COMMENTS ON SOME OF THE PHYSICAL CHEMICAL QUESTIONS ASSOCIATED WITH THE ANALYSIS OF WATER IN EARTH MATERIALS

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ABSTRACT

A discussion of various physical chemical questions which are associated with the quantitative analysis of water in earth materials is presented. A pseudothermodynamic approach to the binding of water in various types of earth materials is also presented. Emphasis is placed on the fact that as pore, crack, or hole sizes approach molecular dimensions, the interaction energy of water with the host material can become very large. A scale of interaction energies is suggested which would be useful for specifying operationally relevant analyses in earth materials.

INTRODUCTION

The quantitative analysis of the water content of earth materials is of great importance in various aspects of the Plowshare Program. The requirements for water analyses encompass a wide variety of problems from predictions of the strengths of earth materials to the disposition of radioactive elements in the cavities and craters created by nuclear devices. Water analyses are also useful in areas other than Plowshare where the problems are geochemical and geophysical in nature, such as predicting seismic damage in various geological regions.

A single, general method of analysis to yield pertinent information for such a wide variety of requirements does not exist, and it is doubtful that one could be found. The purpose of this report is to establish a workable set of definitions to examine the specific problem at hand and to point the way to one or more analytical methods that can yield pertinent information. The intention is to explore some of the subtleties of the questions regarding water analyses in earth materials in enough detail so that some of the commonly overlooked questions can be recognized. Finally, we shall discuss a few specific methods of analyses.

STATEMENT OF THE PROBLEM AND EXAMINATION OF DEFINITIONS

The most difficult problem we are faced with is due to a combination of incorrect preconceptions and a tendency to substitute overly simplified models for earth materials. The conventional operational mode is that of classifying water in earth materials as being either "free" or "bound" water. Presumably the word "bound" refers to some kind of binding between water molecules and the molecules (and/or ions) of the various constituents of earth materials.
The type of binding is usually unspecified. The term "free" water as it is commonly used seems to refer to a condensed phase of pure water.

The usual reaction to a cursory consideration of the definitions involved is to split the analysis into two parts: (a) "total" water and (b) "free" water. The definitions are now readjusted so that "free" water is condensed phase pure water (still neglecting the subtle questions).

"Total" water is then given one of a number of definitions: (1) all the water that can be driven off by heating to a given predetermined temperature (for example, with this definition, there are difficulties associated with water-producing reactions, etc.); (2) the amount obtained by counting all the hydrogen in the sample by some scheme like proton resonance, and dividing by 2 (some problem with hydrocarbons, silicates, and nonfreely rotating hydrogen); or (3) the amount obtained by any other counting technique that could give either an H count or an OH count in the sample (subject to various corrections).

Of course, the main purpose in such a separation is that by subtracting the "free" amount from the "total" amount of water, one gets back to arriving at an amount for "bound" water with an operational definition while essentially sweeping lots of problems under the carpet. Admittedly, that would be an operational definition, and it may even be valid for some specific requirement; but when dealing with earth materials, the probability of this technique being valid can be quite low.

The tendency of classifying the water as "free" or "bound" arises from the point of view of looking at the various phenomena by using pure compounds as models. Thus, we generally drive off water at ~110°C to dry samples. This procedure was assumed to drive off "free" water while "bound" water would be unaffected. Then, by heating to much higher temperatures, more water could be driven off from many compounds, such as hydrates. For example, copper sulphate can only be completely dehydrated by heating to ~1000°C. With a little reflection, one can show that such a classification is no more valid for pure substances than for mixtures such as occur in earth materials. For example, NiSO₄·7H₂O loses 1 water of hydration at ~37°C; the remaining 6 are stable to over 100°C before a step-by-step dehydration can occur.

A PSEUDOTHERMODYNAMIC APPROACH TO THE PROBLEM: THE ESTABLISHMENT OF A CLASSIFICATION SCALE

We wish to propose a more functional, and hopefully fruitful, classification for the way water is bound with other materials. The classification we propose has some thermodynamic significance and also has the advantage that we can apply some rather good models for real materials to obtain semiquantitative notions of where a given material will lie in the classification scale.

Suppose we consider the amount of energy required to overcome the interaction of the water with the rest of the material and have it end up in some standard state. Let us specify that the standard state shall be gaseous non-associated water vapor at ambient temperatures. (By this we really mean steam behaving as an ideal gas; i.e., the partial derivative of the enthalpy with volume at constant temperature is zero.) We are concerned with earth materials which are all in a condensed state (solid, liquid, or both) and are all at ambient temperature and pressure. Then we are considering an energy which is similar (but not quite equal) to the heat of vaporization to remove the water associated with the material and bring it to the standard state mentioned.
above. In the following discussions when we talk about the interaction energy of the water with the material, we really mean the amount of energy required to get the water in the standard state mentioned above.

The lowest value on such a classification scale is that for water interacting with itself. That is the case of agglomerates of water molecules in the liquid state, and the energy of interaction is about 5 kcal/mole. We shall show later that this is the lowest value on the scale. The upper end of the scale is physically equivalent to those energies which cause disproportionation of simple molecules in the region of ~100 kcal/mole. The scale is continuous. The great advantage of this proposed scale and classification is that it is independent of how the water is bound. Thus chemical bonding of any kind, chemisorption, physical adsorption, van der Waals bonding, hydrogen bonding, etc., are phenomena which can all be considered. We can at this point note that what is presently referred to as "free" water is water bound with interaction energies of ~5 to 20 kcal/mole. If one were to take this proposal for a scale and classification system seriously, then the term "free" should be used for interaction energies of ~5 kcal/mole. We believe that the scale itself should be the classification. So instead of saying "free" one should say "water bound with X kcal/mole." From such a scale and the understanding of various kinds of earth materials, it should be possible to develop functional operational analyses for water.

That the lowest energy of interaction for this scale is for the water-water interaction can be seen from the following argument. Suppose that there is, in the condensed state, an energy of interaction of water with some other substance that is less than the water-water interaction. The application of enough heat to break up the former interaction will lead to the formation of liquid-state water, and the only energy of interaction will be that of the water-water interaction. To make this particular argument clearer, let us give an invented example. Suppose there is a pure substance, "Y," which forms a series of hydrates. Furthermore, suppose that the water-splitting reaction for removal of the first water of hydration at pressure P occurs at temperatures well below ambient temperatures. The result at ambient temperatures is two phases: (1) the next lower hydrate and (2) pure water at pressure P (or a solution of "Y" in water). Therefore, the water-water interaction will be the lowest observed interaction. (In a strict thermodynamic sense, this statement is incorrect except for open systems. For closed systems some equilibrium will ensue. Thus, for instance, in a calorimetric determination (see below), it would be possible to observe interaction energies below the 5 kcal/mole.)

Let us discuss one aspect of the problem of what one might term "dispersed" water in earth materials. We shall get into this problem in some detail later, however, at this point we shall merely state some conclusions. Suppose we consider water dispersed in rock in a monomolecular (or at most a few molecular multiples) state. This means that the "pore" sizes or "hole" sizes we are considering are ~1.5 Å long. These holes are therefore much smaller than microcracks and really correspond to the size of crystal defects. For such a situation, the water is more strongly bound to the host material than it is to itself. This is so since polarizable material (host) surrounds the highly polarizable water molecules (guest) at much closer distances than that

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* The observed heat of vaporization of water is ~10 kcal/mole. However, normal vaporization leads to associated water vapor as shown by P-V-T data (J. S. Rowlinson, Trans. Farad. Soc. 45, 974 (1949)). An average molecular weight of 32 g mole⁻¹ for the vapor is thus quite reasonable, and rationalizes the use of the 5 kcal/mole in this discussion.
of the neighboring water molecules. This then results in a higher interaction energy between the water guest and the host earth material molecules.

We shall now discuss various materials with emphasis on earth materials in order to be able to apply such a scale. Let us first consider pure water and aqueous solutions which might be found in earth materials.

The water-water interaction in the condensed state can be considered from the viewpoint that the hydrogen bonds which bind the water molecules together are bona fide chemical bonds (that is, either electron exchange or charge transfer accounts for the bonding). Then, using these kinds of models along with observed spectroscopic properties, one can calculate an interaction energy of ~5 kcal/mole. This is the more classical viewpoint. Alternatively, one can view the interaction as that between polarizable bodies by means of electron correlation, or, in other words, van der Waals forces accounting for the intermolecular forces. When one uses the dielectric constant and average intermolecular distances in the van der Waals (London dispersion) relations, one again obtains ~5 kcal/mole for the hydrogen bond. This model, however, does not require that a bona fide chemical bond be formed. Either viewpoint leads to the same conclusion and it really is much more a matter of personal taste as to which one is used. Both are equally correct. We prefer the latter viewpoint for this discussion for two reasons. First, and most important, it is much easier to calculate the energetics involved for intermolecular forces with the London dispersion force relations (which are admittedly a bit crude) to reasonable accuracy (~10 percent) than to use the much more sophisticated chemical bond techniques to obtain answers to the same accuracy. Second, we shall be more concerned with intermolecular forces for those earth materials which are going to be most troublesome as far as water analyses are concerned.

Let us just touch on aqueous solutions. For electrolytic solutions, ions in solutions will have "atmospheres" of water dipoles associated with them. Thus some of the waters will have an interaction energy with the ions of either charge which is larger than the water-water interaction. The total interaction energy will depend principally on the charges of the ions, their sizes, and their concentration. For nonelectrolytes, the energy of interaction of the water associated with the solutes will be a function of solute size and concentration (going up with both variables). For most earth materials, the concentration of electrolytes and/or nonelectrolytes is usually low so that total water interaction energies with these materials will be small and somewhat near the low limit.

THE CASES OF INTEREST

We shall concentrate on what could probably be termed "troublesome" earth materials, rich in water and tending to be equilibrated under conditions of moderate temperature and pressure called weathering. In contrast, "fresh" igneous and metamorphic rocks contain relatively little water except in pores, cracks, and interstices. Here, the problem will be complicated only when the dimensions of the space occupied by the water becomes comparable to molecular dimensions. When the dimensions are quite large, the water-water interaction of ~5 kcal/mole will be predominant. We shall discuss the question of pores shortly. Water can be present in some of these earth materials, as strongly bound hydrates with energies of interaction of over 20 kcal/mole. In some of the metamorphic silicates and aluminates, hydroxyl groups can be found that are joined to the major structure with energies of up to 80 kcal/mole.

Salt deposits of various kinds could be somewhat complicated. In arid regions with deposits of materials containing hydroxides, carbonates, halides,
and sulphate, hydrates could be obtained with a quite low interaction energy. One must be careful in selecting the analytical methods to use and the interpretation of the results. Large salt deposits of mainly NaCl are usually not troublesome, although hydrated salts can be present and the amount of water depends on the particular hydrate and its concentration in the salt deposit sample. Occluded water in salt deposits and dissolved water also can be pitfalls. Large pores or cracks of occluded water will be low on the classification scale. But, monomolecularly dispersed water is difficult to classify. (Presumably, the monomolecularly dispersed situation could arise where the salt deposits were supersaturated—in the solid state—with dissolved water.)

The really troublesome materials to analyze are the clays and zeolitic-type minerals. As is well known, there is a large number of synthetic and naturally occurring materials in these classes. Rather than using any of the classification schemes used by geologists, we shall use a scheme which comes from the study of inclusion compound chemistry.

The various types of inclusion compounds are classified according to their general crystal structure types. (This is not to be confused with structural varieties defined by either crystallographic point groups or space groups—both of which can have a large number of structure types.) To three of the four types of inclusion compounds there will correspond one or more earth materials of a clay or zeolitic variety. It is for this reason that we choose to classify the earth materials along the same scheme. Also, the behavior of synthetic clays and zeolites are such that it is clear that the chemical bonding properties of these materials are the same as those of the general class of inclusion compounds.

We will not go into great detail on inclusion compound chemistry. Several books and review articles are available for those who are interested in further pursuing this topic. However, we will quickly cover some general aspects of the field so that analogies can be made. The manner in which crude calculations for the interaction can be made for some particular system is indicated.

Inclusion compounds are compounds that form between two or more different kinds of molecules in which the stabilization energy is not due to bona fide chemical bonding but is due mainly to van der Waals forces (or/and hydrogen bonds). By bona fide chemical bonding we mean, as stated earlier, that either electron transfer or sharing of electrons or both are involved. Also, as mentioned earlier, we choose to consider hydrogen bonding as due to van der Waals forces. The two kinds of molecular species involved are called the host and guest molecules. The four general types of inclusion compounds are illustrated in Figs. 1 through 4. Figure 5 is an illustration of a form of inclusion compound which is sometimes considered as a separate type, but which is really only an extension of the system shown in Fig. 1.

The energy stabilization for the inclusion compound can be calculated easily (not necessarily precisely) by applying the London dispersion relations to all the atoms in the system. One does this first for the complex and then for the individual host and guest molecules; the difference represents the stabilization energy. The relation is

$$E_{1,2} = k \frac{\alpha_1 \alpha_2}{r_{1,2}^6},$$

where $r_{1,2}$ is the distance between the two atomic units in question and $\alpha_1$ and $\alpha_2$ are the polarizabilities of the respective atomic units. One sums all pairs
of atomic units for both parts of the calculation. Since bona fide chemical bonding is unaffected by the complex formation, those energetics need not be calculated. (They would be the same for the complex and the sum of the host and guest molecular terms. Thus, the chemical bonding energy is simply a constant for this case and one which need not concern us.)

Another way to do the calculation (although a little less accurate than what has been outlined above) is to calculate the stabilization energy directly. The relation has the same form, that is

\[ E_{G,H} = k \frac{\alpha_G \alpha_H}{r_{G,H}}. \]

However, a little care is necessary. \( \alpha_G \) and \( \alpha_H \) are the molecular polarizability of the guest and host molecules, respectively, \( r_{G,H} \) is a mean distance. The terms over all interactions must be summed.

The main point we are trying to get across at this time is to show the origin of these stabilization energies (that they are not chemical bonds in the usual meaning) and to show the form of the interaction. Physical adsorption is due to the same type of electronic correlation phenomenon. Notice that when we make such a calculation, if we are careful about summing all pair interactions for the complex and its decomposition products, the products can be both gas-phase molecules and solids, or all gas-phase molecules. Thus, such a calculation can be made with water as the guest molecule; and, if done properly, the product of the decomposition can be gas-phase water and solid host material. Thus, we can calculate directly the interaction energy needed for the classification scale. When the energy is calculated both for the complex and the proper form of the complex decomposition products, the stabilization energy and the water-host interaction energy (which is what we use in our classification scale) are the same. When one does these calculations for the four types of inclusion compounds, the energies can range from zero to \( \sim 80 \text{ kcal/mole}. \)

Using the same formulation that London used for arriving at the form of the interaction between molecules, attractive forces can be calculated for other interactions such as that of macromolecule and flat infinite wall, etc. These forces are completely general and are applicable to a huge number of situations. Thus, one can now see that as pore or crack sizes get down to molecular dimensions, interaction energies between water and host material can get to be large compared to the water-water interaction.

Let us return to the four types of inclusion compounds. In Fig. 1 is shown a generalized schematic of the complexes known as clathrates. Classically the clathrates consist of water molecules as host with normally gaseous molecules as guests. Probably there are no analogies of this type of inclusion compound with earth materials except for possibly the occurrence of methane hydrates in gas wells. The gas hydrate clathrates normally decompose at low pressures and moderate temperatures.

(There are two families of minerals which schematically correspond to Fig. 1. The scapolites and the noseansodalites consist of a cage-like aluminosilicate framework with a net negative charge. The guests are cations which can be associated with variable compositions of salts and/or water, \( \text{CO}_2 \), etc. The cations provide charge neutrality. The openings in the cages are rather large, i.e., of the order of 5 to 10 Å in diameter.)
Fig. 1. Clathrates are formed when guest molecules fit into separate spherical spaces within the host material.

Figure 2 is a generalized schematic of channel-type inclusion compounds. Here the guest molecules are in long channels running through the structure. The cancrinites and fibrous clays are examples of earth materials which have structures of this type. Examples for which structural data exist

Fig. 2. Channel inclusion compounds are formed when the host material provides tubular cavities within which the guest material resides.
are cancrinite and davynite for the cancrite mineral type and attapulgite and sepiolite for the fibrous clays. In the latter two, water is the main guest molecule.

Figure 3 is a generalized schematic of the sandwich inclusion compounds. Here layers of guest and host materials alternate. An example of these kinds of complexes are the graphite intercalation compounds. Such things as bromine form stable complexes with graphite with the bromine residing in layers between the hexagonal carbon structure. There are many natural earth materials which fall into this type. For a good number of these, water is the guest. The swelling of clays with water is due to the stability of the sandwich inclusion complex. The family of the most abundant micaeous silicates which are layer structures are muscovites, biotites, the illites, and talc. Nonsilicate micas which are layer structure are autunite, torberlite, zeunerite, trogerite, and carnotite.

One can understand, at least qualitatively, some of the physical properties of layer structure clays with water guests. For instance, besides the swelling (and also shrinking) behavior, the creep and sliding behavior of these materials are now obvious manifestations of a rather weakly bound structure. (Water molecules are the bonding links between host layers and essentially are the only slide-restraining links,) The seismic response of such materials, that of essentially liquefying under earthquake conditions, can be understood as a breaking up of the structure because a relatively small amount of energy is needed to overcome the stabilization energy. However, the range of stabilization energies can be quite large from numbers almost as low as the water-water interaction to ~80 kcal/mole for very stable structures. Also, for some of these individual layer structure clays, the water will have a range of binding energies.
With some of the layer structure clays, the water-host complex does not form because of the extra stabilization energy. Instead, the dehydrated clay structure is already a layer structure. The water can then intercalate and bind (with a range of energies) to the layer framework. The net result is the same. The water is held by van der Waals forces to the framework.

Figure 4 is a generalized schematic of zeolite inclusion compounds. This type of compound does not form from a host of some other crystal structure because of added stability of the guest molecules. Rather, the guest-free structure consists of interconnecting channels. The figure is misleading in the sense that the channels and interconnections are not really smooth. In some of the zeolites the channels are not straight but may have a number of jogs (which are periodic in the structure). Also, the interconnection space is usually considerably larger in diameter than the channel diameter. All the natural zeolites are three-dimensional networks. However, there can be large differences in the density of channels in different directions so that a nearly layer-like or nearly fibrous-like structure can be obtained.

When water enters these channels, there will be a range of tightness of binding to the framework since there is a distribution of effective spaces within the channels and in the interconnecting spaces.

Thus, part of the water can be easily removed, but the removal of all of the water may be quite difficult.

The cusp-shaped guest cavities as shown in Fig. 5 have their counterparts in some silicate glasses in which the tetrahedral bond networks around the silicon ion are degraded leaving concave holes throughout the structure.
Some of these glasses also have a large concentration of hydroxyl ions. Thus water can be very tightly bound by both the silica cage and the excess hydroxyl ions.

METHODS OF ANALYSES

It now should be clear why there are no all-encompassing analytical methods available. We mentioned earlier that operationally relevant analytical techniques would have to be applied in order that the information derived would be of some value.

Such simple schemes as heating at a prescribed temperature and time, with or without evacuation, etc., could be operationally valuable techniques.

There are three techniques which may have a somewhat extensive use for determining water that is bound by just 5 to 8 kcal/mole.

The first method is by measuring the heat capacity of a large rock sample over a temperature region between -40 to +40°C. The heat of fusion of ice is 80 cal/g, so that a bump in the heat capacity curve near 0°C can give a quantitative measure of the water in such a state. This method has the advantage that it is an absolute method and is nondestructive. Its disadvantage is that data acquisition is slow and moderately difficult. (We should mention that while differential thermal analysis (DTA), thermogravimetric analysis (TGA), or differential scanning calorimetry (DSC) are all capable of giving relative quantitative analyses, they all suffer from the fact that very small amounts of sample material are involved. The problem of a representative sample for such techniques becomes insoluble. The alternative of making measurements on enough samples to obtain representative results then becomes a horrendous one.)

The other absolute method (that we know of) is to measure the isothermal compressibility of the rock specimen. Water of low interaction energy has two phase transitions: one at 10 kbars and the other at 23.5 kbars. A measurement of the volume change (at the discontinuities in the PV curve) at
these pressures provides two independent values for the amount of water. Thus this method has the advantage that, since there are two phase transitions, the value can be confirmed. The disadvantages are that the method is sample destructive. (The probability that there are other materials present besides water which have phase transitions at those two pressures is negligibly small.)

The third method is based on the transmission of microwaves through a sample. Water attenuates the microwave signal, although in this method spectroscopic techniques are not used. The attenuation is then a measure of the water in the sample. Surprisingly few things interfere with the measurement. However, the measurement does depend on the water molecules being in a state of free rotation. This means that some water which is more tightly bound than 5 kcal/mole but which is free to rotate along one or two of its principal axes can attenuate the signal. Thus, this measurement will show some of the water held by van der Waals forces with some moderately strong binding. This method has the disadvantage that it requires calibration, but it has the advantages of being very rapid and simple in application. It is probably an excellent tool for research on the fibrous clays, the layer clays, and the zeolites. With careful operational restrictions, it might possibly be an excellent analytical technique.

The calorimetric and compressibility method should essentially yield equivalent results on the same samples.

There are numerous other analytical techniques which can be considered for an operationally relevant analysis. What is probably most necessary at this time is some research on the more troublesome earth materials. Particularly, we suggest research on pure synthetic clays and zeolites for use as analogy models of the naturally occurring minerals. There already exists rather extensive literature on some of the physical properties of the synthetic zeolites. Some of this literature is relevant to the design of useful analytical techniques. Such experiments as the addition and removal of specific amounts of water to model materials and the testing of various analytical techniques would undoubtedly be useful. Once a good understanding of these pure materials is obtained, and after an actual petrographic analysis to determine the types and relative amounts of the various troublesome materials present in the specimens, it might be possible to specify the criteria for operationally relevant analyses in an intelligent and logical fashion.
REFERENCES