Fundamentals and Applications of Supramolecular Chemistry

Deepak Chopra

Department of Chemistry

IISER Bhopal

Week 05

Lecture 22

W5L22_Structures of Gas Hydrates

Hello everybody. So let us now continue our discussion regarding gas hydrates, and we will also look at some interesting aspects of solid-state inclusion complexes in the present lecture.

So, to start with, as we discussed in the last lecture, gas hydrates essentially have water as a supramolecular host structure, which is extensively hydrogen bonded, and the voids contain different kinds of molecules that act as guests.

So, in this case, the basic framework comes from hydrogen-bonded water molecules, and efforts have been made to determine the crystal structures of these gas hydrates. So, to start with, the structure is determined from X-ray diffraction for these particular gas hydrates, and what has been observed is that there are two fundamental building blocks present in the formation of these gas hydrates.

So, we have got this 1, 2, 3, 4, 5-membered ring. So, you can essentially approximate it to be a linear O-H...O hydrogen bond.

So, this is a 5-membered ring. In addition to this, it has also been observed that you can have 1, 2, 3, 4, 5, or 6 membered rings as well. So, these kinds of building blocks are present, and it is essentially the fusion of these five-membered rings and six-membered rings that gives rise to these kinds of gas hydrates, and what has been observed is the following.

Now, if you look at the diagram here, you can see that we can have different kinds of 3D supramolecular building blocks made of these water molecules.

For example, the top row here represents the first figure, which is a pentagonal dodecahedron because it is represented symbolically as 5^{12}, essentially telling you that there are 12 such 5-membered rings that are fused to form the dodecahedron, and each vertex actually represents the water molecule, while the bond is not a covalent bond.

The line that connects the two vertices corresponds to the hydrogen bond. So, this is not a covalent association; it is a geometrical, diagrammatic representation of a hydrogen-bonded assembly, where we now know that each pentagon is a 5-membered ring and each hexagon is a 6-membered ring, each vertex is a water molecule, and the lines essentially represent the hydrogen bonds.

So, this structure is referred to as a pentagonal dodecahedron. We can also have another kind of structure that consists of the fusion of 12, 5-membered rings and 2, 6-membered rings. So, you can see the 6-membered ring; this is one 6-membered ring, and this is another 6-membered ring, and the remaining 12, 5-membered rings are also present.

You can see that as well as 1, 2, 3, 4, 5, and 6 here, which is this side. And similarly, you can see 1, 2, 3, 4, 5, and 6. So, there are a total of 6 plus 6, 12, 5-membered rings as well as 2, 6-membered rings, and this creates the structure which is called a tetrakaidecahedron.

The tetrakaidecahedron means there are 14 such rings; the total number of rings is now 14: 12 five-membered rings and 2 six-membered rings. Similarly, along the same lines, we can obtain larger-sized clusters and larger-sized supramolecular hydrogen-bonded building blocks consisting of the fusion of this 5-membered ring and 6-membered rings.

We can also have 12 such 5-membered rings that undergo fusion with 4 such 6-membered rings. You can see the 6-membered rings; this is one such ring in the front, there is one at the back, one on the right-hand side, and one on the left-hand side. So, there are four such six-membered rings, and the remaining twelve five-membered rings are also present.

This leads to the formation of a hexadecahydron, which means the total number of fused rings is now 16. The bottom row represents an irregular dodecahedron, which is this one, and we have the famous icosahedron, or the icosahedral structure, which can also be present in the structure of different gas hydrates.

So, keeping in mind the composition of these building blocks, we can either have the fusion of 5^{12} units with $5^{12}6^{2}$ units or the fusion of $5^{12}6^{4}$ with 5^{12} units, allowing us to create different types of structures.

So, two structure types have been reported: the Type 1 structure type is a fusion of two 5^{12} units and six $5^{12}6^{2}$ cavities. So, each of these supramolecular building blocks creates a cavity; you know there is a cavity that is present in the center, and this cavity can now include the guest molecules.

And the number of guest molecules can vary depending on the voids or the volume available for the different guest molecules to occupy the voids created by the host cavity. The second one is a type II structure, which is a fusion of 16,5^{12} units and 8,$5^{12}6^4$ cavities.

So now you have a fusion of 16 such 5^{12} units and 8 such $5^{12}6^4$ units. And these are the two fundamental structure types that have been observed. And as I told you, the 5^{12} unit is the dodecahedron, the $5^{12}6^4$ unit is the hexakaidecahedron, and the $5^{12}6^2$ unit is the tetrakaidecahedron. So, now these are the two structure types that are present, and let us look at how these structure types look before we go further into their geometrical properties. So, this is the structure; you can see the gas hydrate of structure Type I.

We can call it S-(I) or Type I. So, you can see here that you have got this central dodecahedron, which is the 5^{12} unit. This is the 5^{12} unit, which is surrounded by the tetrakaidecahedra. There are 6, and there are 2 more, actually, which are behind. So, here I am showing you a representation of 8 tetrakaidecahedra.

You can even have 2 more in front of this dodecahedron, but by definition, as I told you, to start with Type I is a fusion of 2, 5^{12} units and 6, $5^{12}6^2$ units. So, we have the 6, 1 2 3 4 5 6 structures, as well as 2 shown behind for the sake of completion. So, this is the structure of the S-I type. In the S-II type, you can see that we have the fusion of these 5^{12} units, along with the $5^{12}6^4$ units; that is, we have the hexakaidecahedra which are actually fused. Now you can see the hexakaidecahedra; they are present here: 1, 2, 3, 4, 5, 6, and this gives rise to a void in the center, which is actually a dodecahedral void.

And it is these voids that are now present, whether the dodecahedral void or the hexakaidecahedral void, which are available to the guest molecules for occupation. So, this is structure 2, the structure 2 gas hydrate, which is actually a fusion of the hexakaidecahedra, with 6 such units forming a dodecahedron in the center, which creates the voids, and in all these voids, you can have the guest molecules.

Now, there is a third very important structure type; we call this the structure H type, which is actually also the hexagonal form of ice that we use for the sake of comparison here. And in this, we will see that we have a central icosahedron which is surrounded by 1, 2, 3, 4, 5, and 6 irregular dodecahedra, and the central part is the icosahedron.

So, this icosahedron is formed by the fusion of these irregular dodecahedra, and the composition of this particular structure type depends upon the presence of different cases, which are represented as 1X, 3Y, and 2Z, along with 34 molecules of water; this is the composition of the unit cell.

This is the ideal composition, the ideal composition of the unit cell if you were to have the filling up of the X type, Y type, and Z type voids along with 34 molecules of water. But let us also go back and look at the composition of the type 1 and type 2 structures. So, S-I and S-II, these are more important and fundamental.

So, the lattice type corresponds to a lattice, and the lattice type, along with the space group, corresponds to the symmetry operations that define the position of the molecules in the unit cell, because we have determined the structure of these gas hydrates. It is the body-centered cubic Pm3n, and for the S-II, it is the diamond cubic structure.

This is the face-centered cubic, Fd3m, which is the space group. The unit cell length in angstroms is 12; this is 17.3. Now, what is the unit cell formula? This is very important because we will be taking this unit cell formula further to understand the composition of the host and guest ratio.

So, the units and formula here are 6X, 2Y, and 46 water, whereas for the large-sized S-II, there is a large-sized cavity of 8X, 16Y, and 136 water.

So, right away you can see that the composition of the unit cell is very different. S-II being a much larger size cluster, you know, this is S-II. It is a much larger-sized structure, and the voids are also available more in terms of volume.

So, we can have a larger number of cases that are being included, and what is the nature of the cavity; this is important. So, it can include small Y and large X.

If you have two different kinds of guest molecules, depending on the size of the guest, they will either occupy the X or Y; large sizes will go to the X side and small ones will go to the Y side.

The same is true for the S-II structure. And the number of cavities per structure is 2; as you saw, there are 2 cavities for Y and 6 for X, and here it is: Y is 16 and X is 8. And the average cavity radius is 3.91 angstroms; this is 4.33, 3.902, and 4.683. This is the cavity radius. So, there are small differences in the cavity radius here for the S-I and S-II types.

What is most important from this data is to see that the unit cell formula is different and what cavities are available, as well as the number of these cavities. Depending on the number of cavities and the size of the guest molecules, they will be able to crystallize in different structure types, S-I and S-II, respectively.

So, the next important thing is to look at the size of the guest molecule that is going to occupy the voids created in the gas hydrates. Keeping that in mind, people have now examined this trend more carefully. So, let us draw this to a particular scale.

We will take a scale now and start with, for example. We will start with different dimensions. For example, we look at 3 angstroms, 4 angstroms, 5 angstroms, 6 angstroms, and 7 angstroms.

So, these are the ranges we are going to see here, and what has been observed is that when you have got 3 angstroms, between 3 to 4 angstroms, we have got argon, and at 4 angstroms, we have got krypton, then nitrogen, oxygen, methane, xenon, and hydrogen sulfide; these increase in size. So, from Krypton to nitrogen to oxygen to methane to xenon to H_2S, all the sizes of the molecules are increasing.

Then from 5 angstroms, we have CO_2, ethane, and further, we have C_3H_6 as well. Then, from 6 angstroms onwards, we have propane, butane—I mean to say isobutane—and from 7 angstroms onwards is n-butane.

So, we have looked at all these different guest molecules, and we know that methane is very important because it has a role in the formation of gas hydrates and the problems we discussed about gas hydrates.

Now we also have the other hydrocarbons like ethane; CO2 is a very important gas, and it is important to be able to efficiently capture this gas and then use it for different applications. Including propane, isobutane, and n-butane, all these different kinds of guest molecules can be included in the structure of the host lattice.

And if you were to actually look at hydrogen, helium, and neon, they cannot be trapped in the gas hydrate structures because they diffuse through the hydrogen-bonded bars. So, where are the hydrogen-bonded bars?

As I told you, these are the bars; these are the hydrogen-bonded bars. So, this is kind of a cage-like structure where the water molecules are present, and the voids can now contain the guest molecules.

But hydrogen, being very small, helium, and neon can easily diffuse to the hydrogen-bonded bars, and they are now free to undergo translational diffusion, and hydrogen molecules can also rotate inside the voids because of their much smaller size.

Now what has been observed is the type of structure that is obtained when you have these host molecules and these guest molecules with the host structure of water.

So, they tend to crystallize in S-I type; here they crystallize in S-II type, here they crystallize in S1 type, and here they crystallize in S2 type. And we can now find out the hydrate numbers, the ideal hydrate numbers, for a given structure type.

So, in S-II, what happens is that let us go back to S-II. So, in the case of S-II, the total number of water molecules is 136; in the case of S-I, the total number of molecules is 46. The total number of available voids is 24, and the total number of available voids is 8.

This is something we need to keep in mind for the calculation, so now we can calculate the ideal hydrate numbers. Now, in the case of the S-II structure, we know that it is a fusion of the 5^{12} and $5^{12}6^{4}$ structure types.

This is 5^{12} plus $5^{12}6^{4}$; in this case, it is only the $5^{12}6^{2}$ voids that are occupied, and here it is only the $5^{12}6^{4}$ voids that are occupied. Now, if you go back and see why $5^{12}6^{4}$, it depends on the size, and if the size is small, the corresponding void will be occupied.

So, now let us look at the ideal hydrate numbers. So, in the case of the S-II type, where we have these guest molecules, the total number of voids that are occupied is 24. We saw that number, and the total number of water molecules is 136. So, this comes out to be 5 2/3.This is 5 2/3.

In the second case, we have 46 water molecules divided by 8. So, this is 46 divided by 8, which is 5 3/4. Here, this is only occupying the $5^{12}6^{2}$ voids; the number of water molecules is 46. But now, only the $5^{12}6^{2}$ voids are occupied. As you can see, the $5^{12}6^{2}$ voids are the larger number, so they are occupied, and that is 6 in number.

Therefore, this comes out to be 23/3, ie 7 2/3. So, this comes out to be 46 divided by 6, which is 7 2/3, and here we are going to have 136 water molecules divided by 8, which is going to be 17. So, these are the ideal hydrate numbers to start with: that is, 5 2/3 water molecules per guest, 5 3/4 water molecules per case, and 7 2/3 water molecules per guest; this is 17 water molecules per guest.

Depending upon the structure type, the type of voids, and the corresponding number of voids that are going to be occupied by these guest molecules—in this case, n-butane, ethane, isobutane, and so on and so forth—so different kinds of guests, depending upon their size, will go and occupy the voids.

And statistically, they will try to occupy those sites where a greater number of guest molecules can go and sit; that is, the available void space is larger. As you can see in the last two cases, when the size requirement is more than it goes and occupies preferably the larger size voids.

So, these are the idle hydrate gas numbers, but in reality, what can happen depends upon the pressure and the temperature at which the gas hydrate formation takes place.

So, we discussed that this gas hydrate occurs at very low temperatures and under high-pressure conditions. Because you are essentially freezing these gas molecules to occupy the voids, applying pressure and allowing them to, you know, crystallize in the voids.

So, sometimes what can happen is that they get compressed a bit and are able to, you know, adjust into the void volume. So, we can have more content present in these voids than what is expected from these ideal hydrate numbers, and it can also be lower.

So, the real crystal structure can give you a composition that does not necessarily correspond to the ideal hydrate numbers.

For example, in the case of chlorine.water structure, it ideally should have corresponded to 7 2/3 water molecules. This is what was supposed to have been the case because it crystallized in the S-I structure type where the $5^{12}6^{2}$ voids were being occupied.

So, technically, it should have ideally been 7 2/3, but in reality, the composition is 10 molecules of water. So, you can have more content present in the voids depending on the adjustment of the water molecules in the void space.

So, with this, we come to a close regarding the discussion on gas hydrates, and now in the next lecture, we will go into other kinds of structures that form a host-like framework into which different kinds of guests can be included, based on pure organic molecules that have specific functionalities to form large-sized supramolecular structures with voids and cavities to include guests.

Thank you.