

Concepts of Chemistry for Engineering
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Lecture No. 27
Hard Soft Acid Base

Welcome to this next segment, where we are going to discuss about another periodic property known as hard soft acid base rule. So, when we discuss about acid and base, we can define an acid or a base in different ways. One of the ways is to define with respect to the Bronsted theory, which says if a system can donate a proton that is going to be known as Bronsted acid and if a system can accept a proton it is known as Bronsted base and we have discussed about this acid base system of Bronsted theory in the acid base equilibria with respect to thermodynamics.

Now, we take another look how alternatively we can discuss the acid base properties? And another way to define acid base is with respect to the electron pair donation, which is much more generalized.

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Hard Soft Acid Base

Lewis acid: Accepts electron pair (typically metal ions)

Lewis base: Donates electron pair (Ligand donors)

Introduced by R. G. Pearson:
Classification of acids/bases on the stability of the salt formed between them

Hard Acid: Small cation, high charge density, high positive charge, not easily polarizable

Hard Base: Small anion, high charge density, high negative charge, not easily polarizable (coulombic/ionic interaction)

Soft Acid: Large cation, low charge density, low positive charge, easily polarizable

Soft Base: Large anion, low charge density, low negative charge, easily polarizable (covalent interaction)



So, if there is a system which can accept an electron pair that is going to be known as the Lewis acid generally metal ions and then the entity which is supplying this electron pair is going to be known as the Lewis base generally ligand donors. So, this is the definition with respect to the Lewis acid base theory, which says a system that can accept an electron pair is an acid, a system which can donate an electron pair that is the base.

Now, when you talk about Lewis acid and Lewis basicity, we need to know what is the strength of this acid basicity and when they are interacting between themselves a set of Lewis acid or Lewis base, how they interact and who they actually prefer? So, for example, if you have a Lewis acid in metal ion, and I give them a large number of choices of bases, which of them it would like to prefer and can we connect that with respect to a little bit of idea about thermodynamics?

That is where this discussion about this hard base acid base theory come into the picture. Scientists RG Pearson actually coined these terms hard acid-hard base systems and soft acid-soft base system and he was actually looking at the time on the stability of different salts prepared by the different combinations of acid and bases and he defined hard acid-hard base, soft acid-soft base as following.

So, accordingly hard acid he says it is a small cation, which has a very high charge density generally combined with high positive charge and they are generally weakly polarizable. So, if we connect the dots from the polarizability that we have covered in a different segment, if you have very small electron density, which is actually present around the system with a very high charge, that means your charge density is actually very high, then it will be very less, it will be very difficult to polarize it and this less polarizable system is known as a hard acid.

Similarly, hard base is anionic counterpart of it, if there is an anion, small anion, small in size, which contains some charge in such a way that the charge density is pretty high. And it is also less polarizable and around those kinds of systems are generally try to come together and form a very stable salt. So, this hard acid and hard base would like to interact with each other, why they interact with each other very easily?

Because of their non-polarizable system, they actually try to keep their charge very distinctly. And those two-charge system between the hard acid or a cation and hard base or anion come together in the form of a columbic or ionic interaction. And that is the reason hard acid-hard base system are very stable.

Another system comes in the name of the soft acid and soft base. What is a soft acid? Generally, a cation, but with a very high surface area where we have a very low charge density and generally the overall positive charge is actually quite low. So that the charge density is like the charge divided by the area, area is very high, however, the charge is pretty low and they are polarizable systems.

So again, connected to the polarizability, we have now two sets of ions, which are very highly polarizable, if it is a cation, we call them the soft acid. In the case of soft base that is very similar to the soft acid, but instead of a cation now it is an anion, it is going to be large anion, very low charge density comes up with some negative charge, which is very low in magnitude and this is also very polarizable system.

So, soft acid and soft base also come together and interact with between very strongly, why? Because the polarizable character of the electron density means the electron density can adapt and form new bonds. So, this soft acid and soft base can form covalent interaction, which also becomes very stable.

So, that is why either hard acid hard base through columbic or ionic interaction, or salt bridges or soft acid or soft base, through covalent interaction gives us very stable salt formation. So, that is why if we give different system and ask them to react, the hard acid will like to find out the hard base and soft acid would like to find out the soft base and form the salts and drive the reaction on to that particular direction.

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Hard Soft Acid Base

I. Arrange the following anions with respect to their soft basicity:

F^- , Cl^- , Br^- , I^-



Soft basicity directly related to polarizability

Polarizability order:

$F^- < Cl^- < Br^- < I^-$

Hence, the soft basicity order:

$F^- < Cl^- < Br^- < I^-$



Now, we will follow some question to understand how this soft acid hard acid, soft base hard base system works. So, over here, we have taken example of four anions; fluoride, chloride, bromide, iodide and try to find out the nature of the soft base, which is the most strongest soft base and

which is the hardest base. So, soft basicity as we discussed, it is directly connected to the polarizability, more the polarizable the system is, softer the system is.

And we have discussed earlier in the polarizability section, as we go down to this period to this particular group over there as you go down this particular group we found fluoride, chloride bromide, iodide has the same charge, but the volume increases as you go from fluoride to iodide, and with that the polarizability also increases. So, iodide is the most polarizable system, then bromide, then chloride, then fluoride.

And similarly, the soft basicity also follows the same trend, that means iodide will be the softest base, then the bromide, then the chloride, then the fluoride. So, fluoride will be the least soft or we can say in the other way, the hardest base in this series, where iodide is the softest base. So, if we want to look into soft nature, fluoride to chloride to bromide to iodide, its soft nature increases from fluoride to iodide and hard nature increases as we move from iodide to fluoride.

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Hard Soft Acid Base

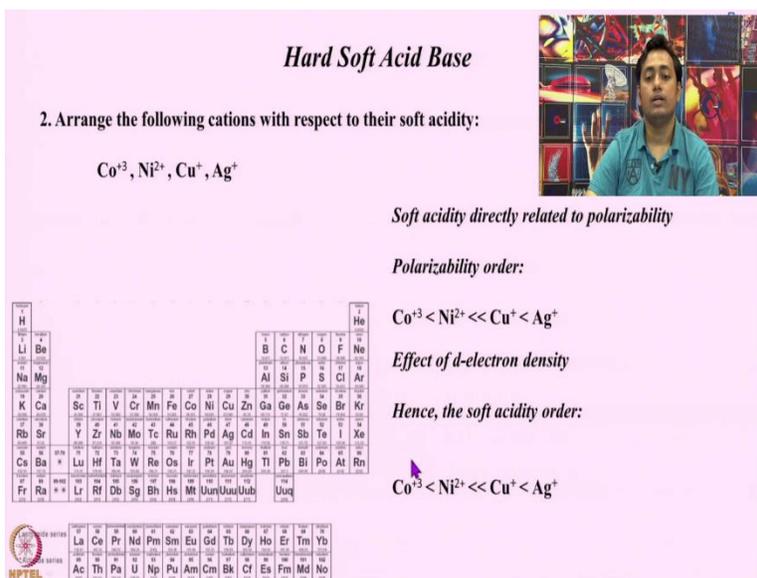
2. Arrange the following cations with respect to their soft acidity:
 $\text{Co}^{+3}, \text{Ni}^{+2}, \text{Cu}^{+}, \text{Ag}^{+}$

Soft acidity directly related to polarizability

Polarizability order:
 $\text{Co}^{+3} < \text{Ni}^{+2} \ll \text{Cu}^{+} < \text{Ag}^{+}$

Effect of d-electron density

Hence, the soft acidity order:
 $\text{Co}^{+3} < \text{Ni}^{+2} \ll \text{Cu}^{+} < \text{Ag}^{+}$



The slide includes a periodic table with a red arrow pointing to the transition metal elements (d-block). The NPTEL logo is visible in the bottom left corner.

Now, instead of anion we take a range of metal ions; Co^{+3} , Ni^{+2} , Cu^{+1} , Ag^{+1} . So, the first three Co^{+3} , Ni^{+2} , Cu^{+1} are in the same period over here, there is the first row transition elements and silver ion is actually in the same group of the copper. So, let us take a look into how we can monitor that.

So, as we know the soft nature of acid or base directly coordinates with the polarizability. So, this correlation, we can expand in this particular way. So, polarizability we know is connected with the

charge density. So, it depends on the amount of charge and what is overall volume. So, now among all these ions, Co^{+3} has the highest charge then the Ni^{+2} then Cu^{+1} then it has the same charge as Ag^{+1} .

So, charge wise we can say Co^{+3} has the highest charge then Ni^{+2} and then Cu^{+1} and Ag^{+1} has the same charge. So how the charge density differs? So, now cobalt, nickel and copper belong to the same period, so, they have the same outer sphere of electrons the 3d electrons. Over here the number of electrons are actually differ, it is actually a different system (Co^{+3}) is a d6, (Ni^{+2}) is a d8 and Cu^{+1} , Ag^{+1} is a d10 system.

So, as the number of d electrons slowly increase, it increases the overall volume of the system. And this higher charge also contracts the d electrons. So, the d electron density among these first-row transition element is actually such that it is the smallest volume in the terms of Co^{+3} , then it is larger in the Ni^{+2} and the largest among the first-row transition element is a Cu^{+1} . So, we have not only had the highest charge, but also the lower volume.

So, obviously, Co^{+3} is going to have the highest charge density then the Ni^{+2} then the Cu^{+1} . So, that will be the trend of the polarizability order; Co^{+3} will be the least polarizable then Ni^{+2} , Cu^{+1} will be the most polarizable. Now we have to distinguish between Cu^{+1} and Ag^{+1} ; Cu^{+1} and Ag^{+1} have the same charge and same outer sphere electron density d10 system.

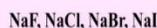
But over here copper is in the first row, so it has the 3d 10 electron and Ag^{+1} in the next way, so it has the 4d 10 electrons. So, over here 4d electrons are actually present outside so, it is much larger in size compared to Cu^{+1} . So, that is why Ag^{+1} the volume is much larger than the Cu^{+1} . So, the charge density is much lower in silver. So, now, if we combine all these things together, this will be the polarizability order; Co^{+3} less than Ni^{+2} less than Cu^{+1} less than Ag^{+1} .

And because it is a d10 system, that charge density is way too low compared to this highly charged ion. So, there is a huge gap over there and this particular trend is going to follow even for the acidity. So, Ag^{+1} will be the softest acid then the Cu^{+1} which will also show a very good amount of soft nature, whereas, this charge system with very high charge density it will be more on the harder side so, there will be more hard acid, so their soft nature will be pretty weak.

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Hard Soft Acid Base

3. Predict the relative water solubility of the following salts:

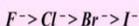


H	He																
Li	Be	B	C	N	O	F	Ne										
Na	Mg	Al	Si	P	S	Cl	Ar										
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	* Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	** Lr	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub	Uuc	Uud	Uue	Uuf	Uug	Uuh
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb																	
Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No																	

Here the cation Na^+ is identical
The anions vary in the salts

Na^+ is a relatively hard acid
Hence it would prefer hard base for generating a stable salt

The order of hard basicity for the anions are:



The NaF will be the most stable (least soluble)
and NaI will be the least stable (most soluble)

Now, coming back to another question, when we discussed the solubility of these particular salts, sodium fluoride, sodium chloride, sodium bromide and sodium iodide. What is the common factor? Sodium is same in all of them and we are adding the anions fluoride to chloride to bromide and iodide. So, when you talk about the solubility, you are trying to find out, we take this salt in solid form put that in water and then in water they actually break the bond present in the salt between the cation and anion and the water dissolve them separately.

Now, stronger is the bond between this salt, harder will be to break this bond and lower will be the solubility if a salt is easily breakable, it will dissolve in their particular cation and anion very easily in the water. So, that will be going to have a higher solubility, whereas, if a salt is very strong in their bond, it will take very high amount of energy and in the water, they may not even break down, so, that will have very low solubility.

So, to understand that we have to now find out which of these bonds' sodium fluoride, sodium chloride, sodium bromide and sodium iodide is the strongest, sodium is common the variation is in the anion. Now sodium itself present over here, which has relatively high charge density, so, we can say sodium ion is a very less polarizable ion. So, we can say it is generally hard ion. So, it is a hard acid.

So, it will prefer a hard base, so among the fluoride chloride bromide iodide we have already discussed what is the combination, now fluoride has the highest charge density, because it has lowest volume over there, we can follow that from the periodic table then the chloride then bromide

then iodine, iodide has the highest volume. So, the least amount of charge density highly polarizable, so it is a soft ion, soft base.

So, the hardest is the fluoride, softest is the iodide. So, generally what will happen the sodium will form which is a hard acid, the strongest bond with the fluoride because it is a hard-hard interaction, then it will be having interaction with the sodium chloride which will be less than the fluoride, but higher than the bromides or iodides. Then comes the bromide, which will be less than chloride or fluoride but higher than iodide and sodium iodide will be the complete mismatch because it is the hard acid and soft base.

So, when we discuss about the basicity of this particular anions, fluoride is the hardest so it will prefer to bond with hard acid sodium, so the sodium fluoride bond will be the strongest. Sodium chloride bond will be weaker than sodium fluoride because chloride is little bit less hard compared to the fluoride, it will be strong compared to bromide and iodide. Sodium bromide will be weaker than chlorides and the fluorides but stronger than iodide and sodium iodide will be strongly mismatch, because it is interaction between hard acid and soft base.

So now, sodium fluoride the strongest bond, it will be the least soluble because water cannot break it very well, because the bond strength is so well that it cannot break it to sodium ion and fluoride ion, whereas sodium iodide very weak bond, so it breaks down very easily so that we will be having the highest solubility.

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Hard Soft Acid Base

4. Predict the relative water solubility of the following salts:

CuF, CuCl, CuBr, CuI



Here the cation Cu^+ is identical
The anions vary in the salts

Cu^+ is a relatively soft acid (d^{10} system)
Hence it would prefer soft base for generating a stable salt

The order of soft basicity for the anions are:

$\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$

The CuI will be the most stable (least soluble)
and CuF will be the least stable (most soluble)



And a very similar question and the last one, but over here, we change the iron from sodium ion to copper ion Cu^{+1} ion. And as you have discussed earlier, Cu^{+1} ion is actually a soft ion, because it is a d^{10} system and it will prefer a soft base for generating the salt. And as you have just discussed in the earlier answer also, we go from fluoride to iodide in this particular group, fluoride is the hardest because it has the highest charge density, lowest volume and you go to the iodide, it has the least charge density but the highest volume, so most polarizable and the softest ion.

So over there, copper because it is a soft acid it will prefer the soft base, so the strongest bond it will form with the soft base that is a copper iodide. Whereas, thus weakest bond it will form with the fluoride because it is a complete mismatch, it is a hard ion, hard base and a soft acid. So, copper iodide will have the strongest bond and the least solubility or the copper chloride is the least stable and it will be the highest solubility.

So again, solubility is connected directly with the bond strength, where we find the highest bond strength it will be the least soluble, where we will find the least bond strength, it will be the highly soluble and the bond strength over here between the copper and the halides goes in the trend of copper iodide is the strongest soft nature, copper bromide is still soft, but not as soft as the iodide.

Copper chloride now we start moving to the hard system. So, it is a mismatch it will be much weaker, copper fluoride is the most weak or the weakest link over here, because it is the hardest base present in this system.

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Hard Soft Acid Base

5. Comment on the equilibrium of the following reaction:

$$R_3P-BBr_3 + R'_3N-BF_3 \rightleftharpoons R_3P-BF_3 + R'_3N-BBr_3$$

This is an acid-base reaction

The phosphine/amine acts as base while the borane derivative act as the acid

N / P → Base. Borane → Acid

Now with the last question of this segment, we are looking into this particular reaction. Over here, there is a phosphine borane bond and there is amine borane bond. So, over here we are looking into a reaction, there is a phosphine and borane bond where the borane contains bromide, this amine and borane bond, the borane contains fluoride. And then there is exchange, they are exchanging the borane counterpart, so the phosphine is now connected to the borane containing fluoride and the amine is containing the borane containing the bromide.

We want to find out where this equilibrium lies, this reaction goes to the forward side or it is happy to stay back in the left-hand side? Can we understand this fate of the reaction with respect to the hard soft acid base system? To understand that, we have to look into this reaction and find out it is an acid base reaction, there is a phosphine present over here and which is actually reacting with our base in the form of borane.

So, over there, there is an amine system present with two electron pair and there is a borane present, borane present like this, which has a vacant p orbital, this is an empty orbital and this nitrogen amine transferred the electron to the borane, so, from the Lewis acid base theory, this borane is accepting the electron pair, so it is a Lewis acid and this amine is supplying the electron pair, so it is a Lewis base.

And the same thing can happen not only on the nitrogen, but also with the phosphine. So, either nitrogen the amine or the phosphine are actually the base and the borane system is actually the

acid. Now, it is much easier, we have to just find out which is the soft and which is the hard acid base system.

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Hard Soft Acid Base

5. Comment on the equilibrium of the following reaction:

$$R_3P-BBr_3 + R'_3N-BF_3 \rightleftharpoons R_3P-BF_3 + R'_3N-BBr_3$$

This is an acid-base reaction

The phosphine/amine acts as base while the borane derivative act as the acid

The amine is hard base compared to phosphine

hard *soft*
diffused
polarizable

Now, amine is a hard base compared to phosphine. Why? Because both amine and phosphine actually has a lone pair. But this lone pair stays in 3p orbital on nitrogen, on 4p orbital in phosphorus, this is much more diffused, higher volume and the same two electrons is spread over a larger volume, larger space. So, this is going to be more polarizable. So, that is why phosphine is actually a softer base compared to amine. So, amine is hard, phosphine is soft.

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Hard Soft Acid Base

5. Comment on the equilibrium of the following reaction:

$$R_3P-BBr_3 + R'_3N-BF_3 \rightleftharpoons R_3P-BF_3 + R'_3N-BBr_3$$

This is an acid-base reaction

The phosphine/amine acts as base while the borane derivative act as the acid

The amine is hard base compared to phosphine

The BF_3 is a strong acid than BBr_3

The slide includes a periodic table on the left and a diagram on the right illustrating the interaction of lone pairs from fluorine and bromine with the boron center. The fluorine atom is shown with its 2p orbitals, and the bromine atom is shown with its 4p orbitals. The diagram is annotated with '2p' and '4p' labels and a 'soft' label near the bromine atom.

Now, with respect to the borane, the borane seems same, but there is a difference which atoms are bound to it, we can have either fluoride bound to it or we can have either bromide bound to it. So, here is the lone pair of the bromine present over there, which has the capacity to get electrons over there. Now, what happens the fluoride has some lone pairs of orbitals present over there which can interact with this orbital and present some electron density over there, same thing happens with respect to the bromide also.

Now bromide when it is interacting with this borane, it is actually interacting its 4p orbitals, whereas, fluoride is using the 2p orbitals. So, during this interaction, this is actually going to spread the overall electron density out, but with respect to 4p when it is interacting, it is going to show movement over a larger space because 4p orbitals are much larger.

So, that means, when the bromides are interacting with this borane center, it is going to show its soft nature with respect to the acidity, because the orbital will be much more polarizable through this interaction in the bromines. Whereas, in the interaction with the fluoride because it is using small and less polarizable 2p orbitals that is also going to reflect it on the boron center.

So, the boron center acidity will be strong acidity when it is connected to the fluoride. So, that is why BF_3 is less polarizable or strong acid compared to BBr_3 . So, now, we know BF_3 is the strong acid BBr_3 is the soft acid. So, now, we have to just combine them together.

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Hard Soft Acid Base

5. Comment on the equilibrium of the following reaction:

$$R_3P-BBr_3 + R'_3N-BF_3 \rightleftharpoons R_3P-BF_3 + R'_3N-BBr_3$$

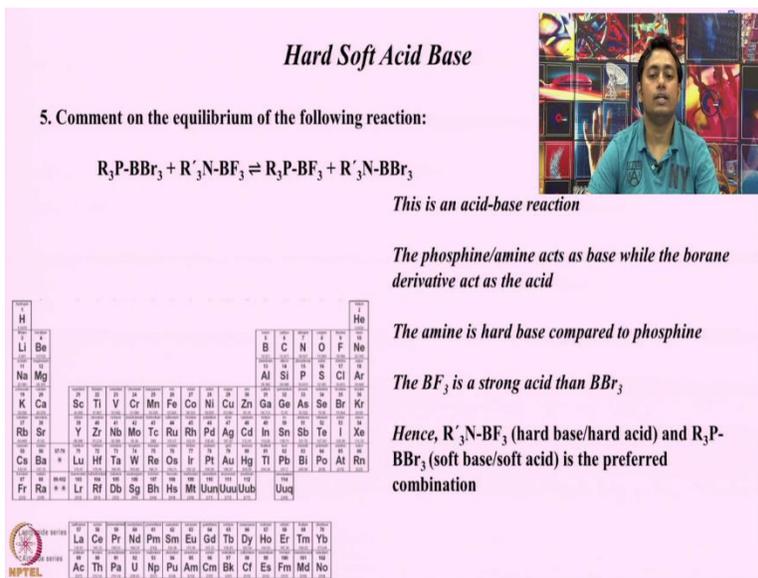
This is an acid-base reaction

The phosphine/amine acts as base while the borane derivative act as the acid

The amine is hard base compared to phosphine

The BF_3 is a strong acid than BBr_3

Hence, R'_3N-BF_3 (hard base/hard acid) and R_3P-BBr_3 (soft base/soft acid) is the preferred combination



So, a hard acid-hard base system will be preferred. So, amine to BF_3 will be preferred. And a soft acid-soft base will be preferred, phosphine to the borane connected to the bromine and these two systems will be more stable, this through the ionic interactions, this is through the covalent interaction.

And this particular combination in present you can see on the left-hand side of the reaction, on the right-hand side it is a phosphine and BF_3 , soft base strong acid. Amine into the BBr_3 strong base soft acid, so, they are not preferable, this side is preferable. So, the equilibrium for this side will lie on the left-hand side.

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Hard Soft Acid Base: Summary

Hard Acid/base: Small ion, high charge density, not easily polarizable

Soft Acid/base: Large cation, low charge density, easily polarizable

Hard/hard and soft-soft interactions are preferred

Salt formation, solubility, equilibrium

So, over here now, we would like to conclude this particular section of hard soft acid base theory. Hard soft acid base theory is directly connected to the polarizability, a hard acid or a hard base is so systems those are less polarizable, generally small in size and which has high electron charge density.

On the other hand, soft acid and soft base systems are such which are actually larger in size and whose electron density is much more polarizable which has very low charge density. Hard acid and hard base actually preferred each other through the ionic interaction. Soft acid and soft base prefer each other because of their covalent interaction.

And this hard acid hard base interaction is very important when you talk about the formation of stronger bonds, like in salt into their solubility, and also even equilibration when we actually put in acid with a combination of base or vice versa. So, all this fate of the reaction will be controlled by the hard acid hard base and soft acid soft base nature of the systems. So over here, we conclude the hard acid hard base system discussion. Thank you.