A warm welcome to this

inorganic chemistry class.

The course code is CHC 109.

Section B topic reaction mechanisms.

And kinetics.

The module that I will be doing

is factors affecting the rate.

Of substitution reactions
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The learning outcome of this

module will flow as follows.

We will learn about the factors

which affect the rate of aromatic

nucleophilic substitution reactions.

We learn to identify suitable

substrates leaving groups and incoming

nucleophiles for SN1 SN2 type reactions.

And then we'll be able to analyze factors

governing suitability of reaction conditions

for nucleophilic substitution reactions.

So the outline will flow as follows.

These are the factors that we're going to

see size and charge of the central metal.

The electronic configuration

of the central metal,

the Crystal field stabilization,

energy, charge to ionic size ratio,

and the geometry of the complex.

Let us begin with the first factor

size and charge of the central metal.

Smaller the central metal atom

more tightly will the ligands be held,

and more inert will be the complex.

There are 3 complexes on your screen.

the liability increases for the

following complexes as seen below.

Please note the rate constant K

stands for the exchange of solvent

and coordinated water molecules,

so smaller the value of K more

inert is the complex correct.

You will agree with me that the

ions in these complexes belongs to group 2A.

All the metal belong to your group

2 A alkaline earth metal group.

So as you go from Magnesium too.

Calcium to strontium.

The ionic size is increasing,

so we already said smaller the size of

the central metal more tightly will ligands

be held and more inert is the complex.

Therefore,

from the values of rate constant,

it is evident that the Magnesium +2
metal complexes,

most inert whereas the hexaaquo strontium

+2 complex is least.
higher the

charge of the central metal ion more tightly.

The ligands will be held and

more inert is the complex.

There are two complexes on your screen.

One is a calcium +2 complex

the other is a hexa aquo sodium with

sodium is in the plus one oxidation state,

so higher the charge more tightly.

The ligands will be held.

This is evident from the value

of rate constant.

It is lower for the calcium complex.

It is a little higher.

For the sodium complex and

below we have the net effect of size

and charge on the central metal.

This can be seen in the gradual

inertness of these complexes.

Correct as you move from left to right,

the ionic size is decreasing,

whereas the ionic charge is

increasing its plus three.

In aluminium +4 silicone plus

five in phosphorus plus 6 in SF 6.

So this is the net effect of size and charge.

And how do we confirm this?

That means a hexa fluoro

aluminate minus three is

least inert. SF_6 will be most inert.

How do we know this?

If we had a

AlF_6 minus the will immediately get a

precipitate of aluminium hydroxide,

whereas SF_6 does not undergo any

noticeable change when a base is added,

so it indicates that this one AlF_6 minus 3 is least inert.

Well whilst SF 6 is most inert.

Next factor is size in

charge of the central metal,

not this is based on taubes classification.

Now According to him he said

complexes having one or more empty

inner d orbitals will be labile.

OK, I've taken the example of Hexa

Aqua titanium plus three with titanium

is in the plus three oxidation state.

It has 1 d electron associated

in this oxidation state.

OK, so two of the 3 d orbitals are empty.

OK, so it is an inner orbital complex.

It undergoes d2sp3

kind of hybridization,

two inner d orbitals are empty.

Therefore it is labile.

What about the complex hex aquo vanadium

+2 vanadium in the +2 oxidation state

has 3 d electrons associated with it.

So in vanadium, +2 in this complex hexa aquo,

when vanadium too complex there

are no empty inner d orbitals.

Therefore, this complex is inert.

Both our inner orbital complexes,

both the complexes hexa aquo titanium

plus three and hwxa aquo Vanadium +2.

Both are inner orbital complexes

but the first one OK,

the previous one has empty inner d orbitals.

OK,

two of them you can see on

your screen the next one,

the vanadium complex,

has no empty inner d orbitals and

therefore this makes this complex inert.

But as the previous one is labile

then also Taube said that when the

central metal forms both inner

and outer orbital complexes,

I've taken 2 complexes of Fe +2 is a

hexa cyano Complex 1 isn't exactly complex.

Now in the hexa aquo complex,

OK the hexa cyano complex.

Is an inner orbital complex,

where as the Hexa Aquo complex

aquo being a weak ligand
OK, it is an outer orbital complex,

so when the central metal form so

therefore the hybridization year is d2sp3

here it is sp3d2

So when the central metal atom forms

both inner and outer orbital complexes.

In that case the inner orbital

complex will be inert.

So FeCN 6 - 4 is inert whereas

the outer orbital complex is labile.

So therefore,

FeH2O6 plus two is labile

so on the basis of Mot theory
concluded complexes with metals

having electrons in e.g.

When I say electrons in e.g yeah

the outer orbital complex of hexa

aquo ion plus two has electrons in

e.g correct less than 3 electrons

in the d orbitals.

You're looking at hexa aquo titanium

plus three which has only one.

Electron in the d orbital.

These complexes are relatively labile

complexes with other electronic

configurations, will be inert.

Next factor is the CFSE or Crystal

field stabilization energy.

So the liability of a complex

depends upon the differences

in energy between the reacting

complex and the activated complex.

What do we call this difference in energy?

It is called activation energy.

Now how do we get this activation

Energy, activation energy can

be obtained by comparing.

The Crystal Field stabilization energy

of the initial octahedral complex

and the Crystal field stabilization

energy of the transition state

using an assumed configuration

for the activated complex OK.

This activation energy diagram

will explain everything to you.

This is your reacting complex which

if it follows an SN1 mechanism it is

found to form an activated complex

or a transition state where the

geometry which has coordination #5.

If it follows an SN2 type of mechanism.

It is going to form a transition

state or an activated complex where

the coordination number is 7 OK,

so every reactant complex will pass

through the activation state or

through the transition state before

it finally gives you the product.

So this difference in energy between

the initial reactant complex and

the activated complex is called

the activation energy.

So if substitution reaction takes place by

dissociative mechanism or SN1 mechanism,

you're getting a 5 coordinate square pyramid.

Or trigonal bipyramidal activated

Complex. if your substitution reaction

is taking place by displacement

mechanism or SN2 mechanism,

then you're getting a 7 coordinate

pentagonal bi pyramidal activated complex.

Now if the CFSE decreases during

such a conversion to a big extent,

or if the difference is negative,

the intermediate complex that is

your activated complex will be

unstable and a very high energy

of activation has to be reached.

By the reactant to take part in the reaction.

In this case,

the complex will prefer to remain inert.

This is commonly seen for d3 and d8 systems,

whereas if there's little or

there's no change in the CFSE.

If the difference is positive,

there is a gain in the CFSE,

then the complex will be labile..

This is seen for d1, d2,d5,d6,d7 and d10 systems,

so this is about crystal

field stabilization energy.

Next we see charge to ionic size ratio

greater the ratio of charge in the

complex to the size of the central metal.

Lesser would be the lability of the complex.

The lability of the complexes

below decreases as follows.

Please note aluminium has the highest charge.

Here it is Al

In the plus three oxidation state

it has the smallest ionic size,

so the charge to radius ratio is 6.

For the sodium hexaaquo sodium complex,

the charge to radius ratio is 1.

So that means this complex.

The hexa aquo sodium complexes,

mostly by OK,

whereas the hexa aquo aluminium

plus the complex is least labile,

so greater the ratio of the charge

of the complex to the size of the

central metal ion greater the ratio,

lesser is the liability.

So the ratio is the maximum for

Hexa aquo aluminium complex.

And therefore this complex is least

Labile and the sodium hexa aquo complex is,

Most labile.

Lastly,

the geometry of the complex

now tetrahedral

and square planar complexes offer a better

sites for the attack of an incoming ligand,

and therefore for the same set of metal

ion and ligands square planar tetrahedral

complexes are more labile than octahedral.

I've given you 2 examples,

look at the first one.

It is a square planar complex.

The metal ion is platinum +2.

You have two ammonia ligands

and two chloro ligands.

It's a square planar complex.

Look at the octahedral complex.

Also, Platinum +2 is the central metal ion

but here you have four more ligands.

two chloro ligands making

it octahedral. So this square planar

complex offers a better site for

attack of an incoming ligand and so

therefore the square planar complex

of platinum is more labile than

the octahedral complex of platinum.

Another example,

look at this tetrahedral complex

of Tetra Chloro Cobaltate

cobalt is in that +2 oxidation state,

so tetrachloro cobaltate is tetrahedral.

You have hexa chloro cobaltate

cobalt is +2 again which is octahedral

so tetrahedral Tetra chloro cobaltate
will be more labile than the

octahedral hexa chloro cobaltate.

So for the same set of metal ion

and ligands square planar and

tetrahedral complexes.

Are more labile than the

corresponding octahedral complexes.

So in conclusion,

smaller the size higher the charge of

the central metal ion more tightly.

The ligands are held and more

inert is the complex.

Next complexes with metal

having electrons in E.g.

Less than 3 electrons in the d orbitals

are expected to be relatively labile.

lability of a complex depends upon

the difference in energy between your

reactant complex and the activated complex.

This difference in energy is

called activation energy.

Greater the charge to ionic size ratio,

lesser is the lability of the complex,

and tetrahedral and square planar

complexes are definitely more

labile than the corresponding.

Octahedral complexes
for your references

students there are many good books,

concise,

inorganic chemistry Wiley India.

Puri Sharma principles of inorganic

chemistry.

Selected topics in inorganic

chemistry is also

a good book and we have College

in organic chemistry for TyBSc.

Himalaya publication house.

Also a very good book.

Thank you.