

to enter upon what is perhaps the most promising next step in the development of the sciences: namely cooperative undertakings on a large scale involving chemistry-physics, chemistry-engineering, chemistry-geology, chemistry-biology, and the like. Many of the pressing problems of the immediate future are too large for any individual or for any single department. In this way, on its scientific side, the university may best serve the community. Thus it may better perform the prime function of every true university—the *advancement of knowledge*.

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THE ORIGIN OF SOIL COLLOIDS AND THE REASON FOR THE EXISTENCE OF THIS STATE OF MATTERS

In the mechanical analysis of hundreds of samples of soil by the beaker method, the microscopical control of the subsidence of the clay group indicated that the smallest diameter of a clay particle is about 0.0001 mm. while the water from which the sediment subsided was clear and transparent.

At first thought it would appear that in a soil which has weathered under many agencies, such as the grinding of glacial ice, the abrasion of flood waters, the pounding of ocean waves, and other agencies of attrition due to soil movements operating through untold ages, material of every degree of fineness would accumulate, passing down below the limit of microscopic vision. Practically however this does not appear to be the case as the finest material of the soil, called the clay group, excluding the colloidal material, to be discussed later, ranges in diameter from .005 to .0001 mm. The question naturally arises as to what has become of the material of smaller size.

My present view is that particles of matter derived from silicate rocks and other soil-forming minerals when they approach a diameter of .0001 mm. contain relatively so few molecules that the bombardment of the water molecules in which the particle is im-

mersed shatters the particle beyond the ability of the molecules in the solid to hold together as a solid mass. The atoms of calcium, magnesium, potassium and sodium in the molecule of the silicate would go for the most part into true solution, while the atoms of silicon, aluminum, and iron would go chiefly into colloidal solution forming the basis of the colloidal matter or the ultra clay of the soil. It should be possible for the mathematical physical chemist, from physical constants now known, to determine empirically the relative size of the particle of matter which could withstand such bombardment without complete disintegration. This is a problem which has not yet been worked out.¹

There appears to be a certain equilibrium established between the colloidal state and the truly soluble state as there is always a small proportion of silicon, aluminum, and iron which seem to be in real solution, as they pass through a Pasteur-Chamberland filter and separate out on evaporating the solution not as a colloid but as an amorphous mass of hard scale-like material, like a boiler scale, without absorptive properties.

It is that portion of the silicon, aluminum, and iron which collects on the outside of the Pasteur-Chamberland filter in a truly colloidal condition which is recognized as the ultra clay.

This colloidal matter is very absorptive and takes into itself a considerable quantity of salts of calcium, magnesium, potassium, and

¹ Another way of looking at this is from the point of view of the internal energy of the system. The molecular attraction between the molecules of the solid and the molecular attraction between water molecules themselves and between the molecules of the solid and of the water must come to equilibrium. If the solid particle becomes relatively small in diameter there will be relatively few molecules in the solid to hold together against the attraction of the increasing number of water molecules surrounding them as the size of the solid particle diminishes. The attraction of water molecules for solids which it wets, as, for instance, glass, is seen in the relatively high temperatures and therefore high energies required to remove the *last traces* of water from the solid.

sodium which were in free solution but which are changed in the absorbing medium to a colloidal state in which they are extremely inactive and in which state they fail to respond to reagents that would normally reveal their presence. It is a matter of very great difficulty, therefore, to determine whether the electrolytes found in the ultimate analysis of the ultra-clay are constitutionally combined with the silicate of alumina and iron, or whether they merely exist in a passive colloidal state.

THE TRUE SOLUTION

The study of ultra clay includes fundamental problems of physical chemistry, particularly the differences in state between true solutions and colloidal solutions. The modern concept of solutions ascribes a rather complex form to the molecule of water. The molecule of a salt dissolved in water forms numerous and indefinite hydrates with the surrounding water molecules. The complexity of these hydrates is influenced by concentration and by temperature, or in other words by the balance in the internal energy of the system expressed by the activities of the water molecules on the one hand and the activities of the salt molecules on the other, as well as the activity or energy exerted between the water molecules and the salt molecules.

Little is known about the complexity of the hydrates in the solution. We have actual data only when certain salts crystallize from the solution. With salts that crystallize with water of hydration the lowest hydrates are formed at the higher temperatures and the higher hydrates are formed at the lower temperatures. Magnesium chloride is known to crystallize with five different amounts of water, namely, 2, 4, 6, 8, and 12 H_2O . The higher hydrate (12 H_2O) separates at temperatures between 16.8° to -33.6° C. The lowest hydrate comes out at 181.5° C.

Sodium carbonate is known with three states of hydration, namely, 1, 7, and 10 H_2O , depending upon the temperature. If intermediate hydrates occur they do not appear

to be stable forms. It would appear therefore that 12 H_2O is the highest stable hydrate formed in crystals except for the double molecules of the alums which carry twice this amount or 24 H_2O . Sodium chloride crystallizes out at ordinary temperatures without water of hydration, the crystal being completely dry on the inside. It is said to crystallize with 2 H_2O at temperatures somewhat below zero. Sodium sulphate crystallizing at room temperature immediately changes under the same temperature conditions to the anhydrous form when the solution becomes saturated with sodium chloride. This gives us a vision of only a few proportions of water which fit into the molecular structure of the crystal in permanent form. It throws no other light upon proportions of water of hydration which may occur in solution which would not fit into the structure of a crystal in stable form.

The strength of these hydrates differs markedly. Sodium carbonate with 10 H_2O on exposure to air is reduced to sodium carbonate with 1 H_2O . Sodium sulphate with 10 H_2O gives off free water under pressure as when pestled. Any of the three known hydrates of calcium chloride, namely, 2, 4, 6 H_2O , absorbs water when exposed to ordinary air, which changes from a gaseous to a liquid state in which the calcium chloride finally dissolves.

It appears therefore that the water of hydration is influenced by the internal energy of the system and may be modified by the external pressure of the water vapor in the air and by mechanical force.

There are of course numerous cases where salts crystallize without water of hydration or where they come down in the form of amorphous material without crystalline form. There are likewise numerous cases where it is difficult to secure crystals and often impossible to separate material in a solid state which ordinarily comes out in a solid form. The difficulties in obtaining sugar in a solid form with certain impurities, particularly glucose and potassium, or iron, is a case in point. The impossibility of obtaining ortho-

phosphoric acid in a solid state from solutions containing certain impurities is another case in point.

Many of the salts which contain water of crystallization, especially the sulphate carbonate, and acetate of sodium, are remarkable for the fact that when solutions are prepared free from dust and under perfectly quiescent conditions they refuse to crystallize far below their ordinary point of saturation unless they are disturbed by agitation, by particles of dust or particularly by introduction of crystals of the material, when they suddenly crystallize throughout the entire mass. Jeanne years ago stated that he assumes "that saturated solutions when heated form peculiar hydrates and that these remain unaltered when the temperature is lowered but that vibration or the presence of a crystal of the salt is sufficient to bring about their decomposition."

It has been observed by Ostwald that previous to the formation of sodium chloride crystals points of congestion may be noted where droplets form and can be seen under the ultra microscope. This is analogous to the suspensoid form of droplet of a colloidal body, but while the colloidal droplet is stopped from going further the sodium chloride droplet completes its course by coming together into a crystalline mass with the complete exclusion of the water of hydration which has surrounded the molecule in its solution state. Under conditions of supersaturation above referred to it is supposed that these centers of congestion are avoided and crystallization does not occur until by agitation or the introduction of nuclei such centers of congestion are brought about.

COLLOID SOLUTIONS

It would appear that the colloidal state of the silicon, aluminum, and iron is such, the hydrates formed with the water molecules are so complex and the internal energy of the system is so low that the molecules of silicon, aluminum, and iron, and the same would probably be true for colloidal platinum, gold and silver, are unable at ordinary tempera-

tures to combine as a crystalline or amorphous mass. If the temperature is raised to 900 or 1000° the last traces of water disappear, they lose completely their colloidal properties and take on the form of an amorphous mass.

The modern concept of the atom shows a central nucleus charged with positive electricity surrounded by many electrons with negative charges. If the two forces are perfectly balanced the material is inert as in the case of nitrogen gas. The activity of the atoms of other elements depends upon the extent to which this balance is thrown off to one side or the other.

From the modern concept of solutions it would appear that the silicon, aluminum and iron are completely dissociated in their colloidal solution but the positive and the negative portions of the molecules are so balanced that they are in an extremely inactive condition and substances absorbed by them become equally inert and inactive for the same cause and thus change their state from a condition of true solution to a colloidal solution.

The principles of dyeing appear to be based upon a similar change of state. The dye in true solution enters a colloidal membrane such as silk or wool, is changed to a colloidal state in and on the membrane from which it can not thereafter be dislodged with water as the colloidal solution is immiscible with water. The principles of dyeing seem to rest upon the ability of certain materials including mordants which are of such conditions that they have the power to bring about this change of state.

The colloidal material separated from soils in a dilution not exceeding one gram per liter after thorough agitation appears under the ultra microscope as minute droplets showing points of congestion such as precede the formation of salt crystals and appear as droplets of fat suspended in milk or as fog appears in the cloud. In larger concentrations these droplets coalesce into larger masses as the fat globules coalesce on rising into cream or as the droplets of fog coalesce to form the liquid water of larger drops. Fog follows neither the laws of gases nor the laws of liquids. The soil colloid

in suspension in water may be coalesced by salt or lime solutions but the change is not sufficient to overcome the colloidal state as in the case of the coalescence of the fog particles into liquid water, and on removing the coagulating agency the colloidal matter may again be put in suspension.

As before stated the only means yet discovered to change the colloidal nature of the soil colloids is through an enormous expenditure of energy in heating the material to 900° or 1000° to completely drive off the water of hydration and leave the material an amorphous mass lacking entirely colloidal properties. This is too expensive a method to be used in agriculture or in road construction to particularly affect the plasticity of the wet clays. The problem before the soil chemist and the road engineer is to bring about a change in the internal energy of the soil colloid so as to break up the complex hydrates and permit the atoms or molecules of silicon, aluminum, and iron to form a crystalline or an amorphous solid and thus make the extremely plastic clays less plastic and more friable.

The molecular weights of colloids determined from diffusion or from freezing point are very high, reaching the figure 25,000 for starch. The question arises as to whether this figure is applicable to the molecule of the anhydrous colloid or to the colloidal molecule associated with the extremely complex system of hydrates that have attached themselves to the molecule of the colloidal substance. Numerous cases have been reported where zeolites have formed after the percolation of soil moisture through exceedingly small openings in rocks and building stones. The question arises as to whether sufficient force can be exerted to force a colloidal solution through openings too small to carry the associated water of hydration, and whether under these conditions, like the stirring of a supersaturated solution, the molecules of the colloid could be brought sufficiently close to combine into a crystalline or amorphous solid.

This is of theoretical interest only. The practical problem seems to be to find some cheap method of breaking up the complex

hydrates to give the atoms of silicon, aluminum and iron, or the hydrated molecules of the silicate an opportunity to combine in a solid form.

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WHEN WILL THE TEACHING OF CHEMISTRY BECOME A SCIENCE? ¹

WHEN will the teaching of chemistry become a science? Before answering this question, let us ask another question. When did chemistry become a science? Chemistry became a science when men found that there were different elements; that these elements had different properties; that they could be changed into different forms; that they would react with one another and give different products and that in all these interactions and transformations there was no loss or gain of mass. These are a few of the fundamental conceptions that were necessary before chemistry could become a science.

The teaching of chemistry will become a science when we as teachers recognize that every student is possessed with certain original tendencies with which we are to work just as the chemist works with the elements. These original tendencies are subject to transformations and interactions, but they can not be destroyed any more than an element. The law of the conservation of mass holds. Sometimes the psychologist speaks of an original tendency being eliminated. He means by this that the tendency has been so modified that you can not recognize it. The chemist would say that it had suffered a chemical change or had been changed into an allotropic form.

For the benefit of those people who studied psychology some years ago, I might say that a few of these original tendencies are curiosity, manipulation, mastery, fear, sex instinct, hoarding, ownership, etc. These are the rocks upon which we build our chemical

¹ Read before the Section of Chemical Education, American Chemical Society, New York, September 8, 1921.