

MICELLES AND BASE EXCHANGE¹

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The term "micelle" was invented by N \ddot{a} geli (1) to represent a colloidal particle. The term has been used in a number of senses, many of them loosely defined. We shall attempt in this paper to amplify the discussion of the thermodynamic consequences of the term in its broadest aspect, and we shall particularly study the electrolytic micelle as used by McBain (2), which postulates that a simple ion formed by the dissociation of certain electrolytes may be considered replaced by a heavily hydrated polyvalent ion or micelle. The thermodynamic and physical properties of soap solutions and of alkali silicate solutions have been explained by means of this concept (3). We shall also consider the extension of the idea of micelles to complexes and the property of base exchange in relation to electrolytic micelles, with particular reference to a rigid micelle ion or group of rigid micelle ions.

The class of substances which might be called by the term "micelle" stands intermediate between a substance of the simplest molecular constitution as, for instance, dilute helium gas and one of the most complex. Practically, we may well limit ourselves to a consideration of substances more complex than simple molecules or ions or ionic radicles, as H₂O, Na⁺, SO₄⁻, etc. We might presume that the term "micelle" included all more or less definite complexes, but before discussing the thermodynamics of such systems, we shall consider the chemical individuals of which they are composed. We might divide the possible complexes on the basis of the type and degree of chemical binding which marks the

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various kinds of complexes or micelles. Without going too far into the mechanism of these chemical bindings we may roughly divide them into two main groups,² called "electronic bindings" and "interionic forces."

It is not possible to draw a definite line of demarcation between the two groups, and some may wish to offer a single mechanism to explain the two groups. For the purpose of our discussion, it is unnecessary to define the type of binding. As we shall see, certain types of complexes are more simply considered, if the assumption of the predominance of a particular type of binding is made. Thus, the assumption of electronic binding in a crystal of diamond, or in a stable complex such as $\text{Ag}(\text{NH}_3)_2^+$ or $\text{Ag}(\text{CN})_2^-$, enables us to predict that a crystal of diamond will act as a single molecule, or that the law of definite proportions will account for the constancy of the composition of the complex. On the other hand, the assumption of pure interionic forces in such crystals as those of potassium chloride explains the crystal lattice and the ease with which ions are formed from these crystals in a saturated water solution. In like manner, the assumption of forces closely related to interionic forces, as the explanation of the grouping of water molecules around potassium and chloride ions in solution, offers a mechanism for observed phenomena. We shall also recognize as electronic bindings such polymeric combinations as are frequently met with in organic chemistry, as the polymerization of formaldehyde, or cyanogen, and which may be the explanation of the ready "adding on" of silica to HSiO_3^- , or of CrO_3 to CrO_4^{--} .

The conception of micelles, from a thermodynamic standpoint, is essentially that a system composed of micelles and solvent forms a homogeneous phase—homogeneous in the sense that the composition and properties of any particular portion of the phase is the same as that of any other portion, providing we take the portion so large that its average composition is the same as the average composition of every other portion, and that statistical

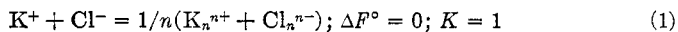
² A third group may include the combination of such molecules as carbon tetrachloride, forming a liquid or solid in which the molecules are held by some force which is not here named.

methods are valid. Thus, if we consider a solution of sugar *microscopically* and portions of the phase so minute that the number of sugar molecules is so small that statistical methods no longer obtain, or if we consider a portion of the homogeneous phase of dimensions of the order of magnitude of the molecules composing that phase, one may no longer consider it homogeneous. So, when we speak of micelles in rapid equilibrium with their simple products of dissociation, we are thinking of a portion of a homogeneous phase sufficiently large that molecular discontinuities are not recognized. When we think of the micelle in the limit, that is when all the material in a solution aggregates into a single micelle, we have reached a point where it is difficult to choose so large a quantity of solution that the individual portions may all be said to have the same composition and properties. However, we may still apply statistical methods in just the same way that we apply such methods to the vapor pressure of tungsten at ordinary temperatures, where the concentration of tungsten atoms in equilibrium with tungsten metal is less than one in the whole sidereal universe.

THE TYPICAL CRYSTAL AS A MICELLE

Just as it is valuable to consider such an apparent absurdity as the concentration of tungsten vapor in equilibrium with the metal at ordinary temperatures, let us carry the idea of micelle formation to an almost absurd limit and from this viewpoint consider the mixture of a single crystal or of a small number of crystals with the saturated solution.

Let us study not a solution which is in equilibrium with a single potassium chloride crystal but rather one in equilibrium with small crystals which do not differ appreciably in thermodynamic properties from a single one. Thus we may consider (4) the reaction



where n is the number of potassium or chloride atoms forming the crystal particle with which the solution is in equilibrium, and n^+ and n^- are the number of charges associated with each micelle.

If we follow the usual custom in dealing with micelles, we will refer their activity to the same standard state as that used for the ions, namely the hypothetical molal solution of potassium and chloride ions. Consequently we write for the above reaction:

$$\Delta F^\circ = 0; K = (m' \pm \gamma')^{2/n} (K_n Cl_n) / (m \pm \gamma)^2 (KCl) = 1. \quad (2)$$

The molality of the micelle is the number of moles of potassium chloride crystals per thousand grams of water, which is equal to the number of crystals per thousand grams of water (or 55.51 moles) divided by Avogadro's constant (6.06×10^{23}), and will consequently be a very small number. By virtue of the principles which we have already given in another place (3f), we should expect the activity coefficient of such a solution of micelles to be very small because of the large number of charges associated with each ion of the crystal micelle. However, it will be noted that the product of the molality and activity coefficient of the crystal micelle is raised to the $2/n$ th power which is a very small power, and consequently the value of the activity of the crystal micelle in equilibrium with potassium and chloride ions is the same as that of a potassium chloride solution as ordinarily defined. It is obvious, then, that, so far as our thermodynamic treatment is concerned, the micelle crystals obviate the necessity of considering a distinction between a homogeneous and a heterogeneous solution, for we may make n as large as we please.

However, in ordinary practice, we have found it more convenient to take the activity of the solid in the large crystal as unity and therefore to write the equation:

$$KCl(s) = K^+ + Cl^-; \Delta F^\circ = -RT \ln (m\gamma)^2 (KCl) \quad (3)$$

whence, combining equations 1 and 2, we find

$$KCl(s) = 1/n(K_n^{n+} + Cl_n^{n-}); \Delta F^\circ = -RT \ln (m\gamma)^{2/n} (K_n Cl_n). \quad (4)$$

If in the above treatment we had taken the size of the crystal such that $2n$ rather than n potassium ions and $2n$ chloride ions were united to form the micelle, then the molality of the crystal micelle per gram-mole of KCl would have been one-half that which we have used. With large crystals the molal free energy is practically independent of the size of the crystal, hence since

$(m \pm \gamma)^{2/n} = (m' \pm \gamma')^{1/n}$ where $m' = 0.5m$, the activity coefficient must change in such a way as to satisfy, no matter what the size of the crystal, so long as it is so large that the molal free energy remains constant.

It is immaterial for the thermodynamic argument whether or not the various potassium and chloride ions in the crystal micelle neutralize the electrical effect of the one upon the other, as this is taken care of in the measured activity coefficient. It is our purpose in introducing this more or less fanciful idea to show the import of the conception of micelles in solution, to show the intermediate character of the micelle and to show that, from a thermodynamic standpoint, we are not greatly concerned with the mechanism of surface phenomena. The position of the micelle as an intermediary between the individual molecule of a solution and a crystal has been recognized since the inception of the postulate; but in many cases the idea of the colloid as a distinct phase has been emphasized, whereas we have shown that the conception is that of the crystal or micelle and its saturated solution, which can be treated by the same methods as those used for the homogeneous system.

The reader has no doubt objected that neither potassium nor chloride ions form micelles. We might rather suggest that there are no intermediate steps between the typical ionic solution and the potassium chloride crystal micelles we have studied. Indeed the idea of a micelle (and consequently a homogeneous phase) in the present case has little in its favor, and the formulation on the basis of a heterogeneous system is much more convenient.

MICELLE IONS

The concept of micelles is particularly adaptable when only one of the ion constituents has a tendency to form these aggregates and the other constituent remains in the ordinary ionic form, as, for example, in the case of the soaps and silicates.

We will now consider the case represented by

$$B^- = 1/n B_n^{n-}; K = (m\gamma)^{1/n} (B_n^{n-}) / (m\gamma) (B^-) \quad (5)$$

in which the positive ion A^+ does not form intermediate micelles of the type represented for the negative ion in equation 5.

If n has a small value, such as ten, and one-tenth of the stoichiometrical molality of the negative ion constituent is in the form of the micelle, then the molality of the univalent ion is ninety times that of the micelle. If n is one thousand, and ten percent is in the form of a micelle, then the molality of the univalent ion would be nine thousand times that of the micelle. And if, in the case of a single crystal of AB, in equilibrium with its saturated solution, we assume that one-tenth of the B ions are present in the AB crystal, then the molality of the B ion constituent in the solution is $9n$ times that of the AB crystal. But we have seen that the activity coefficient of such a large electrolytic crystal considered as a solute must necessarily be very small, so that the equilibrium constant in equation 5 is essentially zero, and for ordinary purposes such a way of discussing the solution is valueless. On the other hand, when n is small, we may speak of the molality of the micelle, of its activity coefficient, etc., as such; and it thus represents the first stage in the formation of "insoluble" substances from homogeneous ionic solutions.

When the proper nuclei are introduced into supersaturated solutions of typical crystalline substances, the molecules group themselves in a regular orientation. So, also, we think of micelles forming larger masses, when, for instance, a 0.2 *M* potassium palmitate solution at 90°C. is cooled to 0°C. (3c). The molality of the palmitate micelles of a definite number of charges, which we believe to be arranged in a particular orientation for this molecular species of micelle, is governed by the value of the equilibrium constant of the reaction in which this micelle is formed from its ions, and this equilibrium constant varies with the temperature, depending upon the variation of the partial molal heat contents of the ions and micelles.

Or, we may think of a whole series of reactions of the type:



and write equilibrium constants involving the molalities, or molalities times activity coefficients, of the micelles existing as such; and we may say either that we have equilibrium between the two species of micelles or equilibrium between the one species and the ions that have not formed micelles.

We might also postulate the formation of a positive micelle according to the equation

$$A^+ = 1/p A_p^{p+}; K = (m\gamma)^{1/p} (A_p^{p+}) / m\gamma(A^+). \quad (7)$$

As examples of the positive micelle, we might mention that protein chlorides or sulfates, in their more concentrated solutions, may possibly be considered to be illustrations of positive micelles, although we should wish to examine this point later.

Metathesis of micelle ions

Ordinarily, in speaking of micelle formation, there have been considered only those cases in which the micelle formation is restricted to either the positive or negative ion; and we have not examined specifically cases in which substances are present which would tend to form both positive and negative micelles; although, if our suppositions are correct, we might well expect metathesis to take place, and, at least at the points of contact of the two micellar masses, some of the charge on the positive micelle might be expected to neutralize some of the charge on the negative micelle. But if the micelles were very large, we might also expect to find small positive ions, such as K^+ or Na^+ , taking part in the neutralizing of a portion of the charge on the surface of the negative micelles, and small negative ions, such as Cl^- , taking part in the neutralizing of the charge on the positive micelle in such a way as to preserve the electro-neutrality over the whole surface of the resulting substance. This picture is similar to that of the well-known Helmholtz double layer.

As an example, we may mention $Fe(OH)_3$, ferric hydroxide sol (5). We shall assume that it may be considered to be an agglomeration of excess hydrated ferric oxide and hydrated ferric ion arranged in more or less definitely oriented states with Cl^- ions neutralizing the charge. When this sol comes into contact with arsenious sulfide sol, which we might also consider to be a large negative micelle with Na^+ as the neutralizing positive ions, there is formed an "insoluble" substance which retains practically all of such sodium and chloride ions "adsorbed" on the precipitate. It is not likely that the atoms in the respective sols are able to rear-

range themselves in such a way as to form a definite ferric thioarsenite; it is more likely that they come together and retain to a large extent the individual structures of the micelle ions and thus necessarily give an opportunity for the sodium or chloride ions to compete for the neutralizing of charges in various parts of the clumping surfaces. This merely states that the ferric hydroxide sol itself is exchanging places with a certain number of sodium atoms at the surface of the arsenious sulfide sol. We have seen that the larger the number of charges on an electrolytic ion, the smaller the activity coefficient of that ion, and hence these precipitated clumps will give lower activity coefficients than arsenious sulfide sol of the same size. Indeed, we might picture such a mixture of crystalline clumps with the property of exchange of positive ions at certain points and the property of exchange of negative ions at other points. With large amphoteric protein micelles, e.g. anti-bodies, etc., this is not a particularly new conception.

THE TYPICAL IONIC CRYSTAL AS A COMPLEX

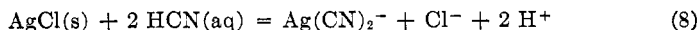
Returning to the case of a typical ionic crystal in its saturated or supersaturated solution, we may think of the neutralizing effect of the potassium ion near the six chloride ions in the crystal and of the chloride ion near the six potassium ions in the lattice as enabling the interionic forces to bind the whole into a single particle just as interionic forces or electronic bindings are able to bind their own ions into a micelle in the case of micelle-forming ions. There remains, however, the fact that, when we think of a single crystal, such as a potassium chloride crystal in contact with a solution, we no longer think of it as a colloidal solution; it is more useful to think in other terms. However, as far as the surface layer of the crystal is concerned, there are points where the attraction for a positive ion is greater than that for a negative ion, and an equal number of points at which the attraction for a negative ion is greater than that for a positive ion. As a matter of fact, all the atoms in the crystal are ultimately free to take part in a reaction, for if the supply of neutralizing ions in the solution is locally reduced, then another portion of the crystal will dissolve

in order to supply this deficiency. The effect at the surface of a potassium chloride crystal of the points of alternate attraction is to give a certain place orientation to the charges in the solution in the immediate vicinity.

COMPLEXES

We do not wish to enter into a mathematical discussion of the application of an interionic attraction model in this place. But, considered in a qualitative way, the effect of the distributed neutralization of the negative charge, postulated for the chloride micelle in equation 1, by the postulated charge upon the positive potassium micelle is to lower the calculated activity coefficient, just as the "association" assumed by Bjerrum (6) lowers the calculated activity coefficient of potassium nitrate.

Complex ions of the type $\text{Ag}(\text{NH}_3)_2^+$ or $\text{Ag}(\text{CN})_2^-$ are universally accepted as orthodox chemical entities. These ions take part in equilibria such as



and show in many respects the same kind of behavior as has been attributed to the typical micelles. Thus, the palmitate micelle dissociates when the concentration of the simple palmitate ion in the solution is decreased; and, with these complex ions, the ion dissociates when one of the products of its dissociation is used up.

We think of the formation of the complex of this type as due primarily to electronic binding between the component atoms; but some will prefer to explain the mechanism of their formation upon the basis of entirely interionic attraction relationships.

The complexes we have mentioned have very small dissociation constants, and just as we have acids and bases with small and large dissociation constants, we also have complexes with large dissociation constants. Thus, the divalent and trivalent metal chlorides and sulfates, which in the crystal form, have a great tendency to form double salts, probably form these easily dissociated complex ions³ of the types CdI_3^- , $\text{Mg}(\text{SO}_4)_2^{--}$, $\text{Al}(\text{SO}_4)_2^-$, CuBr_3^- , or CoCl_4^{--} .

³ McBain and Van Rysselberge, in an address before a meeting of the California Section of the American Chemical Society at San Francisco, May 11, 1928, re-

These easily dissociated complexes seem to be of interionic type related more closely perhaps to the crystal micelle of potassium chloride which we have chosen as an ultimate limit than to the complexes of the type of $\text{Ag}(\text{CN})_2^-$. There is good reason to think that ions more complex than the types we mentioned may be present in very concentrated solutions, for example, of silver chloride in very concentrated hydrochloric acid. If three chloride or iodide ions should unite to form a micelle, the field or charge on the ion would be so great that there might be attracted into this combination certain types of positive ions. Alkali ions are not strongly attracted to the complex, although in very concentrated solutions of potassium chloride we might expect to find evidence for the inclusion of rubidium or caesium ion (9). The difference may well be one of degree for the transference number of cadmium iodide (10) in aqueous solution is explained by McBain by the formation of the complex CdI_3^- , and in concentrated solutions of this salt in propyl and amyl alcohols McBain found evidence for the existence of micelles which would not pass through a membrane which was permeable to the ions as they exist in water solution (7).

With small bivalent and trivalent anions the tendency to form complex ions is much greater. We are familiar with the strong tendency of ferrous, cupric, cadmium, zinc, aluminum, chromium, ferric, etc., sulfates to form double salts with the sulfates of the alkali metals; and the experiments of McBain and Van Rysselberge (7) support the view that these metals enter a complex negative ion leaving the univalent cations to neutralize this charge in the same way that the potassium ion in a strong solution of potassium palmitate provides the means for electro-neutrality in these solutions. Of course, in mixed solutions of divalent or trivalent bases the positive ion which enters the complex depends upon

ported transference data which showed that the magnesium ion in mixed potassium and magnesium sulfates, the cadmium ion in mixed potassium and cadmium sulfates and mixed magnesium and cadmium sulfates, and the lithium ion in mixed potassium and lithium sulfates, moved to the anode in approximately molal solutions. The phenomena were ascribed by the speakers to the formation of complex anions of the type $\text{Cd}(\text{SO}_4)_2^{--}$. *J. Am. Chem. Soc.* **50**, 3009 (1928).

the relative complex-forming tendency of these ions with the particular anion.

We may also mention the explanation of the transference numbers of the alkali and alkaline earth casein salts (11). These substances in all probability form micelles in much the same way that the soap micelles are formed. The alkali is found to travel in both directions, and complicated chemical formulas were devised (12) to account for the effect; but if we merely postulate the partial neutralization of the charge on the micelle, by charges of the opposite kind, held in the orientation more strongly than others (complexes) and therefore dragged along with the micelle under the influence of the current, we have an explanation which will fit the facts, and it is essentially the same explanation which is given to explain the transference numbers of cadmium iodide or of cadmium sulfate in potassium sulfate solution.

McBain and Bowden (13) showed that a fraction of the potassium ion in the more concentrated solutions of potassium laurate was carried to the anode, which can be explained by assuming that some of the potassium ions function to reduce the charge on the negative micelle, and in this sense we would say that some complex ion had been formed. Such distributed neutralization of the charge is, however, probably of only secondary importance in this case.

The transference measurements made by Harman (14) with sodium silicate solutions do not definitely show this phenomenon of the partial neutralization of the charge on the micelles. These, however, are to be regarded as smaller aggregates than those of the soaps in the solutions which are considered.

The transference data of Wintgen (15), of Wintgen and Biltz (16) and of Wintgen and Löwenthal (17), for colloidal stannic oxide peptized by potassium hydroxide, for ferric oxide peptized by hydrochloric acid, and for chromic oxide peptized by ammonium chloride, respectively, show that a fraction of the potassium in the first case, and of the chloride in the second and third cases moves with the colloid; in other words, partially neutralizes the charge on the micelle.

We may imagine the structure of these complex ions or micelles

to be somewhat similar to that of the potassium chloride crystal in which the various atoms are held in more or less definite positions, but in which every atom is eventually free to move as it pleases. The crystal structure of the alums has been definitely determined by Wyckoff (18). These show the same kind of definite orientation as is shown by the potassium chloride crystal. Our point of departure is that at the surface of the alum crystal, in contact with its saturated solution, potassium ions and some of the complex $\text{Al}(\text{SO}_4)_2^-$ groups come off, but these complex groups are free to enter into the general equilibria of the solution. Even aluminum ions or sulfate ions themselves may be assumed to dissolve from the surface of the crystal as such. The preliminary measurements by Latimer and Greensfelder (19) of freezing point lowering of caesium and rubidium alums and an unpublished summary of freezing point measurements, show an abnormally low activity coefficient of the alums. It is obvious that the binding of the positive ion into the micelle or complex is a differential matter.

ORIENTATION IN MICELLES

McBain (2) has postulated that a micelle formed by, say ten, palmitate ions has a definite orientation which is thought to be that of a flat disk. This orientation is perhaps a consequence of the electronic bindings. As a palmitate solution is concentrated, the tendency for micelles with a larger number of ions to form becomes greater, and these are formed not only from the simple ions but also by an agglomeration of smaller micelles. The electronic bindings again must be a predominant characteristic of this union. The definiteness of the orientation will not be so marked in the case of these larger micelles formed from two or more smaller micelles and will not be as "perfect" as in the case of those formed directly from simple ions.

Let us again consider the formation of a micelle in its simplest terms, i.e., the union of two hydrated HSiO_3^- ions to form a hydrated $(\text{HSiO}_3)_2^{--}$ ion. As we have seen, this implies a certain degree of orientation which is not present in the solution containing only HSiO_3^- ions. And as more and more of the HSiO_3^-

ions combine into the micelle, the number of atoms definitely oriented becomes very great; and the sodium ions associated with them, because of the necessity of maintaining an average electrical neutrality in the solution, are also more or less fixed in their orientation. On the other hand, when a potassium chloride crystal forms from a solution, we have again a difference in the orientation of the ions, and there is a sudden change with very strong and definite orientation forces which may or may not involve, as in the case of micellar formation, the elimination of ionic solvation.

In the case of the acid sodium silicates, we saw (3f) that there was a tendency for the negative ion to "add" silica in varying proportions, and that there was a gradual transition of properties from the sodium silicate of 1 Na₂O:1 SiO₂ over to silicates with ratios of as high silica content as 1 Na₂O:5 SiO₂. We especially noticed the increasing tendency on the part of the solutions containing large amounts of silica to form micelles. With increasing amounts of silica, the viscosity of the silicates in water became great.

As we consider more and more concentrated solutions, we find the properties merging with those of the glasses, which are ill-defined crystalline substances, the lack of definition of which may, perhaps, be due to the fact that the aggregation of several micelles to form a larger micelle possesses within itself a less definite orientation than the individual micelles that come together. But if sufficient time were given and the thermal conditions were right, these would doubtless form crystals, because we know that glasses become definitely crystalline after a lapse of time.

It is obvious that the forces pertaining to the formation of micelles will not necessarily seek out molecules or micelles of their own kind; hence we may expect to have slipped into the aggregate a molecule or so of the wrong kind, which may account for the indefiniteness of composition of many colloidal substances.

We note that the tendency to form micelles is strongest with those substances that do not form well-defined crystals. The orientation force, in the case of the substances forming well-defined crystals, is sufficient to form immediately the definite crys-

tal lattice. Perhaps the relation between the micelle and the crystal is somewhat analogous to that between the liquid crystal and the crystal. It is perhaps significant that the substances which easily form micelles do not readily form crystals.

There are those who will object to the designation of so simple an oriented aggregation as $(\text{HSiO}_3^-)_2$ as a micelle, because of the belief that the more obvious relation is perhaps that of the complex ion. But we have taken such cases as the first step in the formation of the micelle, just as we have taken the crystal or the "amorphous" particle as the limit of the largest possible micelle.

We have treated solutions of visible micelles as a system consisting of a homogeneous phase. We might equally well, in a very real sense, have said that the treatment of the discontinuities, for example as in the Debye and Hückel (20) interionic attraction theory, lead us to consider the system heterogeneous and indeed, when the individual particles, or ions, become of ultramicroscopic size, the usual custom has been to treat these systems as heterogeneous. Either viewpoint will, of course, given an equally correct thermodynamic interpretation of the system, and we are free to use the one or the other, as long as we are consistent. Expediency dictates the system which we will use in any particular case.

BASE EXCHANGE IN GENERAL

All substances that form negative micelles in solution should then possess the differential base exchange properties and *vice versa*. Such systems ought to be realizable in several ways. A lump of gelatin placed in a mixture of chlorides should swell, and the ratio of bases in the gel should be different from that in the body of the solution. If a concentrated sodium soap solution is placed on the inside of a collodion cell and the cell placed in a solution of ammonium chloride, the ratio of the bases should be different.

Some of the ideas here presented may be further illustrated by experiments which, although as far as we are aware have never been performed, must, if our ideas are correct, give the results which we have indicated. If potassium silicate solution, con-

tained within a membrane cell permeable to potassium ion but not to silicate ion, is placed in a beaker containing a sodium chloride solution, then there will be a distribution by which some potassium ion will pass out through the membrane and enough chloride ion will pass in through the membrane to establish the Donnan equilibrium (21), and sodium ion equivalent to the potassium ion which has come out and also to the chloride ion which has gone in, will pass through the membrane.

If we assume that the activity coefficients of the sodium and potassium ions outside the membrane are equal, then the ratio of the sodium to the potassium inside the membrane need not be exactly proportional to the concentrations of these ions outside of the membrane because of the greater specific affinity for one of the ions, due either to a difference in the affinity, or to a difference in the activity coefficient due to the different "sizes" of the ions and a consequent different association in the Bjerrum (6) sense.

If we consider the swelling of gelatin in a mixed chloride solution, the ratio of the two ions inside the gelatin block need not be the same as that outside the block; and if the concentration of one of the substances in the mixed electrolyte is changed, we should expect a change in the concentration of that ion within the block, i.e., we should expect base exchange.

Petrie (22) found that the amount of absorption of certain positive ions, as NH_4^+ , K^+ , and Ca^{++} , by carrot disks was not equivalent to the amount of absorption of negative ions such as NO_3^- , Cl^- , SO_4^{--} , and explained the phenomena by assuming that chemical exchange of bases, rather than absorption, occurred. Stiles (23) showed that in the absorption of sodium chloride by carrot tissue the excess Na^+ absorbed was replaced by Ca^{++} , K^+ and Mg^{++} in the solution; and similar replacements were found by Redfern (24) and by Stoklasa (25) and his collaborators. There are abundant micelle-forming colloids in the carrot tissue.

Or, consider the case of sodium and calcium soaps in the presence of sodium and calcium ions. Here there are two ways of looking at the question; first, that the calcium ion and soap ion form an insoluble compound, calcium soap. But we might al-

most equally well have said that the tendency of the ions of the soap to form micelles has been increased by the specific attraction of the calcium ions which crowd out the sodium ions in the vicinity of the micelle, and that these micelles then further agglomerate to form the calcium soap which is insoluble. Herein arises the real difficulty in reconciling the viewpoint of the formation of a micelle with that of a so-called insoluble compound, for the question arises as to when a substance is merely insoluble and when we have merely a large single electrolytic crystal, such as that of potassium chloride, in contact with a saturated solution. These two viewpoints must lead to the same thermodynamic result; for, as has been pointed out, thermodynamics does not enquire into the mechanism of a process.

Another case of reversible base exchange is of the type studied by G. McP. Smith (26) and his co-workers, who studied the equilibrium between mixed alkali and alkaline earth metal amalgams and solutions of the chlorides or other negative ions of the same metals. In this case rapid equilibrium is obtained between the two liquid phases, and the relative proportion of a given metal in the amalgam depends upon the ratio of the molalities of that metal in the aqueous phase and upon the relative activity coefficients of the metals or metallic ions in the amalgam and solution, respectively.

In the same way the composition of a mixed crystal of caesium and potassium alum obtained from a slightly supersaturated solution of the salts depends upon the ratio of the molalities of the caesium and potassium ions, and the ratio of the activity coefficients of these ions in the aqueous solution and their activities in the mixed crystal. Also, if a crystal of potassium alum is dropped into a saturated solution of a definite mixed crystal, there will be a dissolution or replacement of some of the potassium ion by caesium ion, but this action will not proceed many layers of molecules into the surface of the crystal because the rate of diffusion into such a dense crystal, with strong orienting forces, is low. We are thus able to grow crystals with alternating layers of different isomorphous salts by transferring from one solution to another.

BASE EXCHANGE IN ZEOLITES

The most widely studied base-exchanging systems are those of the hydrated aluminosilicates. The various zeolites and silicates are among the most important constituents of the soils, and the permutites or artificial zeolites in particular have been much used

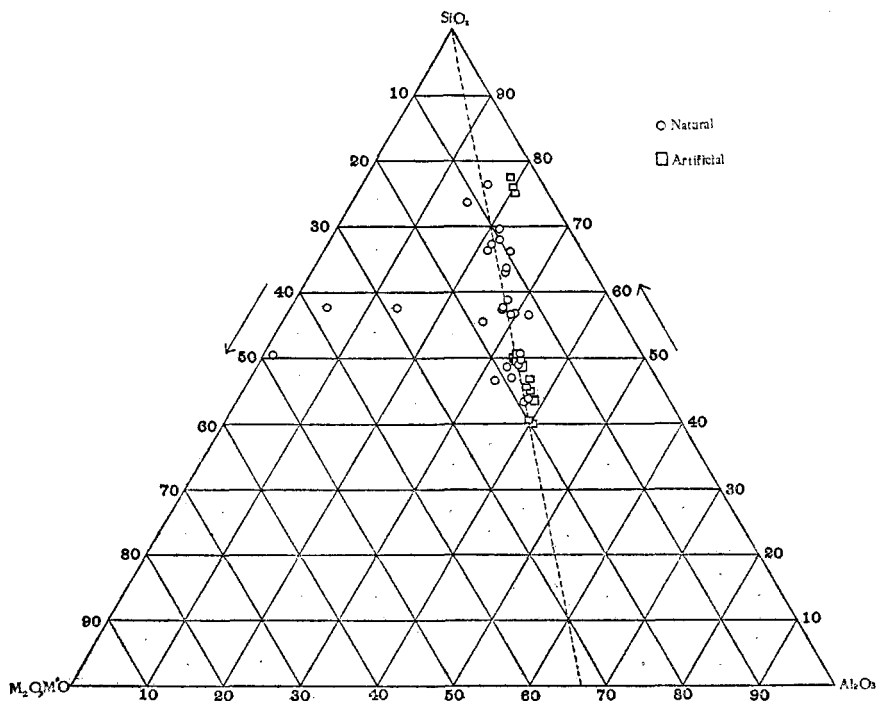


FIG. 1. COMPOSITION OF ZEOLITES

in technical water purification. These substances are classed as insoluble in water, and many of them are usually referred to as colloids. We shall summarize the principal communications relative to the properties of the zeolites, their composition and the theoretical explanations which have been proposed to explain their properties and shall finally indicate the way in which the foregoing point of view can be applied to these interesting substances.

Analyses

From the analyses of twenty-seven natural zeolites (27) given in the literature, we find a very definite, constant alkali-alkaline earth to aluminum oxide ratio. We have shown this graphically by plotting these analyses, calculated in mole percents, in figure 1. It will be noticed that only three of these twenty-seven points lie out of the immediate vicinity of the other twenty-four. At least two-thirds of the points lie on, or else very close to the dotted line, which we have drawn to show this relationship. There is a considerable variation in the ratios of alkalis to alkaline earths, which indicates that there is no such definite relationship as we find in the alkali-alkaline earth to aluminum oxide ratio.

The analyses of thirteen artificial zeolites (28), also shown graphically in figure 1, show the same constant alkali-alkaline earth to aluminum oxide ratio. Burgess and McGeorge conclude that zeolites are true chemical compounds, that they have a definite solubility and are capable of ionization.

Methods of preparation of artificial zeolites

A great many patents have been granted in Germany, Great Britain and the United States for the manufacture of artificial zeolites. Many of them are essentially the same, although slight variations occur. In general, the process consists of fusing together an alumina mineral, aluminum silicate, or aluminate, and an alkali and alkali carbonate with a sufficient quantity of an inorganic salt, preferably a borate, to ensure that on the extraction of the melt with water, there will remain only *crystalline* hydrated aluminum silicates (29). Frequently quartz or rocks rich in quartz are added, the proportions being so regulated that *no* free alkali or alkali carbonate is contained in the molten product (30). The transparent crystals or lamina obtained readily exchange their bases. It is planned that all the alkali shall combine with the Al_2O_3 and SiO_2 so that no gelatinous silicates or aluminates form when water is added (31).

Hydrous aluminum silicates are obtained when (32) a mixture of sodium sulfate and carbon is substituted, in the fusion process, for the alkali carbonate or soda. The sodium sulfide formed com-

bines with the silicic acid to form a sodium silicate. Sometimes the molten mass is broken up and subjected to the action of steam under pressure (33).

Occasionally products of approximately definite composition are obtained. If 2.5–3 parts of kaolin, 5–6.5 parts of sodium carbonate and 1.5–2.4 parts of borax are mixed together, the mixture fused, and the melt extracted with water, a product with the approximate formula $3\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{Na}_2\text{O}$ is obtained (34). This product may be used for removing soda and potash from saccharine juices or for purifying water. Another similar mixture consists of 56 parts of sodium carbonate, 12 parts of kaolin and 6–7 parts of potassium carbonate (35). After fusion, this forms a glassy melt which is crushed, the alkalis are dissolved out with hot water, and then the mass is recrushed.

Sometimes zeolites are formed by mixing solutions of alkali aluminate and alkali silicate, with the addition of sodium sulfate and sodium chloride, and then heating the mixture to the boiling point (36). The bulky precipitate is separated, washed, dried and calcined. (The aluminate solution is obtained by adding sodium hydroxide solution to a solution of an aluminum salt until the precipitate first formed redissolves.) This process is called the wet method, and usually employs very dilute solutions of the reagents (37). An example mentions 6 lbs. Na_2SO_4 , 12 gals. H_2O , 844 cc. of a solution of alumina containing 45.6 grams Al_2O_3 , and 315 grams of water glass solution at $45^\circ \text{Be}'$ containing 75 grams of SiO_2 . The precipitate obtained is washed, dried into a cake, broken up and hydrated in hot water.

One of the recent methods consists in forming the mixture so that there are two moles of CaO to each mole of SiO_2 (38). There is also added alkali metal hydroxide or carbonate to bring the ratio of alkali metal oxide to a point above an equivalent molecular proportion based on the alumina present. When the product is taken from the furnace, it is leached with a solution containing several moles of alkali for each mole of alumina present. The recovered alumina and other products obtained from the furnace may be used as fertilizers.

“Doucil” is prepared by mixing at a temperature below 20° a

dilute solution of sodium aluminate and neutral sodium silicate (39). The product contains 6 to 16 per cent of alumina depending upon the conditions. One cubic foot will soften a thousand gallons of water containing ten parts of calcium oxide per one hundred thousand. Four pounds of sodium chloride per cubic foot of material are required for regeneration. It is guaranteed that 5 per cent of the dry weight of the material can be exchanged for calcium compounds. Experimental work gives values of 7 to 8 per cent.

Artificial zeolites which have been used for softening water (so that their Na has been replaced by Ca and Mg) are regenerated by treatment with a solution of sodium chloride (40).

Water absorption and dehydration

There has been much discussion about the manner in which water occurs in zeolites. Panichi (41) maintains that ultramicroscopic observations indicate the crystalline character of zeolites. He measured the extinction angles under varying temperatures and accurately determined the loss of water on heating.

Zambonini (42) claims that zeolites are "solid solutions". Rothmund (43) allowed samples to stand for an hour over 1.0 N H_2SO_4 until they took up a definite quantity of water. They were then heated at a definite high temperature for 30 minutes and hydrated as before. The initial temperature was 100° ; it was raised 50° each time and continued up to 1000° . Thus the temperature at which loss of water becomes irreversible was determined. Zeolites vary as to the temperature at which they cease to be reversible with respect to loss of water. With silica, the water absorption is reversible only in a certain range, while with sodium permutite it is not really reversible under those conditions. Rothmund believes that there is a strong possibility that the water is held in "solid solution".

van Bemmelen (44), working with silica gel, states that its dehydration is not due to transitions of hydrates, but to physical changes in the structure of the gel. There is a point in the dehydration where the "volume" of the gel no longer decreases; at this point pores appear, causing opaqueness; at a further point the

opaque mass again becomes transparent. Characteristic points occur at various concentrations and vapor pressures, depending on the manner of preparation and age of the gel, the velocity of dehydration and the temperature.

Zeolites formed at lower temperatures (45) are richer in water (in molecular proportion) than those formed at higher temperatures. The zeolites in general differ from the other hydrous silicates in that their water content depends upon the fineness of subdivision, atmospheric conditions, etc. (46). For this reason, marked variations are found in their analyses. Natrolite was examined. On account of the presence of fluoride, on treatment with hydrochloric acid a part of the silicon escaped as silicon fluoride, giving low figures for silica, and the divergence in published analyses no doubt results from failure to take this fact into account. Of twenty-four other zeolites, all showed 0.4 to 4.0 per cent increase in water content on fine grinding. Upon this basis, he regards water as being chemically combined, since it appeared to obey the laws of definite proportions. The difference between the zeolites and the so-called true hydrous minerals was assumed to lie in the fact that the former have the same crystal form in both hydrous and anhydrous condition, so that on heating they do not disintegrate, as do the latter.

Vapor pressure measurements were made by Löwenstein (47) at temperatures varying from 24.5° to 26°. The material consisted of crystalline hydrates which remained clear during dehydration. These natural zeolites lost varying amounts of water. Substitution of their calcium by potassium (by digesting the powdered mineral for about 100 hours at 100° with frequently renewed 10 per cent potassium chloride solution) caused a decrease in the amount of water present but an increase in vapor pressure for the same water content. Treating these potassium zeolites with calcium chloride solutions, artificial calcium zeolites were obtained which proved, as regards their water content and vapor pressure, to be identical with the original zeolites within the experimental error.

Different specimens of hydrated silicic acids showed different vapor pressures for the same water content. It could not be

determined whether this was due to chemical differences or to differences in colloidal state. There were no discontinuities and hence no definite hydrates.

Grandjean (48) found that zeolites, after dehydration, absorb considerable quantities of ammonia, hydrogen sulfide, alcohol and sodium silicate. Absorption of iodine, bromine, calomel, mercury, sulfur and cinnabar caused marked changes in optical power, e.g., a large variation in optical angle, birefringence, and even a change in double refraction.

An artificial gel—a so-called potash permutite—was extracted with potassium chloride solution by Rostworoski and Wiegner (49) until no more calcium could be removed. The resulting permutite was washed with distilled water until free of chloride ions. The potassium permutite thus prepared had the normal power of exchanging bases, potassium for ammonium, etc., but, from solutions of phosphate in the forms of KH_2PO_4 and K_2HPO_4 , or KH_2PO_4 neutral toward phenolphthalein with potassium hydroxide, there was no appreciable absorption of phosphate.

Gédroit (50) found that the quantity of base absorbed in soils, but not “the energy of absorption”, depends on the nature of the cation. “Absorption energy” was greater with trivalent than with bivalent cations, and still less with monovalent cations. Calcium was absorbed more energetically than magnesium, and potassium than sodium. The zeolitic part of alkali soils was richer in sodium than in calcium.

Gédroit (51) looks upon the retention of dispersed substances by soil grains as mechanical adsorption, while the exchange of cations from solution is looked upon as a purely physical process which takes place on the *surface* of solid particles. He considers the exchange of bases to take place in complex alumino-silicates. Ammonium chloride solution of a concentration of 1.0–4.0 *N* was necessary for complete instantaneous base exchange. Physically adsorbed substances will be leached out, while those physico-chemically adsorbed will be retained so that the total concentration of the solution is not changed.

Structure of zeolites

Baschieri (52) considers zeolites to be salts of ortho-silicic acid, of meta-silicic acid, and of di-silicic acid (53), while Löwenstein (47) considers them salts of various hydrated silicic acids. Thus, different specimens showed different vapor pressures for the same water content. He could not determine whether this was due to a chemical difference or to a difference in colloidal state, because no discontinuities were observed. Consequently he concluded that the zeolites were not definite hydrates. On one hand, Gans (54) maintains that zeolites are definite chemical compounds and not adsorption compounds, on the ground that the Freundlich formula yields a constant with zeolites but should not do so with adsorption compounds. On the other hand, Wiegner (55) concludes that they are adsorption compounds because he found the displacement in hydrated amorphous silica gels in close accord with equations for adsorption reactions. Wiegner (56) also gives the explanation that the colloidal compound of aluminum hydroxide and silica, charged positively through the aluminum hydroxide, has a strong adsorptive power for OH^- ions. He considers the cations in equivalent quantities concentrated in the gel water. These gels, containing these bases in the gel water, constitute the "double silicates with replacement power." The gel is thus in adsorption equilibrium with reference to OH^- ions when in contact with water and supersaturated with cations, held electrochemically in the gel water. The cations, entering into the capillary spaces of the gel, displace equivalent cations. If the capillary spaces of the gel are reduced through partial dehydration, then the replacement power is reduced; and if the gel is fused, then there is no more replacement.

There have been attempts made to assign definite formulas to zeolites. Tschermak (57), from the analyses of twenty-one different zeolites, states that in all cases the ratio $(\text{Al})_2[\text{Ca}(\text{Sr}, \text{Ba}) + \text{Na}_2(\text{K}_2)]$ exists; and that if he omitted the oxygen, all zeolites had formulas represented by $\text{Si}_x\text{Al}_2\text{CaH}_{2y}$ and $\text{Si}_z\text{Al}_2\text{Na}_2\text{H}_{2v}$, where x and z range from 2 to 10, and y and v from 2 to 9; or, neglecting the hydrogen, they all contained a group $\text{Si}_2\text{Al}_2\text{CaO}_3$ or $\text{Si}_2\text{Al}_2\text{Na}_2\text{O}_3$. This latter group he regards as the nucleus. The

various zeolites are regarded as compounds of one or other of these nuclei with a silica acid, combined water and water of crystallization. The silicic acid and water of hydration are supposed to form a network enclosing the nuclei. Such a structure he regards as offering explanation for the variation of the optical characters of the zeolites with loss or gain of water, the various adsorption phenomena and the ease with which the bases may be replaced. Scurti (58) in maintaining that zeolites are salts of a series of aluminosilicic acids, states that some of the acidic hydroxy groups are attached to silicon and some to aluminum, thus explaining amphoteric properties. He relates the acidity of soils to the number of hydroxy groups attached to silicon in comparison with the number attached to aluminum.

Leitmeier (59) discusses the relations of colloidal and crystalline substances. There is great difference of opinion as to whether clay minerals are gels or definite chemical compounds. Gels of SiO_2 and Al_2O_3 change to crystalline forms with extreme slowness. Winchell (60) states that zeolites form a number of isomorphous series, and that in any one series, variations may occur so that in each series $\text{Ca} + 2\text{Na}$ (atoms) is a constant; also that the $\text{Al}_2\text{O}_3:\text{CaO}$ ratio is unity for all zeolites and that the ratio of $(\text{Al} + \text{Si}):\text{O}$ is always 1:2. Only a few exceptions occur.

Weigel (61) pictures a very definite structure for zeolites. He states that in their formation, where the silicate particles have assumed a comparatively rigid lattice orientation, the solvent, in which the crystals form, remains within the lattice meshes, without, however, contributing to the lattice structure. Energy is lost through overcoming the internal pressure of the solvent, and this energy aids in the erection of the lattice. The latter retains its rigidity under various conditions, and the energy of the internal pressure is free and serves to bind foreign substances. The ready exchange of bases is explained by weakened bonds in the silicate lattice. He expresses the relation between temperature, the vapor pressure of the surroundings and the amount of adsorbed foreign molecules by a modified van der Waals' equation:

$$n = n/b - [R(T - T_0)v^2]/[a(v - nb)]$$

where n is the number of adsorbed molecules in a silicate molecule, R is the gas constant, T the absolute temperature, T_s the temperature of the saturation pressure of the liquid phase of the foreign substance which itself is at temperature T in the medium surrounding the crystal, a the van der Waals' constant of the medium in which the zeolite forms at the temperature and pressure involved, and b a constant. Weigel has shown that the equation has, within certain limits, given results conforming well to the experimental material available. Ridley (62) considers silicates to be 10- or 12-membered rings of alternate silicon or aluminum and oxygen atoms. Rothmund (63) has recently expressed the opinion that zeolites hold water in the same way as gels and not as hydrated salts, since the water molecules take no essential part in the crystal structure.

Base Exchange

Much has been written about base exchange in zeolites. The idea can be traced (64) from Way's original papers in 1850 through the various commercial and industrial applications. In studying the subject, it is necessary to know the properties of both the simple silicates and the alumino-silicates. Thus Gans (65) found that silicates obtained from material extracted from soils by dilute hydrochloric acid resembled zeolites in replacement of their bases by salt solutions, their behavior towards boiling water, higher temperature, lime and soda. Consequently he divided zeolites into two classes, namely (1) those which very readily exchange their bases and (2) those in which the exchange takes a long time.

In Gans's first class the bases are united only to the aluminum; thus the silicic acid is combined with such groups as $\text{Al}(\text{OH})(\text{ONa})$ or $\text{Al}(\text{ONa})_2$. In the second class the bases are united directly to the silicic acid. He made artificial products of the first class by the action of alkali aluminate on hydrous silicic acid, silicious sinter, infusorial earth, etc., or on the alkali silicate solution. A product of the second class was prepared by the action of an alkali silicate on aluminum hydroxide. He calls the first class the aluminate-silicate-zeolites; the second class the alumina-

double-silicate-zeolites. The first group rarely occurs pure in nature. The Al-free apophyllite does not exchange its bases in a short time; they are therefore united to the silicic acid. He places zeolitic compounds of arable field soils in the first group. Concentrated ammonium chloride solutions were found to exchange the bases of the finely ground zeolites of the first class in two days, while no bases of the zeolites of the second class went into solution. The two classes are formed by the mingling of the decomposition solutions of alkali aluminates and alkali silicates, or through hydration of aluminum silicates. If carbonic acid is absent the aluminate silicates of the first class form, otherwise those of the second class or mixtures of the two, because alumina is precipitated by carbonic acid. The first class is of great technical importance, as zeolites of this class are capable of exchanging their lime for the alkali and trimethyl glycol content of molasses and therefore permit of an increased crystallization of sugar. By the action of calcium chloride solutions the alkali aluminate silicates can be changed to calcium aluminate silicates.

Zoch (66) shook zeolites in solutions of ammonium chloride. He found the reaction at first comparatively rapid although equilibrium was reached only slowly. Thus with stilbite in grains of 0.25–5 mm. diameter equilibrium was reached after forty to fifty days. Temperature, fineness and quantity of powder, and strength of solution all exert an influence. There was an exchange of the bases calcium, sodium and potassium only, these being replaced by an equivalent amount of ammonium. Alumina and silica did not pass into solution, and the amount of chloride in the latter remained constant. Substitution was accompanied by change in optical characters of the material.

The reaction of powdered chabazite specimens with 0.1–0.66 *N* alkali chloride solutions was studied by Reiner (67) at 13° and 60°. Base exchange was indicated by the liberated calcium. The data obtained show the effect of heat and of concentration of solution in promoting base exchange. In order of their ability to replace calcium from the mineral, the alkalies are potassium, ammonium, sodium and lithium. Desmine, in which half of the calcium was replaced by potassium, reacted somewhat with silver

nitrate solution. A slight break in the time-reaction curve occurs when the bases reach the ratio $\text{CaO}:(\text{K}_2\text{O} + \text{Ag}_2\text{O}) = 1.2$. Under the influence of Roentgen rays, the reaction ended in thirty minutes, although it was less than half complete. Without these rays, the reaction went more nearly to completion, if at all, but only after ten or more days. Reiner postulated the formation, by the rays, of ions in the mineral which do not exchange bases.

In separating zeolitic powders in potassium mercuric iodide solution, Walker (68) found several were attacked with nearly complete replacement of the original sodium by potassium. Thus a gmelinite separated by organic liquids gave $\text{Na}_2\text{O} = 10.08$ per cent and $\text{K}_2\text{O} = 0.69$ per cent, while the same mineral separated as above gave $\text{Na}_2\text{O} = 1.20$ per cent and $\text{K}_2\text{O} = 14.86$ per cent. Okenite, originally containing 0.60 per cent K_2O showed, after the separation, 2.24 per cent. Some irregularities in published zeolite analyses may have been due to reactions having occurred with separating solutions.

Analyses were made by Hulbert (69) of three commercial zeolites under exactly identical conditions; first when regenerated with sodium chloride, and again when sufficient magnesium sulfate solution was passed through the silicate to bring about the most complete exchange or replacement of sodium by magnesium. The experiments were repeated with calcium chloride, and definite relative capacities of the zeolites for exchange of different ions was established.

Vogtherr (70) concluded that the active exchangeable bases are embedded in the porous structure of the zeolites, in whose fine capillaries the exchange action takes place. He thought that the silicate itself, whether composed of silica alone, or in combination with alumina or iron oxide, did not play any function in the exchange of bases except to furnish a medium of suitable physical nature.

Base exchange in permutites is believed by Wiegner and Jenny (71) to depend upon ionic interchange and in turn upon the hydration of the ions in solution. They found a definite relation between the exchange and the atomic volume of the ions.

Adsorption studies by Ramann (72) show that quartz adsorbs

alkaline compounds strongly, but neutral salts and acids in traces only. Base exchange studies with permutite by Ramann (72) indicate that the exchange is always in chemically equivalent quantities. The more easily a metal is taken up, the more difficult it is to displace it. Ions were taken up in the following order: $\text{Mg} < \text{Li} < \text{Ca} < \text{Na} < \text{Ba} < \text{NH}_4 < \text{K} < \text{H}$. With alkaline solutions, an absorption of bases in addition to the exchange occurs. The exchange of hydrogen ions for neutral salts was incomplete.

Frankforter and Jensen (73) made a series of preliminary experiments to determine the mechanism of the exchange reactions taking place when an alkali metal zeolite or permutite is treated with an alkaline earth metal, or *vice versa*, using aqueous solutions of sodium, calcium and barium chlorides of various concentrations. A large excess of the replacing metallic ion was necessary for complete exchange. Barium showed approximately 4.5 times the replacing power of calcium when both were present in equivalent amounts. Exchange reactions were more nearly complete with dilute than with concentrated solutions, an observation they take to indicate that these reactions are ionic.

Equilibria in solutions of two salts of varying concentrations when shaken with permutite containing the same cations as the solution, were investigated by Günther-Schulze (74). This was done with the object of ascertaining the concentration of the solution which is in equilibrium with the permutite. The experiments were carried out at 22° with 50 per cent silver and 50 per cent ammonium, 33.33 per cent copper and 66.67 per cent ammonium, 4 per cent lanthanum and 96 per cent ammonium permutites. All the solutions contained the respective salts as nitrates. The results show that to a certain extent the demands of the law of mass action are fulfilled.

Copper chloride, acetate, formate, sulfate, chlorate, nitrate and bromide solutions were also investigated (75) by shaking known concentrations of the salts with pure potassium permutite. From measurements of exchange of cations between the permutite and the solution he drew conclusions as to the presence of complexes in the solution. Thus, even at greatest dilution the simple complex cation CuR^+ was assumed present in practically all of the

copper salt solutions examined. The presence of the complex Cu_2R_3^+ was considered proved only in the case of the copper chloride and bromide. He thought it probable that the other salts exhibit the higher complex formation, which, however, is not present to such a great extent. The complexity of copper salt solutions increases at constant concentration with the strength of the acid, and is greater with the salts of halogen acids than with the salts of oxygen acids of equal strength. His data may, however, be interpreted in a much simpler manner.

Interchange of bases, occurring in mixed solutions containing two different bases, has been studied by Ramann and Spengel (76) by means of a permutite of moderately constant composition prepared in the wet way. The replacement of bases taking place when such a hydrated aluminum silicate was treated with neutral potassium, ammonium, calcium and sodium salts had the character of a chemical change, no signs of physical adsorption being detectable. The interchanges were by equivalents, that of potassium and ammonium following the law of mass action. The curves expressing the ratios of the ions in solution and those of the bases in the silicates are coincident. In solutions containing sodium and calcium salts, the interchange of bases corresponded predominantly with the ratio of the ions in the solution, but preponderance of the calcium or sodium salts resulted in divergences dependent upon a second factor of unknown nature. Potassium and ammonium were mutually replaceable, and displaced sodium and calcium completely from the silicate; whereas the displacement of potassium and ammonium by sodium and calcium was incomplete. The ratios between the bases in the solutions and in the silicates have different values. Bases present in small proportions in the solutions were combined by the silicate in amounts greater than those corresponding with such proportions. Within wide limits the absolute concentrations of the salts in the solution are without appreciable influence on the composition of the silicate, this being the case even with mixtures of calcium salts with those of the univalent metals.

Kornfeld (77) found that shaking for twenty minutes was sufficient to complete the interchange of sodium in sodium permutite

by silver, and of silver in silver permutite by potassium, barium, and ammonium. In all cases except the replacement of silver by barium, the concentration of the solution had no effect on the amount of change. The change between sodium permutite and silver is represented by the equation

$$[\text{Ag (in permutite)}/\text{Na(in permutite)}]^{1.64} \times c(\text{Na}^+)/c(\text{Ag}^+) = 129$$

In the case of silver permutite and ammonium nitrate, the reaction is represented by

$$[\text{Ag (in permutite)}/\text{NH}_4 \text{ (in permutite)}]^{1.67} \times c(\text{NH}_4^+)/c(\text{Ag}^+) = 37.7$$

The replacement of silver by potassium is given by the equation

$$[\text{Ag (in permutite)}/\text{K (in permutite)}]^{2.17} \times c(\text{K}^+)/c(\text{Ag}^+) = 9.9$$

and the replacement of silver by barium by the formula

$$[\text{Ag (in permutite)}/\text{Ba}^{\frac{1}{2}} \text{ (in permutite)}]^{2.8} \times c^{\frac{1}{2}}(\text{Ba}^{++})/c(\text{Ag}^+) = 1.5$$

Rothmund and Kornfeld (78) also found that when the finely powdered solid is shaken up with a salt solution, the replacement of the cation by some other cation reaches an equilibrium in less than ten minutes. They considered the reaction to be chemical and not merely adsorption. Experiments were carried out with silver and sodium permutites and the nitrates of sodium, potassium, rubidium, lithium, ammonium, thallium, and silver. If c_1 and c_2 represent the concentration of the bases in the solution and c_1' and c_2' in the solid permutite in equilibrium with the solution, it is shown that some power β can be found so that the ratio

$$(c_1/c_2)/(c_1'/c_2')^\beta = K$$

where K is a constant. The value of β is generally about 0.5.

Rothmund and Kornfeld (79) also examined bivalent and trivalent ions. The theoretical relations previously derived for univalent interchange, and extended to other types, are confirmed in these cases, also, both for bi-bivalent and for uni-bivalent interchange.

In the case of silicates, present in the soil, relations analogous to those in permutites are discussed by Ramann (80). Thus the replacement of the bases by alkalies and by ammonium is

assumed to depend upon ionic reactions: equivalent quantities of the cations are introduced into the permutites independent of the nature of the anion present in the solution. The composition of the permutite at the end of the reaction was found independent of the total concentration of the solution.

The ammonium in ammonium permutite can be replaced by other bases by treatment with solutions of salts. Ramann and Spengel (81) found that when sodium and potassium were the bases used, the resulting product containing sodium, potassium, and ammonium in the ratio of the corresponding ions in the solution; but when calcium was present the exchange as regards this base did not comply with this simple law.

The decomposition of natural silicates, which cannot always be adequately accounted for by the action of water and carbonic acid, was thought by Ramann and Junk (82) to be related to the following. The reaction, in the formation of magnesium permutite by the action of magnesium salts on ammonium, sodium and potassium permutites, is ionic; and there is no evidence of physical adsorption. Pure magnesium permutite could not be obtained, not more than half of the bases present in the original permutite being displaced by the magnesium. The whole of the ammonium in ammonium permutite could not be displaced with carnallite or kainite solution. Mixed salt solutions decompose the permutite to some extent, especially solutions containing magnesium or ammonium.

THE ZEOLITE AS A MICELLE

In a previous section, we saw that the activity coefficient of a micelle decreases as the number of ions aggregating to form the micelle increases. In the limit, if all the ions, for instance the negative ions, in a given solution, combine to form a single micelle, then an extension of our ideas of the properties of an electrolytic solution predicts that the activity coefficient of such a micelle is nearly zero. In other words, the micelle still retains the characteristics of an electrolyte in much the same way that a typical crystal retains the properties of an electrolyte. Perhaps it is only a point of view which distinguishes the ordinary conception of a

solid solution from that which we are presenting. The same thermodynamic requirements are maintained. However, the viewpoint here taken allows us to consider systems which come rapidly to equilibrium only on the surface of the solid. Because the ordinary processes of diffusion in a crystalline solid are slow, the actual attainment of equilibrium throughout a solid is also slow.

The rate of attainment of equilibrium of the zeolites with the solutions with which they are in contact is rapid, but the zeolites after many cycles of base exchange, in the presence of small amounts of carbon dioxide, gradually lose their efficiency. Furthermore, as we have seen, the ratio of the bases in the liquid phase to the bases in the solid phase is not always constant but varies with the method of manufacture of an artificial zeolite or the method of deposition of a natural zeolite.

Zeolites and related substances are all salts of alumino-silicates. Let us assume that the negative ions of the alumino-silicate form large micelles, and that the constraints between the atoms are large. The substances would therefore behave as very viscous liquids or as glass-like solids. The positive ions, because of the rigidity of the system, are held tightly to the micelle in order to maintain the electro-neutrality of the system.

We will assume that the zeolite has been treated with a concentrated solution of sodium chloride so that the only positive ions present on the surface of the micelles are sodium ions. If now a new solution of calcium or ammonium chloride is substituted for the sodium chloride, the ratio of sodium to ammonium ions in the solution to sodium to ammonium in the zeolite becomes a constant for the particular sample of zeolite.

The natural zeolites show all the optical characteristics of definitely crystalline substances. On the other hand, the artificial zeolites, from their method of preparation, would appear to have more of the character of amorphous substances. The individual micelle or ramifying aggregate of micelles may have a more or less regular lattice arrangement. The tendency, as we have seen, is to regard these natural and artificial zeolites as compounds of different composition, or at least as solid solutions of a number of definite chemical individuals, such as calcium alumino-silicate and sodium alumino-silicate, etc.

When an artificial zeolite is prepared by mixing sodium aluminate with sodium silicate in different proportions, there usually results a complex sodium alumino-silicate which approaches the same composition as that of natural nephelite, i.e., the composition of the zeolite differs little whether a small or large amount of sodium aluminate is employed, except that with a large amount the firm gel forms instantly. However, all alumino-silicates with wide variation in ratio of silica to alumina show the base exchange property.

In figure 1 we showed the composition of various natural and artificial zeolites. Their capacity for base exchange depends not so much on the composition as upon their "history." In the formation of zeolites, we therefore think of the process as being one in which the aluminate and silicate ions, because of their electron affinity, react to form very strongly micellar-forming acid ions. The positive ions are then bound to the multi-charged ionic micelle in order to maintain electro-neutrality in the immediate vicinity of the large charged mass. And while there may be a real orientation of the atoms in the most efficient base-exchanging zeolites, these positive "held" ions must be in such a position that they are readily diffusible into a solution in which the micelle is placed. The variability of the composition of the zeolite supports this view.

Biesalski (83) found that pure acid-silicate grains (84) containing high proportions of silica,—(a) SiO_2 90.1 per cent, Na_2O 3.0 per cent; loss on heating 7.3 per cent; (b) SiO_2 85 per cent, Na_2O 4.4 per cent, loss 10.6 per cent; (c) SiO_2 75.3 per cent, Na_2O 3.8 per cent, loss 20.1 per cent—possessed the property of base exchange. These sodium silicate grains contain so high a proportion of silica that they are either insoluble or extremely slowly soluble. The probability of the micellar character of these highly silicious hydrous sodium silicates is indicated by the discussion in a previous paper (3e).

Biesalski (83) also studied complex sodium silicates of the type in which zinc replaces the aluminum in a zeolite (85), SiO_2 35.4 per cent, ZnO 20.0 per cent, Na_2O 10.7 per cent, loss 33.8 per cent. He found base exchange properties. These experiments indicate

that the base exchange property of the zeolites is not necessarily a property of the aluminosilicate but more of the silica, which we have seen has the property of forming electrolytic micelles (3f). In the grains these micelles are rigidly fixed, but this inability of the micelle to take part in a Brownian movement does not alter the character of the base exchange process. The tendency noted in figure 1 for the aluminosilicates to form with a constant ratio of replaceable base to alumina must be related to the chemical character of the aluminate.

Zeolites usually lose their base exchange properties upon the repetition of the base exchange cycle. This is ordinarily explained on the basis of the hydrolysis of the zeolite, which process, indeed, we saw (3f) to be operative in the case of the pure sodium silicates. This hydrolytic process is hastened by acids, even as weak as carbonic acid, competing for the base ion equivalent to the hydroxyl ion formed by the hydrolytic splitting of a part of the micelle.

With the definitely crystalline zeolites, there is no constant ratio between the ratio of the activities of the base ions in the solution and the ratio of the bases in the zeolites. If we substitute the ratio of the activities of the bases in the solid solution of the zeolite, such constancy must exist if sufficient time to reach equilibrium throughout the solid mass is given. The viewpoint of the electrolytic micelle merely focuses our attention upon the easy metathetical exchange characteristic of ionic reactions.

We have mentioned the specificity of the binding of positive ions to a micelle such as that postulated in the case of the insoluble soap. It is obvious that that portion of the decrease in the activity coefficient which is due to the "association" in the Bjerrum sense must be specific; and hence arises the reason for the ratio of the concentrations of the salts in the solution being different from their ratio of existence in the micelle. In looking at this in another way, we might say that the solubility of calcium aluminosilicate is less than that of sodium aluminosilicate, while, from the viewpoint of micellar formation we would say that the activity coefficient of the calcium micelle is less than that of the sodium micelle. But this does not preclude the possibility that

both calcium and sodium ions may be adjacent as contributors to the electrical neutrality of the small micellar particle. We are here trying to unify the ideas of the adsorption theory and those of the chemical theory. We take the crystalline zeolites as examples of micelles of very large numbers of atoms.

SUMMARY

Micelles are considered as the intermediate steps between ordinary ions and solid crystals. The solution of micelles is taken as a homogeneous phase, and the thermodynamics of such a system is therefore that of the homogeneous phase rather than that of the heterogeneous system.

In this paper the following topics have been discussed:

1. The consequences of the extension of the theory of the formation of micelles when very large aggregates are formed.
2. The electrolytic nature of crystalline and near crystalline micelles. The activity coefficient of such crystalline micellar masses is practically zero.
3. The relation of complexes and micelles.
4. The rapid base or acid exchange properties of solid solutions and of zeolites. This is explained by the electrolytic nature of the solids.
5. Base exchange in other systems.
6. Base exchange in zeolites.

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