

Fundamentals and Applications of Supramolecular Chemistry
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Lecture 05

W1L5_Problem solving and examples in Chemical Forces

Hello everybody. So, let us continue our discussion from where we left in the last lecture. We were talking about the importance of hydrogen bonds. So, we looked at the classification of hydrogen bonds. We also looked at the geometrical characteristics of hydrogen bonds.

So, traditionally when you have a hydrogen bond, we would like to represent it as $DH...A$ where D represents the donor, H represents the acceptor and A represents the directionality, associated with the hydrogen bond and we also observed that this angle in the ideal situation should be close to 180 degree, as linear as possible.

So, as to maximize the attraction between the hydrogen and the acceptor and minimize the electronic repulsions between the donor and the acceptor assuming that the donor and the acceptor have got lone pair of electrons associated with it.

So, overall this situation gives rise to a stabilizing situation where there is electrostatics operating by and large in a hydrogen bond, but then we also saw that in the weak hydrogen bonds there is also contribution of dispersion.

And we looked at the magnitudes of d , we looked at the magnitudes of capital D and we also looked at the magnitudes of θ for strong, medium and weak hydrogen bonds and we also looked at the signature of IR spectroscopy to detect strong hydrogen bonds, medium hydrogen bonds as well as weak hydrogen bonds.

Now, let us take up some classical examples of hydrogen bond formation because as we know that hydrogen bond formation plays a very important role in molecular recognition. It also affects the physical and chemical properties of matter, for example, the melting point, the boiling point and the way the molecules associated affects the properties. Let us take some examples.

For example, let us consider two water molecules, to actually hydrogen bond with each other. So, the combination of two water molecules results in the release of energy that is around 25 kilo joule per mole compared to that if an ion like fluoride interacts with HF, to give you HF_2^- , then the heat of formation is 160 kilo joule per mole.

When you consider a molecule having a permanent dipole moment, for example, acetone to interact with hydrofluoric acid then it leads to the formation of a hydrogen bonded complex where hydrogen is the most electropositive atom, fluorine is the most electronegative atom. There is a permanent dipole and this dipole interacts with the carbonyl dipole. So, there is a strong hydrogen bond between the fluorine and the oxygen electronegative atoms.

This process is favored by enthalpy change of minus 46 kilojoule per mole. And we can also consider the association between two HCN molecules in the following way, that they form linear arrays of hydrogen bonds. But in this case we have got a weak donor, relatively weak donor but the carbon is quite electronegative because it is sp hybridized and it interacts with nitrogen atom which is electronegative as well.

So, there are C-H...N hydrogen bonds and these are relatively weaker hydrogen bonds and this reflects in the enthalpy change for the process being around 12 kilojoule per mole. So right away we can appreciate that if you have an ion-dipole interaction then the enthalpy change is the strongest followed by the association of water molecules via these O-H...O hydrogen bonds, followed by dipole-dipole interaction between two different molecules HF and acetone and followed by the hydrogen bonding interactions between HCN, to form CH and hydrogen bonds.

So, we can have extremely strong hydrogen bonds. For example, we can have F minus HF and we can actually write the resonance canonical of this, which we call as resonance assisted hydrogen bond which we discussed in the last lecture. So, there is a delocalization of the electron density from one fluorine atom to the other.

These are actually 3 center 4 electron bonds. So, the proton has actually stabilized between the two fluorine atoms between the two electronegative fluorine atoms and a sufficient amount of electron density present between the hydrogen and the fluorine atom, compared to, for example, OH...O.

So, if you have an oxygen atom connected to a carbonyl, this is a neutral system, then the amount of electron density which is going to be present in the hydrogen bonding region is less compared to that for the case where you have a hydrogen atom interacting with a negatively charged species. There, the covalent character, so, we call the covalent character associated is high.

The covalent character associated with the hydrogen bond is high. These are examples of resonance assisted hydrogen bond. And so, you can see this kind of delocalization taking place and there is sufficient amount of electron density in the non-covalent region as well and this phenomenon exists.

So, this tells us about the relevance of hydrogen bonds being very significant in the literature and throughout the course we will be seeing the interplay of this hydrogen bonds, the cooperative effect of hydrogen bonds. We also looked at bifurcated hydrogen bond donors, trifurcated hydrogen bond donors, etcetera which play a very important role in packing of molecules, resulting in a particular state of matter. Now with this background that we have now completed the first module, we would like to take up some of the questions just to have a better understanding of the topics that we have studied. So to start with let us take examples. We started with chemical forces, ionic bonds.

So let us take the first example. The first example is we consider four different compounds. Aluminium sulphide, magnesium oxide, magnesium chloride and sodium chloride. And we would now like to arrange this in the order of decreasing strength of the ionic bond. So, we know that the ionic bond exists between the cations and the anions of opposite charges.

We also know that the energy of the interaction is proportional to the product of the charges on the cation and the anion. In this case, in case of aluminium sulphide, the charge on the cation is 3 and the charge on sulphur is 2.

In case of magnesium oxide, magnesium is 2 plus, oxygen is 2 minus, in case of magnesium chloride, chloride is minus 1, where is magnesium is 2 plus, and in case of sodium chloride it is plus 1 and minus 1. So right away you can see that here the product of the charges is highest, 3 into 2, that is 6, here it is 2 into 2, that is 4. Here it is 2 into 1, that is 2 and here it is 1 into 1, it is 1.

So, we are taking only the magnitude of the product of the charges. So, assuming that the inter nuclear separation remains fixed, that means r remain fixed then we can say that the ionic bond strength is greatest for aluminium sulphide, greater than magnesium oxide, greater than magnesium chloride, greater than sodium chloride. So, this is the order of decreasing ionic bond strength. Let us take the next example. In this case, example number 2, let us take 4 compounds, LiF, NaF, NaCl, NaI and KI, let us consider these 5 ionic solids.

So, naturally all these compounds are cases of 1, 1 solids there is a positive charge on the cation and there is minus 1 negative charge on the anion. So now when the charges are the same then what decides the magnitude of the electrostatic stabilization is how strong the cation and the anions are held to each other.

That means what is the separation between the cation and the anion, smaller is the separation between the cation and the anion, the energetic stabilization or the electrostatic stabilization increases. So, in this case, the size of the ion plays an important role. So,

size of lithium is smaller than size of sodium, is smaller than size of potassium.

Similarly, size of F minus is smaller than size of chloride is smaller than size of iodide. So, now if you combine, then we can now figure out that the size of lithium and fluoride being the smallest, that will result in the smallest inter nucleus separation and resulting in the highest electrostatic stabilization.

So, keeping that factor in mind lithium fluoride has the greatest electrostatic stabilization followed by NaF followed by NaCl followed by NaI and the least for KI because K and I have got the largest cation and the anion size. Prior to that it is sodium iodide, prior to that it is sodium chloride and prior to that it is lithium fluoride and sodium fluoride. So, this is the order of decreasing electrostatic stabilization.

Now, the next thing is that we can take another example. Let us take the following compounds, CaF_2 , KCl, NaCl, MgF_2 and LiCl. We have to arrange, we have to determine which of these compounds, has the lowest melting point.

So, melting point is going to be the least for the combination of cation and anion in which the electrostatic interaction is the weakest and electrostatic interaction is the weakest in the case where the cation and the anion both have got the largest size. So, calcium is 2 plus, it has got smaller size, potassium is plus 1, sodium is plus 1, magnesium is 2 plus, lithium is plus 1.

So, lithium is very small sized ion, magnesium is dipositive, calcium is dipositive. So, these 3 are ruled out. Now, between potassium and sodium both having the same ion anion chloride, potassium ion is having a larger size.

So, naturally KCl the combination of potassium cation and chloride anion, results in the weakest electrostatic interaction and therefore, it has got the lowest melting point. So, as long as the electrostatic interaction between the atoms is weak.

The ionic solid is less stable and therefore, it takes much lesser energy to melt the solid resulting in the lowest melting point for KCl. Let us take up the next example now. Example number 4, rank the following, for the attractive power towards water.

So, I am going to give you 4 different molecules, and I am going to tell you 4 different species, and I am going to tell you rank them in order of the increasing attractive power towards water, increasing attractive power. So, we have got magnesium, sodium, HBr and nitrogen.

Obviously, this is a molecule which is non-polar, covalently bonded species. This is a

molecule which has got a permanent dipole moment, this is a monovalent species and this is a dipole species or a dipole cation.

So, naturally there is going to be strong ion-dipole interactions between the magnesium ion and the sodium ion, with water molecules, to form magnesium solvated species or sodium solvated species. HBr is going to have a dipole interaction such that it forms hydrogen bond, Br...H-O hydrogen bond and nitrogen is going to engage in extremely weak hydrogen bonds with the water molecules.

So, this is going to be the O-H...N hydrogen bond. So, naturally, now we can see that the attractive power is the strongest for magnesium, then sodium, then HBr, because these are the case of dipole-dipole interactions. And this is the case of dipole-induced dipole interactions, because nitrogen molecule is a non-polar species.

And now it will try to induce a dipole moment in the nitrogen molecule resulting in dipole-induced dipole interactions. And we know from our studies on different chemical forces that dipole - induced dipole is weakest, followed by dipole-dipole and then the ion-dipole interactions. So, the increasing attractive power will be nitrogen, lesser than HBr, lesser than Na plus, lesser than magnesium.

So, this is the increasing order of attractive power towards the water molecules. The dipole species being first, the monovalent being second, then HBr followed by the nitrogen species. Let us take the next example, let us take a set of molecules, and try to rate them, classify the molecules as being polar or non-polar, weakly polar, metallic or ionic. So, these are the 5 classifications we have. So, let us start with the first one carbon dioxide.

The molecule carbon dioxide has got a linear geometry where the dipole moments cancel each other. So, the net dipole moment is equal to 0, we are assuming here the static nature of the molecule. So, this particular arrangement, linear arrangement gives rise to a dipole moment 0 and because the dipole moment is 0, the molecule is non-polar. MeOH, is the next example. In methanol we see that it has got a polar OH bond.

So, when you have a polar OH bond it is expected to undergo hydrogen bond formation with another methanol molecule and this hydrogen bonding can extend.

So, because you have this hydrogen bonding now between the methanol molecules this is the case of OH...O hydrogen bonds. So, the molecule methanol is a polar molecule. Oxygen is again a non-polar molecule, to start with it does not have a permanent dipole.

We all know that ammonia has got a permanent dipole moment. So, it is a polar molecule. Dichloromethane, is a tetrahedral molecule, but the electronegativity difference between

carbon and chlorine is less compared to that between say carbon and fluorine.

So, it is definitely a polar molecule, but it is weakly polar, because the polarity depends upon the magnitude of the dipole moment for the molecule which in turn depends upon the individual dipole moments constituting the different bonds. So, the electronegativity difference being less for carbon and chlorine the bond polarity is reduced and therefore, it is weakly polar in nature. The next compound is PCl_3 . PCl_3 also is again we see that it has got a tetrahedral arrangement, like ammonia, it is a polar molecule. Carbon monoxide is a polar molecule because there is a ground state dipole moment, therefore it is a polar species.

Formaldehyde is a polar molecule because there is a dipole moment associated with the overall molecule. We have a dipole moment because the carbonyl group is present and therefore, the overall molecule has got a dipole moment and therefore, it is a polar species. SiCl_4 it is a tetrahedral molecule. But the dipole moment cancels out because of the symmetry associated with the SiCl_4 units.

Therefore, the net dipole moment is equal to 0. So, this is the resulting dipole moment coming from this part. This is the resulting dipole moment coming from the bottom part. Therefore, these two cancel out giving rise to a net dipole moment of 0. So, it is a non-polar molecule. So, although the individual bonds are polar but the overall distribution of the dipoles is such that they cancel each other and therefore the net dipole moment in the molecule is 0, therefore this is a non-polar molecule.

Iron is a metallic species. You can take copper, you can take zinc, you can take nickel, you can take palladium, you can take platinum these are pure metallic species. And then we have taken examples of different salts where X is equal to fluoride, chloride, bromide and iodide, these are all ionic species. So, overall, these are under set of very interesting examples of species being polar or non-polar. Now let us take another set of examples, where we will talk about molecules which are capable of dipole-dipole interactions. So let us take a set of molecules, for example methane, carbon dioxide, formaldehyde, SF_6 , and ammonium plus.

So, which is the compound which is capable of dipole-dipole interactions. To have dipole-dipole interactions, the dipole moment of the molecule must not be equal to 0.

We have just now seen that this is having 0 dipole moment, this is having 0 dipole moment, this is an octahedral geometry which is having a net dipole moment of 0, this is a tetrahedral molecule having a dipole moment of 0. It is only formaldehyde which has got a net dipole moment and therefore, it can engage in dipole-dipole interactions. Now, the next question is that related to hydrogen bonds, let us identify the species that is

capable of hydrogen bonds, hydrogen bond formation.

For example, let us take CH_3COCH_3 , CH_3OCH_3 , $\text{CH}_3\text{CH}_2\text{OH}$, H_2CO and CH_3F . So, we have these five different species to form hydrogen bonds. To start with, the compound must have a donor atom, and the bond must be polar that means there must be a substantial electronegative difference between the two atoms which constitute the polar bond. Now in this case this is a ketone, acetone, it does not have very polar OH groups, it essentially has non-polar CH groups, this is ether, this also has got non-polar C-H groups.

This is ethanol, it has got a polar OH group. This is formaldehyde, which again does not have a polar OH bond, it is non-polar C-H group. Because of the electronegative difference there can be some delta plus character on this carbon, but then overall the electronegative difference is not substantial.

So, it is still, by and large, you can say, weakly polar, but not as polar as ethanol. And finally, methyl fluoride which again has got C-H hydrogen bonds, which are relatively less polar. So, out of these 5 molecules potentially ethanol can engage in hydrogen bond formation, followed by methyl fluoride, which can participate in hydrogen bonds, weak hydrogen bonds and then we also can have participation from formaldehyde.

But these two definitely are non-polar and will not participate in strong hydrogen bond formation. Now, let us now take another set of molecules. and determine which molecule has the largest dipole-dipole interaction. We can take propane, we will take methyl chloride, butane and acetonitrile.

So, in case of propane it is a non-polar species. So, definitely the dipole-dipole interaction will be not there. It will belong to the category of dispersive interactions which we study that is the instantaneous dipole-induced dipole interactions. This has got a dipole moment, definitely this has got a non-zero dipole moment.

It is expected to have dipole-dipole interactions. This is again butane, non-polar species, dispersive interactions, pure Van der Waals interactions, and methyl cyanide, or we can say acetonitrile, organic solvent which has got a large dipole moment because the fact that there is a highly polarized cyano group.

So, μ is not equal to 0, here μ is not equal to 0 here. So, greater is the dipole moment in this case μ_1 , μ_2 , μ_1 is greater than μ_2 . And therefore, this is reflected in the boiling point of the compound being greater, because of the greater magnitude of dipole-dipole interactions. So, the boiling point of acetonitrile is around 355 Kelvin, whereas for methyl chloride, it is around 249 Kelvin.

So, because of the greater magnitude of dipole-dipole interactions, acetonitrile boils at a higher temperature compared to methyl chloride. So, potentially if you see there are no strong hydrogen bond donors here, there are weak hydrogen bond donors like CH in case of acetonitrile as well as CH in case of methyl chloride, but there are sufficiently large magnitude of dipole-dipole interactions and therefore that decides the boiling point of the compound.

And last few examples I would also like to discuss, traditionally what are the strongest hydrogen bonds? The strongest hydrogen bonds are OH...O, OH...N, NH...O and N-H...H. These are the strongest hydrogen bonds. So, whenever you have a species which has a donor and an acceptor these are the strongest hydrogen bonds possible.

The weakest are, the relatively weaker are CH...O, CH...N and CH...X where X is equal to fluoro, chloro, bromo and iodo and then followed by C...C that is the pi...pi stacking types. Or you will have say, S...S, or you will have F...F and so on and so forth, or CH...H--C or CH...pi.

So, now you will be able to appreciate the spectrum of interactions from strong to medium to extremely weak interactions as discussed here. One problem you can look at it yourself. Can be a take home for you. You can take the following compounds, calcium bromide, butanol, ethanol and C₄H₁₀, ok.

Arrange these in order of increasing boiling point. So, I think with this we come to the end of this lecture and this also completes my first module. Now, we will go to the other classification of interactions for the next lecture.

Thank you.