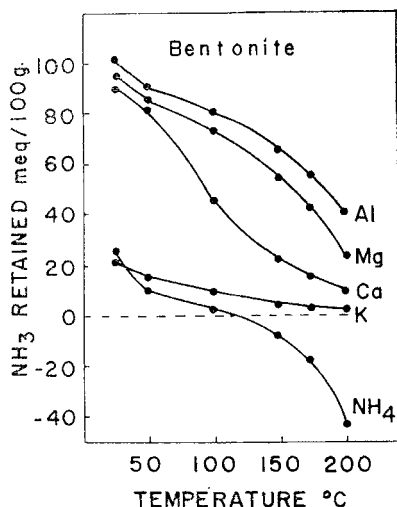


FIGURE 6.—Influence of saturating cation and temperature on ammonia retention by Utah bentonite (all samples exposed to NH_3 at 15 mm Hg).

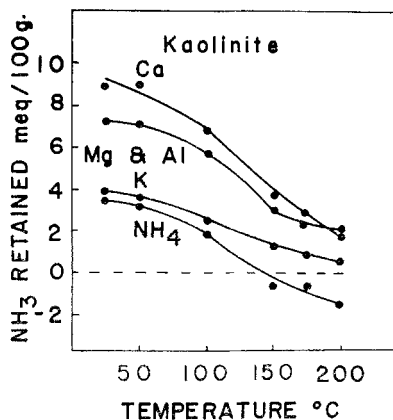


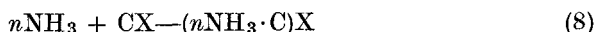
FIGURE 7.—Influence of saturating cation and temperature on ammonia retention by kaolinite #7 (all samples exposed to NH_3 at 15 mm Hg).

It has sometimes been assumed in the past that ammonia sorption by clay minerals is primarily a function of surface area. It is apparent however, that in characterizing the ammonia retaining ability of any clay system, a detailed knowledge of the cation exchange suite is of importance. Similar conclusions may be drawn from the results of Brown and Bartholomew (1962).

Chemisorption of NH₃ by the Formation of Inorganic Ammines

It became evident early in this research that there was a striking correspondence between the cation exchange capacity and the quantity of NH₃, on a milliequivalent basis, that was retained against evacuation for certain of the reference clay systems. When based on cation exchange capacities, the relative amounts of sorbed ammonia were almost identical for the montmorillonite type clays saturated with polyvalent cations (Figs. 2 and 3). This corresponds to approximately 2 NH₃ molecules per exchangeable Ca or Mg.

It has been shown*† that ammoniation of air-dry Ca, Mg and Al saturated montmorillonite clays resulted in a change of *c*-axis spacing from the normal hydrated state of 14–15 Å to 12.6–13 Å. Further, Ca-montmorillonite was collapsed from 15 Å to about 10.5 Å by heating at 150° and 1 mm pressure for 12 hr. Ammoniation of this dehydrated clay resulted in a sharp 12.3 Å diffraction peak. These data and those presented here suggest that NH₃ reacts directly with the exchange cations to form ammoniates. In the case where the 14–15 Å clays were exposed to NH₃, the gas dehydrated the exchange cations during the formation of the complex, thus giving rise to a competition with H₂O for adsorption sites. Visual evidence of dehydration of clay systems was obtained in several instances throughout the conduct of these studies. Young‡ has also obtained evidence for considerable dehydration of soil and clay samples as a result of ammoniation. These results seem to indicate that the retention of ammonia by the Ca, Mg and Al montmorillonite and bentonite systems involved a mechanism analogous to that which gives rise to inorganic ammines as indicated by equation (6). The data thus support the postulate of Barrer and MacLeod (1954) and the data of Slabaugh and Siegel (1956). On the basis of the data given here a formula more generalized than equation (6) is proposed in the form



Here, *n* is the stoichiometric relationship of NH₃ to the exchangeable cations, i.e. the number of molecules of NH₃ per C. The value of *n* is thus the co-ordination number of NH₃ with the exchangeable cation species C. For the

* See reference on page 304

† James, D. W., and Harward, M. E. Competition of NH₃ and H₂O for adsorption sites on clay minerals. (Manuscript submitted to Soil Science Society of America *Proceedings* and presented before Division II of that society at Cornell University, August 22, 1962).

‡ J. L. Young, U.S.D.A., A.R.S. Corvallis, Oregon. Personal communication. Unpublished data (intended for publication in Soil Science Society of America *Proceedings*).

Ca and Mg saturated clays $n = 2$. On the basis of these data, the value of n for the Al clays would superficially equal 3.6; this will be discussed later in the text. It is obvious that where the exchange cation C is hydrogen then n should equal 1. It is also evident from Figs. 5 through 7 that equation (8) is reversible even where C is H. The later results are in agreement with Bottini's (1937) analysis of the decomposition of NH_4 -bentonite using DTA techniques.

In view of the above, a study was conducted to obtain corroborative evidence for the mechanism expressed in equation (8) from a comparison of ammonia coordination complexes of various inorganic compounds. The fact that ammonia will form coordination complexes with metal cations is well known. Sidgwick (1950) discussed numerous kinds of such ammine compounds. For example, various Mg salts will take up NH_3 to form the complex $(\text{Mg} \cdot n\text{NH}_3)$ where n may be either 2, 4 or 6 depending on the conditions. Other alkaline earth halides also form amines. In the case of Al halides, ammonia is absorbed readily and it should be noted that the monamines and triamines are very stable forms. Thus, in regard to reactions with dry ammonia, the behavior of Al, Mg and Ca as exchange ions on clay surfaces seems to follow the pattern established by these elements in ionic crystalline substances other than the silicate minerals.

A study was made of the ammonia retaining abilities of various salts under the approximate conditions employed for the clay in this research. Samples of reagent grade salts were placed in the vacuum system and evacuated. They were then flooded with about 700 mm NH_3 until pressure equilibrium was attained at room temperature. The samples were degassed overnight after which the retained NH_3 was determined. The results are given in Table 1

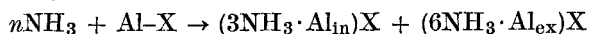
TABLE 1.—COORDINATION OF NH_3 WITH CATIONS IN CHLORIDE SALTS

	This experiment	Sidgwick (1950)
K	0	0
Ca	2.0	1,2,4,8
Mg	—	2,4,6
Al	5.9	1,3,5,6

where a comparison is also given for similar values from the literature. It was noted that the uptake of NH_3 by Ca salt gave agreement with the literature and gave also approximate agreement with the apparent uptake of NH_3 by Ca ions on the montmorillonite clays.

The retention of NH_3 by the Al salt was almost twice as high as for the exchangeable Al in the clay minerals. Since it is well known that coordination of ammonia about cations usually occurs in integral values; the same would be expected for aluminum in the exchangeable form. The interpretation of n for the Al saturated clays in Figs. 2 and 3 is therefore somewhat different than for the Ca and Mg systems. It was estimated* that 86.6 and 85.0 per cent

of the total cation exchange capacity for montmorillonite and bentonite respectively arose from interior lattice exchange sites. Sidgwick (1950) states that the coordination numbers of Al for NH₃ are 1, 3, 5 and 6. The adsorption of NH₃ per Al on the clay corresponded to 3.6. X-ray diffraction data of ammoniated samples indicated interlayer spacings corresponding to the thickness of 1 ammonia.* This indicates that the NH₃ molecules on interior sorption sites are oriented linearly (with Ca and Mg) or in a plane (with Al) about the exchangeable cations. A value of $n = 3$ appears most reasonable for Al in all interior sites. This is also in agreement with Sidgwick's (1950) notes on the stability of the aluminum triammine complex. It was then assumed that for all exterior sites $n = 6$. Simple calculation, using the distribution of sorbed ammonia between interior and exterior sites would lead to a predicted value of 136 meq of coordinated ammonia per 100 g for the Al montmorillonite and 115 meq/100 g for the Al-bentonite. Comparison of these values with the curves for the Al clays in Figs. 2 and 3 make this interpretation seem reasonable. These results would lead to a modified version of equation (8) for the Al saturated 2:1 clays as follows:



where *in* and *ex* refer to internal and external adsorption sites respectively.

Chemisorption by Weakly Acidic Hydroxyl Groups

In light of the above developments for the Ca, Mg and Al montmorillonite type clays, the ammonia retention by all of the remaining systems might at first glance appear to be anomalous. Referring to the kaolinite systems, the behavior differed in two important respects from the montmorillonite type clays. First, the amounts of NH₃ retained relative to the exchange capacity were much higher in all kaolinite systems. Secondly, the order of retentivity of the Ca, Mg and Al kaolinite systems was the reverse of that demonstrated for the montmorillonite clay systems.

The ammonia retention by the kaolinite systems may be explained in the following manner. It is believed that NH₃ coordination about K and NH₄ on clay minerals does not occur. This is in accord with the concepts discussed in connection with ammine formation of inorganic salts (Table 1) and also with the analogous behavior of NH₃ and H₂O in their solvation properties on cations of all kinds. The sorption of NH₃ by the K and NH₄-kaolinite may then be accounted for by the reaction denoted by equation (3). This reasoning is based on the theory that ion exchange on the edges of 1:1 type clays arises from hydroxyl groups that have weak acid properties. If the amount of ammonia thus retained by K-kaolinite is subtracted from the values shown for the Ca-kaolinite system, the ammonia retention falls approximately into line with values given for the Ca ion on the montmorillonite clays.

It also appears necessary to account for some changes in cation saturation due to preparation of the clays. It will be recalled that in the preparation of

* See reference on page 304

the various homoionic systems the clays were washed exhaustively to eliminate excess salt. It is probable that significant quantities of exchangeable cations were replaced by hydrolysis during this process, resulting in exchangeable H on the more weakly acidic exchange sites. In order to test this idea portions of the K-kaolinite were washed with 1 N KCl, 0.1 N KCl and KCl + KOH at pH 8.5 which was 0.1 N with respect to K. After three washings with these salt solutions, the suspensions were spun down in the centrifuge and dried. Ammonia retention on these samples was compared with the K-kaolinite prepared in the usual manner; the data are presented in Table 2.

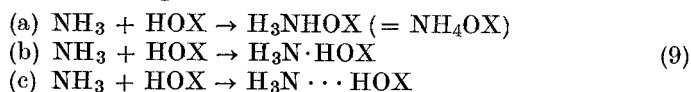
TABLE 2.—THE INFLUENCE OF EXCESS KCl ON NH₃ RETENTION BY K-KAOLINITE*

Washing procedure after saturating with 1 N KCl	NH ₃ retained meq/100 g
Standard-washed free of Cl	3.90
0.1 N KCl	2.38
0.1 N KCl t pH 8.5	2.29
1 N KCl	2.06

* Ammoniation was at 15 mm Hg and 30°C after washing and drying.

These data indicate a sharp reduction in the amount of NH₃ retained as a result of incomplete removal of KCl. The ammonia retaining ability was not completely eliminated however. It is apparent that if the weak acid concept is correct, more than 50 per cent of the ammonia retention by the Ca, Mg and Al-kaolinite arises from reactions with OH groups. The ammonia retention by the K and NH₄-saturated montmorillonite and bentonite may also be explained by equation (3). Similarly, it is believed that reaction with weakly acidic OH groups would account for a small part of the NH₃ sorption by the Ca, Mg and Al saturated 2:1 clays.

It would appear that if all the broken-edge OH groups having weak acid properties were arrayed according to their tendency toward ionization, there would be a broad spectrum of acid strengths depending upon the location of the OH group or the nature of the cation to which it is bonded in the clay structure. The weaker the acidity, the more likely would be the hydrolysis of the adsorbed metal cation from a given O⁻ group, and the less likely would it be for the group to give rise to an exchange site. With respect to sorption of NH₃ the spectrum could be expressed as



Equations (9) depict a range of adsorption energies which is concomitant with the acid strength of the OH group. The energy of NH₃ chemisorption would thus grade into the energy of physical adsorption; equation (9a) is identical

with (2) while equation (9c) would be a simple hydrogen bond and energy-wise would likely not differ from the NH₃ ··· OX arrangement of equation (7).

A possible explanation for the transposition of the order of retentivity by the Ca, Mg and Al in the kaolinite (compared to the montmorillonite) systems is that exchangeable Mg and Al may tend to occur as hydroxy compounds. This concept was expressed by Thomas (1960) who showed that in a dry kaolinitic soil the exchangeable Al existed in both the di- and univalent forms. This would have a tendency to decrease the adsorption of ammonia since it has been demonstrated that gibbsite* and, by inference, brucite display no tendency toward chemisorption of ammonia (Brown and Bartholomew, 1962).

Heats of Adsorption by Montmorillonite

Measurements of thermodynamic quantities are informative as to strengths of adsorption and may provide information upon which to choose between alternative mechanisms. For purposes of comparison with clay minerals, measurements were made on the vapor pressure of ammonia in the system CaCl₂-CaCl₂·2NH₃. Classical thermodynamic theory (Partington, 1951, p.332; Glasstone, 1940, p.835) was used in calculating the heats of reaction.† The average thermodynamic values over the temperature range 35° to 70°C were $\Delta H = 11.6$ kcal/mole and $\Delta S = 29.6$ entropy units. Partington (1951, p.257) presented data on the vapor pressure of solid ammonia over the temperature range -109° to -79°C. ΔH and ΔS were calculated from his data and averaged over this range; the values obtained were $\Delta H = 7.75$ kcal/mole and $\Delta S = 34.0$ e.u. The vaporization of solid ammonia is obviously a simple physical process involving only van der Waals'-type forces. On the other hand the ion-dipole interaction between Ca and NH₃ is clearly more energetic and the NH₃ in the complex is more highly ordered than is NH₃ in the pure solid form. These data are taken as evidence that formation of the Ca-diammine in the chloride salt falls into the category of chemical reactions. The same will be shown to be true with regard to clay minerals.

Estimations of the heat of vaporization of NH₃ from Ca and NH₄-bentonite were obtained from equilibrium pressure and temperature readings of the heated, NH₃ treated systems. Preliminary experiments were first conducted on the ammoniated Ca-bentonite system to verify the validity of assumptions for application of thermodynamic theory. A plot of log P versus $1/T$ revealed the constancy of the heat capacity of the system. It was also shown that the temperature-pressure curve obtained on a cooling cycle was identical with that for the heating cycle, indicating that the reaction was reversible under the conditions employed. It was therefore concluded that the Clausius-Clapeyron equation could be directly applied to the data obtained from ammoniated clay-systems.

* See reference on page 304.

† Heat of vaporization and heat of desorption are equivalent expressions under the present context. The negative of these terms, the heat of adsorption, will also be used in this discussion.

ΔH for the ammoniated Ca-bentonite was approached in two ways. First, equilibrium pressure readings were made at about 10°C intervals and ΔH was calculated from adjacent pairs of pressure and temperature values using the Clasius–Clapeyron equation. The results are presented as curve *a* of Fig. 8. This curve shows that ΔH values below 90°C were somewhat erratic. This was considered to be a result of a series of over-lapping equilibrium reactions that were interfering in the analysis. If it is assumed that a spectrum of adsorption energies occur in the ammoniated clay, then a given equilibrium dissociation

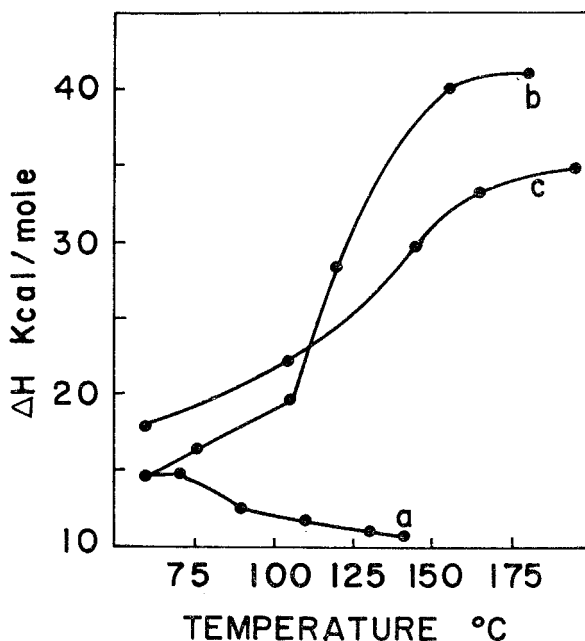


FIGURE 8.—Heats of adsorption of ammonia

- (a) Ca-bentonite, stepwise heating without evacuation
- (b) Ca-bentonite, stepwise heating with evacuation to zero pressure between pairs of pressure and temperature equilibrium values.
- (c) NH_4 -bentonite, determined in same manner as (b).

situation would be altered by imposing upon it the tendency of a reaction having slightly higher energy to dissociate. Thus the values given in Fig. 8a would pertain only to the sites having weakest sorption energies. It was noted that for temperatures above 90°C , ΔH and ΔS averaged 12.0 kcal/mole and 26.3 e.u. respectively. These values are in good agreement with the data from the calcium chloride diammine; evidently the solvation properties of ionic Ca were quite similar in the two very different environments.

The second approach in measuring the heat of adsorption was designed to avoid over-lapping reactions. After obtaining a pair of equilibrium pressure-

temperature values, the system was reduced to a zero pressure reading on the Hg manometer by degassing, thus forcing the reaction, that was involved at that particular temperature level, to completion. Following this the temperature was raised and another pair of equilibrium values were obtained. The first attempt with this technique resulted in evolution of water from the system at about 160°C and perturbations in the pressure readings. This water may have come from dehydroxylation of broken-edge OH groups but it was quite likely that a small amount of hygroscopic water remained in the clay because of the large amount of sample present. Whatever the source of water, when the system had reached equilibrium at 170°C, the vapor was eliminated by exhaustive evacuation. Following this the system was cooled to less than 30°C, re-ammoniated and another series of equilibrium values was obtained. No water vapor was detected this time. The results are presented as curve *b*, Fig. 8.

Comparison of curves *a* and *b* in Fig. 8 shows that very different results were obtained by the two procedures. The first values of ΔH in each curve are identical as would be expected from a reversible reaction. However, the change of ΔH with increasing temperature in the last series departed markedly from those obtained in the first run. In curve 8b it is seen that the heat of adsorption increased regularly up to about 105° after which an abrupt change occurred. It is believed that the first section of the curve in Fig. 8b shows the true heat of adsorption on Ca bentonite for all external surface located Ca ions. As all of the surface oriented ammonia was eliminated, the gas retained within the expandable lattices began to diffuse out thus giving much larger pressure differences with increasing temperatures. The greater pressure difference was reflected in the abrupt change in curve 8b at about $\Delta H = 20$ kcal/mole.

These results may be interpreted in two ways. At the higher temperatures, time to attain equilibrium required up to four days. It is possible that constant pressure only indicated a pseudo-equilibrium situation, in which case the value of ΔH above 20 kcal/mole would be spurious. A preferable interpretation of these results is that thermal decomposition of the Ca ammoniate resulted in a change of up to 20 kcal/mole but that the ammonia had to obtain heat in addition to this in order to have enough kinetic energy to escape from between the tightly collapsed lattices. Reference to Fig. 5 will show that ammonia removal would be approaching completion near 175°C. This undoubtedly accounts for the change in the shape of curve 8b between 150 and 175°C.

Ammonium saturated bentonite was treated according to the second method used for the Ca-bentonite. The results are given as curve *c* in Fig. 8 and a continuum of sorption energies is evident. The curve 8c could be extrapolated to room temperature on the low temperature side and the heat of sorption would thus be seen to decrease to the energy levels of physical adsorption. The energy spectrum depicted here for the ammoniated NH₄-bentonite tends to corroborate the concept expressed in equations (9) for this phenomenon.

Some difficulty was encountered in attaining equilibrium at the 140–150°C point in Fig. 8c. Therefore, the value of ΔH at that point may be somewhat in error. The final two values of ΔH given in the figure were obtained from good equilibrium conditions and the values 33.5 and 34.9 kcal/mole were believed to be good estimates at the temperature levels concerned. Similar results were obtained by Ellis and Mortland* on an NH_4 -bentonite. They used differential thermal analysis techniques and obtained an average heat of desorption of $\Delta H = 35.3$ kcal/mole for the temperature range 200° to 450°C. These results are in very good agreement with the energy of decomposition of NH_4 as the chloride salt. Sidgwick (1950, p.661) gives data to show that the heat of decomposition of NH_4 is 35.6 kcal/mole. Accordingly, ΔH for the reaction $\text{NH}_4\text{X} \rightarrow \text{NH}_3 + \text{HX}$ was in actuality the heat of formation of the ammonium ion.

The problem of diffusion of NH_3 from between the lattices of NH_4 -bentonite seems to have had little effect on the determination of ΔH . (Cf. Fig. 6 for the amount of ammonia removed at these temperature levels.)

GENERAL DISCUSSION

The sorption mechanisms described in equations (2) and (8) are fundamentally chemical reactions which are brought about by the mutual attraction between unshared electrons of the dipolar ammonia molecule and the cationic centers of positive charge. The intensity of the ion-dipole bond is strongly modified by the effect of coordination, thus the emphasis on the coordination or lack of coordination between ammonia and the various cations discussed in this report. Coordination results from certain spacial configurations and is a phenomenon which depends on the size relationships of the coordinating bodies. Different coordination complexes are possible, for example, between Al and NH_3 because of a favorable radius ratio between the two kinds of particles. On the other hand, an unfavorable radius ratio between two particles, e.g. NH_3 and K, precludes the formation of a stable coordination complex.

In expressing chemisorption in terms of equation (8), the tacit assumption has been that the cation exchange capacity of the system CX was a discrete quantity. This of course was not literally true because the estimate of CEC on any clay exchange system will vary with the chemical conditions of measurements. One important factor that affects estimates of CEC is the reference cation being used; uni-, di-, and trivalent reference cations give increasingly higher estimates of CEC in that order. Accordingly, variations in estimates of CEC will have direct bearing on the estimate for n in equation (8). Reference to Figs. 2 and 3 shows that in the case of the Ca, Mg and Al saturated montmorillonite type clays, nearly all the NH_3 retention values, throughout the pressure range of applied ammonia, fall within the limits of variability

* B. G. Ellis, and M. M. Mortland. Heats of desorption of ammonia and simple organic materials from bentonite. *Abstract, Agronomy Abstracts* 1961, p.11.

that one might expect for CEC when the sorbed NH₃ is assigned as previously indicated for the respective cations. This was taken as reasonable proof that n in equation (8) had integral values for these systems.

Relationships of Sorption Equations

Equation (2) is a very important concept in explanation of NH₃ chemisorption by 1:1 type minerals, but it is proportionately much less important in dealing with montmorillonite-type clays. Equations (2) and (8) are complementary and probably will have to be utilized in considering NH₃ adsorption by clay minerals of all kinds.

Equation (1) is a special case of equation (8) and needs no further explanation. However it is noted that this equation is the reverse of the decomposition of NH₄-clay.

One of the pertinent questions which arises here concerns the importance of mechanism involving water (equations 3 and 4) relative to the formation of ammoniate type complexes (equation 8). There is little doubt that reactions of NH₃ with H₂O in soil and clay systems would be expected to occur under certain conditions. A number of workers (Cornet, 1943; Mortland, 1955; Brown and Bartholomew, 1962) have studied NH₃ retention under conditions that were analogous to those used in the present work. They have suggested that the NH₃ sorption processes directly involve either liquid or adsorbed water. It was apparent from the discussions following the oral presentation of this paper that there is a considerable amount of support for this viewpoint. Mortland* has obtained data from infrared analyses which he feels support the viewpoint that NH₃ sorption involves a reaction with H₂O. These data should be informative with respect to the question raised here. The present workers took precautions to eliminate "free" water in these sorption studies and also to prevent water vapor from entering the systems during NH₃ treatment and degassing. It is felt that even if water of cation hydration existed in these systems initially, the competition of NH₃ for adsorption sites, particularly in view of the high pressure of ammonia application and subsequent degassing, would result in the loss of water from these systems. Accordingly, a principle assumption throughout this report has been that NH₃ adsorption and retention data for the systems studied here have pertained to the dehydrated state of the respective clay systems. It is thus apparent that there are opposing viewpoints with respect to NH₃ retention by clays.

The primary purpose of this paper has been to present evidence to suggest that the mechanism of NH₃ retention involving the formation of ammoniates with certain saturating cations may be more important than we have heretofore realized. The following are points which support this view:

1. Evidence was obtained for the stoichiometry of NH₃ retention on Ca, Mg and Al clays. When proper allowance is made for estimates of NH₃

* Personal communication. M. Mortland, Michigan State University, East Lansing, Michigan. Data are to be reported in *J. Phys. Chem.*

retained by reaction with weakly acidic OH groups, integral values for coordination numbers are obtained.

2. The retention of NH_3 on clays saturated with different cations was shown to be analogous to NH_3 retained by inorganic salts of these ions through the formation of ammine type complexes.

3. The ion-dipole bond involved in the inorganic amines is much stronger than the attraction between H_2O and NH_3 . In a closed N/10 ammonium hydroxide system, NH_3 is distributed as the following distinct species: 46.2 per cent NH_3 (dissolved gas); 52.4 per cent associated as NH_4OH ; and 1.4 per cent as NH_4 (Sidgwick, 1950, p.660). This explains why, in an open system, NH_3 will readily escape from an otherwise pure aqueous solution at ambient temperature and pressure. This is true of "free" solutions, let alone in clay systems where the levels of moisture would be much lower and be under tension or at an entropy level lower than solid state water. On the other hand, amines of Ca, Mg and Al dissociate only at elevated temperatures. In the case of $(\text{Mg} \cdot 2\text{NH}_3)^{++}$ the "dissociation tension" is 18 mm Hg (i.e. dissociation pressure is 752 mm Hg) at 181°C and the dissociation pressure of $(\text{Ca} \cdot 2\text{NH}_3)^{++}$ is 100 mm Hg at 105°C . In the case of the Al halides, monamines and triamines are the most stable forms; $\text{AlCl}_3 \cdot 1 \text{ N H}_3$ melts and boils without decomposition (Sidgwick, 1950, pp.241, 299, 430). Therefore, one could state *a priori* that with clay minerals in an atmosphere of ammonia, where H_2O is very limiting, the ammonia would react first with the exchange ion and secondarily with the water of hydration. Further, the coordination complex would persist on evacuation but NH_4OH would readily dissociate and both NH_3 and H_2O would escape from the system. This is especially true here where the systems were degassed to pressures less than 1 mm of Hg. The reactions given by equation (4) would logically operate in the presence of liquid water; in the absence of liquid water, even though the water of hydration about the exchangeable cations is not removed, the formation of exchangeable NH_4 would not be expected.

4. The ability of H_2O to compete with NH_3 for adsorption sites has been demonstrated when an acid trap to hold the displaced NH_3 was present.* The reverse reaction of NH_3 displacing H_2O is to be expected, especially considering the pressures of ammoniation used in these studies, in fact, the ability of NH_3 to displace H_2O from soil and clay systems was observed.

5. X-ray diffraction analyses indicate similar 001 spacings for ammoniated montmorillonites regardless of the use of hydrated or dehydrated Ca-clays. The observed spacings are consistent with the size of NH_3 and the observed coordination numbers of the cations for NH_3 .

6. Evidence was obtained to indicate that the heats of adsorption of NH_3 on the Ca-clay do not resemble the heats of adsorption on the NH_4 -clay. It should be emphasized that curve 8b was obtained after the clay has been degassed, ammoniated, degassed and ammoniated several times. As was indicated, the final step before obtaining the data in curve 8b was to degas

* See reference on p. 304

at 170°C and then to cool and re-ammoniate at room temperature. There is little doubt but that the Ca-clay was "dry". If, in fact, exchangeable NH₄ had been formed in the Ca bentonite according to equations (4), then the thermal decomposition of this system should be analogous to the ammoniated NH₄ system.

Proposed mechanisms of NH₃ retention must be capable of taking the above points into account. It is felt that the observations made in this study support the viewpoint expressed by Barrer and MacLeod (1954) and by Slabaugh and Siegel (1956) with respect to formation of ammoniates with exchangeable cations such as Ca, Mg and Al. It is apparent, however, that further critical experiments are needed to resolve contrasting viewpoints.

SUMMARY AND CONCLUSIONS

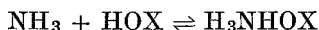
Three clay minerals consisting of montmorillonite #11, Utah bentonite and kaolinite #7 were characterized as to their physico-chemical reactions with NH₃. The results showed that all clay systems studied retained ammonia against evacuation at room temperature and that the ability to retain ammonia was governed primarily by the kind of exchangeable cation present. For homoionic systems of montmorillonite clays the order of retention was Al > Mg > Ca ≫ K > NH₄. The order of retention by the kaolinite clay was Ca > Mg > Al > K > NH₄.

The retention mechanism may be described by the reversible reaction equation $n\text{NH}_3 + \text{CX} \rightleftharpoons (n\text{NH}_3\text{C})\text{X}$, where C and X represent the exchangeable cations and the exchange complex respectively. n is the coordination number of ammonia with the cation, C, and for the systems tested has the following values for the 2:1 clays:

Cation	K	NH ₄	H	Ca	Mg	Al _{in}	Al _{ex}
n	0	0	1	2	2	3	6

where *in* and *ex* refer to internal and external adsorption sites respectively. For the cations located on the internal surface areas of the expanding type clays it was concluded that the ammonia molecules were oriented linearly or in a plane about the exchangeable cations.

The overall retention process in all clays was augmented by the sorption of NH₃ to broken-edge hydroxyl groups which have weak acid properties. This phenomenon was of greater magnitude relative to the exchange capacity in the kaolinite systems than in the other clays. It is typified by the reaction equation



where HO represents the hydroxyl group on the edge of the clay.

The sorption mechanisms described in the above equations were fundamentally chemical reactions brought about by the mutual attraction between

unshared electrons of the ammonia molecule and the cationic center of positive charge. The coordination of ammonia with the various cations in the clay minerals was in all cases characteristic for the respective cations of inorganic compounds.

It is believed that the NH_3 retained against evacuation was in actuality chemisorbed ammonia. For ammoniated Ca-bentonite the sorption energy ranged from 14 kcal/mole at 50°C to 41 kcal/mole at 180°C. For ammoniated ammonium bentonite the results showed a continuum of sorption energies ranging from 17 kcal/mole at 50°C to 35 kcal/mole at 190°C. The latter indicated the decomposition of the initially exchangeable NH_4 and is actually the energy of formation of the NH_4 ion.

REFERENCES

- Barrer, R. M., and MacLeod, D. M. (1954) Intercalation and sorption by montmorillonite: *Trans. Faraday Soc.*, v.50, pp.980-989.
- Bottini, O. Von. (1937) Über die thermische Zersetzung von ammonium-permutit, ammonium bentonite und ammoniumton: *Kolloid Zeitschrift*, v.78, pp.68-71.
- Brown, James M., and Bartholomew, W. V. (1962) Sorption of anhydrous ammonia by dry clay systems: *Soil Sci. Soc. Amer. Proc.*, v.26, pp.258-262.
- Buswell, A. M., and Dudenbostel, B. F. (1941) Spectroscopic studies of base-exchange materials: *J. Amer. Chem. Soc.*, v.63, pp.2554-2559.
- Cornet, I. (1943) Sorption of NH_3 on montmorillonite: *J. Chem. Physics*, v.11, pp.217-226.
- Jackson, M. L., and Chang, S. C. (1947) Anhydrous ammonia retention by soils as influenced by depth of application, soil texture, moisture content, pH value, and tilth: *J. Amer. Soc. Agron.*, v.39, pp.623-633.
- Jenny, H., Ayers, A. D., and Hosking, J. S. (1945) Comparative behavior of ammonia and ammonium salts in soils: *Hilgardia*, v.16, pp.429-457.
- Mortland, M. M. (1955) Adsorption of ammonia by clays and mucks: *Soil Sci.*, v.80, pp.11-18.
- Mortland, M. M. (1958) Reactions of ammonia in soils: *Adv. in Agron.*, v.10, pp.325-348.
- Partington, J. R. (1951) *An Advanced Treatise on Physical Chemistry*, v.II: Longmans Green, London, 448 pp.
- Sidgwick, N. V. (1950) *The Chemical Elements and Their Compounds*: Clarendon Press, Oxford, 1700 pp.
- Slabaugh, W. H., and Siegel, R. H. (1956) Sorption of ammonia by homoionic bentonites: *J. Phys. Chem.*, v.60, pp.1105-1108.
- Thomas, G. W. (1960) Forms of aluminum in cation exchangers: *Trans. 7th Int. Cong. Soil Sci.*, v.2, pp.364-369.