Chemistry of Transactinides - I

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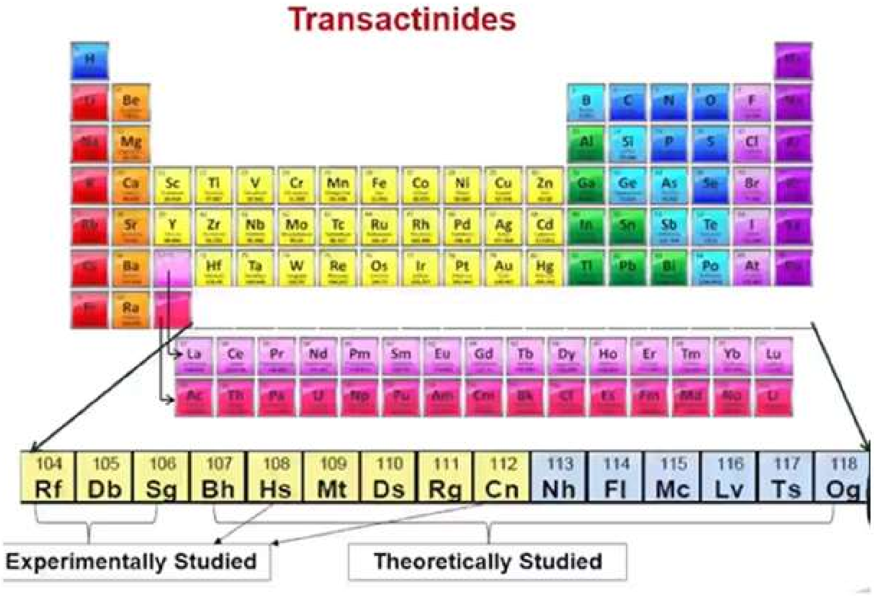
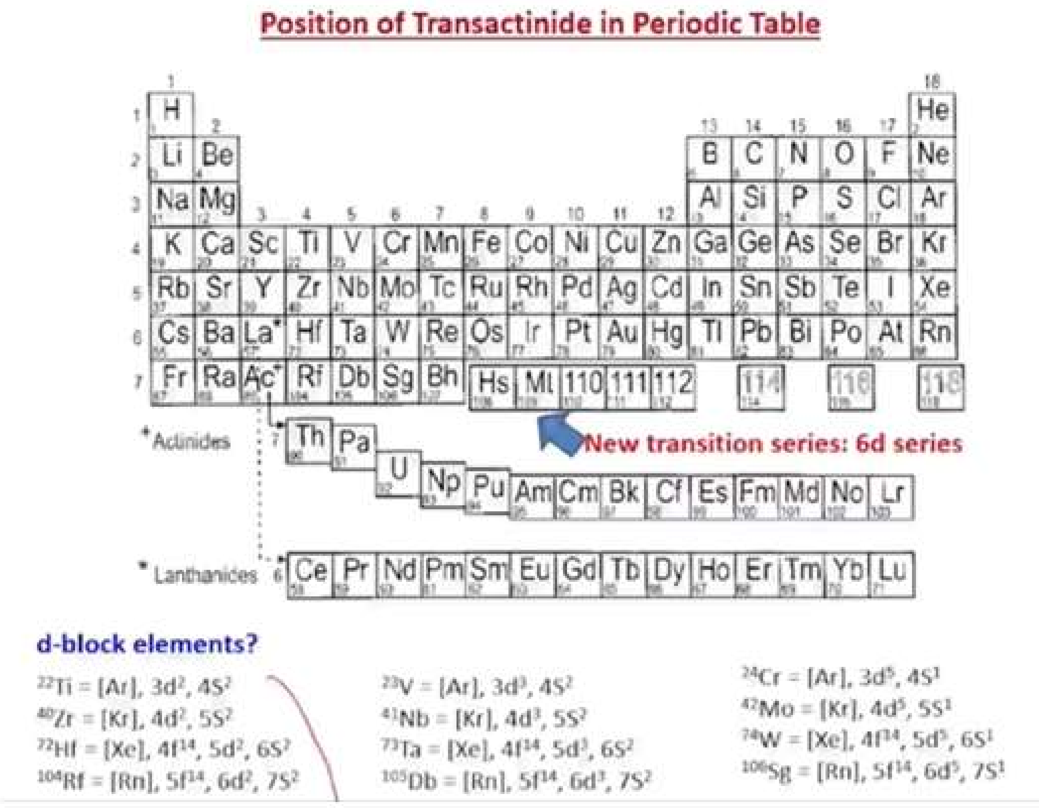
Lecture – 59



So, we have completed the portion on actinides. Now, we will be discussing the transactinides and their chemical properties. The transactinides, as shown in this periodic table, are part of a fourth transition series, and it starts from element number 104 which is the Rutherfordium, and it goes up to element number 118. Now, some of the first few transactinides are experimentally studied, and the later part of the transactinides is also theoretically studied. Now, they have been determined by physical methods that is by counting in the physics experiments, but for the chemistry experiments, it is not possible because of the very, very short half-lives of some of the later parts of the transactinides. Nevertheless, the early part of the transactinides like Rutherfordium (element 104), Dubnium (element 105), Seaborgium (element 106), and Hassium (element 108) have been chemically studied in aqueous medium.



Position of Transactinide in Periodic Table

d-block elements?

$^{22}Ti = [Ar], 3d^2, 4S^2$
$^{40}Zr = [Kr], 4d^2, 5S^2$
$^{72}Hf = [Xe], 4f^{14}, 5d^2, 6S^2$
$^{104}Rf = [Rn], 5f^{14}, 6d^2, 7S^2$

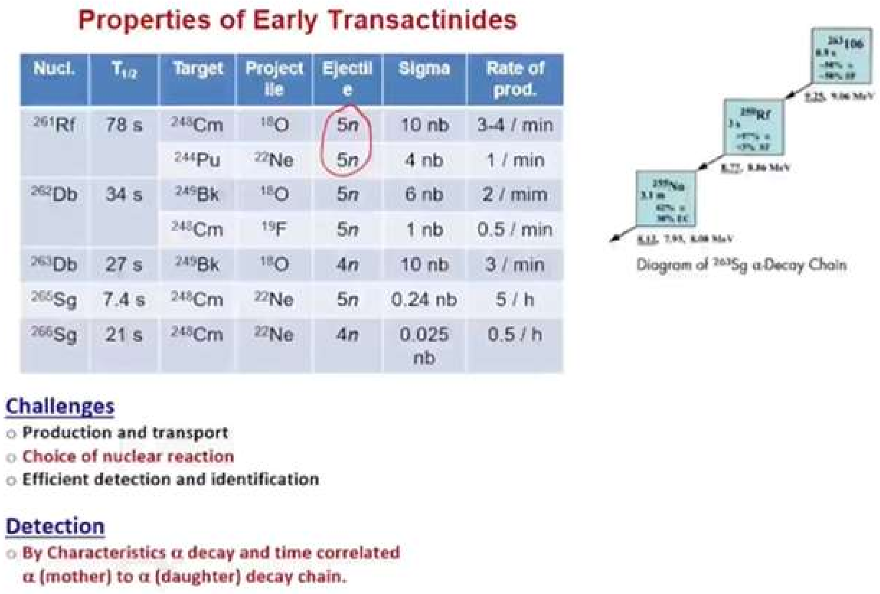
$^{23}V = [Ar], 3d^3, 4S^2$
$^{41}Nb = [Kr], 4d^3, 5S^2$
$^{73}Ta = [Xe], 4f^{14}, 5d^3, 6S^2$
$^{105}Db = [Rn], 5f^{14}, 6d^3, 7S^2$

$^{24}Cr = [Ar], 3d^5, 4S^1$
$^{42}Mo = [Kr], 4d^5, 5S^1$
$^{74}W = [Xe], 4f^{14}, 5d^5, 6S^1$
$^{106}Sg = [Rn], 5f^{14}, 6d^5, 7S^1$

Also, the gas phase chemistry of these elements hasbeen studied extensively. There is also a recent gas phase chemistry report of element number 112. As mentioned in this slide, these lanthanides, and actinides, are called the inner transition series, and the transactinides, are part of the transition series. So, the chemistry of these transactinides follows the transition elements as shownin the next slide. Whether they are d-block elements?

Now, you see from the electronic configuration, titanium, has the Z of 22, zirconium, Z of 40, hafnium, the Z of 72, and rutherfordium, Z of 104. They have a similar electronic configuration like they have the d^2, and s^2 type of configuration, all of them. Only in the case of the hafnium, and rutherfordium, do they have $4f^{14}$, and the $5f^{14}$, that is the filled *f* levels are also there. Same also we can do about the + 5 oxidation state transition elements like vanadium, which has Z of 23, niobium, Z of 41, tantalum, Z of 73, and dubnium, Z of 105. Their electronic configurations, you can see that they are similar, that is d^3, and s^2 type of configuration is there, and finally, the +6 oxidation state, that is chromium, Z of 24, molybdenum, Z of 42, tungsten, which has Z of 74, and seaborgium, which has Z of 106.

They also have similar electronic configurations, that is d^5 and s^1. As will be seen later in this lecture, the s, and the third transition series elements are considered as the homologs of the transactinides. For example, zirconium, and hafnium are homologs of rutherfordium; niobium and tantalum are for dubnium, and molybdenum and tungsten are for seaborgium. Now the properties of these early transactinides and their half-lives are mentioned here in the table below. Some of the early transactinides, which have been synthesized in the last century, are given here like ^{261}Rf, which has a $t_{1/2}$ of 78 s, and all these transactinides are produced by nuclear reactions in accelerator facilities.



Properties of Early Transactinides

Nucl.	$T_{1/2}$	Target	Projectile	Ejectile	Sigma	Rate of prod.
^{261}Rf	78 s	^{248}Cm	^{18}O	5*n*	10 nb	3-4 / min
		^{244}Pu	^{22}Ne	5*n*	4 nb	1 / min
^{262}Db	34 s	^{249}Bk	^{18}O	5*n*	6 nb	2 / mim
		^{248}Cm	^{19}F	5*n*	1 nb	0.5 / min
^{263}Db	27 s	^{249}Bk	^{18}O	4*n*	10 nb	3 / min
^{265}Sg	7.4 s	^{248}Cm	^{22}Ne	5*n*	0.24 nb	5 / h
^{266}Sg	21 s	^{248}Cm	^{22}Ne	4*n*	0.025 nb	0.5 / h

Challenges

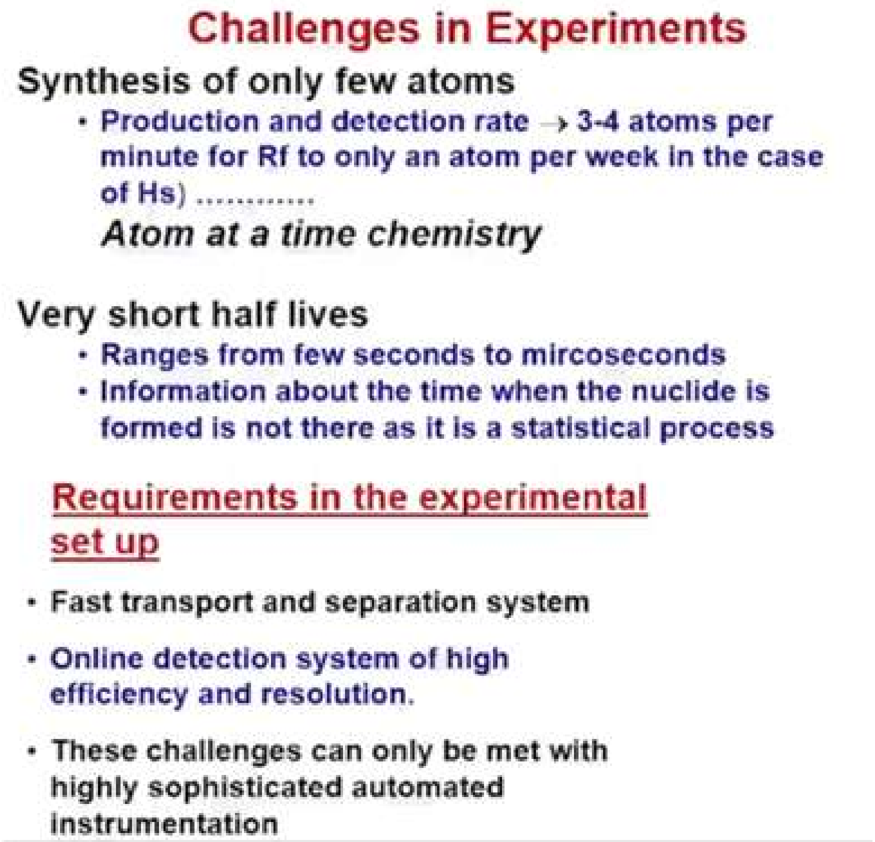
- Production and transport
- Choice of nuclear reaction
- Efficient detection and identification

Detection

- By Characteristics α decay and time correlated α (mother) to α (daughter) decay chain.

Diagram of ^{263}Sg α-Decay Chain

Thus, ^{261}Rf is formed either by a ^{248}Cm target with ^{18}O beams or a ^{244}Pu target with a ^{22}Ne beam. In both cases, 5 neutrons are emitted. But for these reactions, the cross-section is significantly different. For the first reaction, that is the reaction from ^{248}Cm, 10 nano barns as the cross-section, and for the ^{244}Pu as the target, the cross-section is around 4 nanobarns, and the rate of production also varies, even though the product is the same, but from ^{248}Cm, the rate of production is much higher because of the higher cross-section, that is 3 to 4 atoms are produced per minute and from the reaction, while that from ^{244}Pu plutonium, only one atom per minute is produced. Now coming to ^{262}Db, that is element 105, it has a half-life of 34 s, and the target required for this is ^{249}Bk,where an ^{18}O beam is used, in which again 5 neutrons are emitted, and with a 6 nanobarn cross-section, you have the product around 2 atoms per minute, and with a ^{248}Cm target with ^{19}F as the beam, you have 5 neutrons emitted, and with 1 nanobarn, which is a 6 times lower cross-section, and that is why the production also is less, you have only 0.5 atoms per minute. The ^{263}Db has a half-life of 27 s, and it is produced from ^{249}Bk targets using an ^{18}O beam, with a 10 nanobarn as the cross-section, which is 3 atomsper minute. Now coming to the seaborgium isotopes, there are mainly two isotopes of seaborgium. One is ^{265}Sg, with a 7.4 s half-life. For this, it is ^{248}Cm targets with a ^{22}Ne as the ion beam. The reaction is done, which is 0.24 nanobarn as the cross-section., and 5 atomsare produced per hour. For the ^{266}Sg, which has a relatively longer half-life, that is 21 s. Again, the target is ^{248}Cm and the projectile is ^{22}Ne and 4 neutrons are emitted in this case, but the cross-section is nearly one order magnitude lower, with a production rate of 0.5 atoms per hour.



Challenges in Experiments

Synthesis of only few atoms

- Production and detection rate → 3-4 atoms per minute for Rf to only an atom per week in the case of Hs) ....
  Atom at a time chemistry

Very short half lives

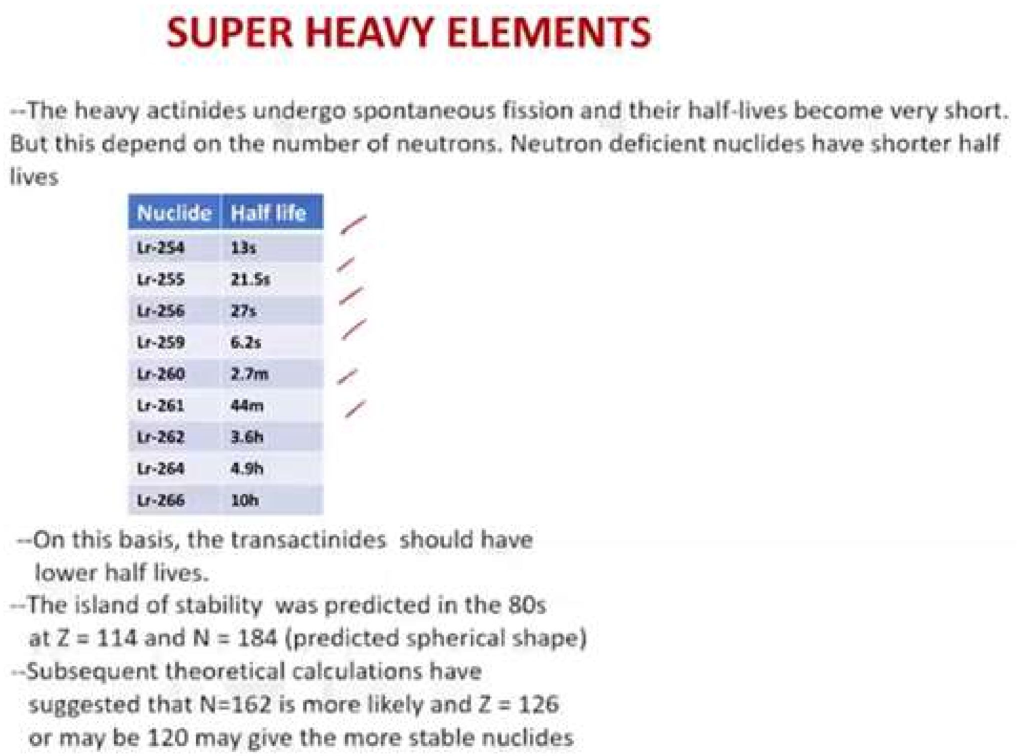
- Ranges from few seconds to mircoseconds
- Information about the time when the nuclide is formed is not there as it is a statistical process

Requirements in the experimental set up

- Fast transport and separation system
- Online detection system of high efficiency and resolution.
- These challenges can only be met with highly sophisticated automated instrumentation

Now the challenges in the case of the transactinides is that the production, and transport. This is a challenge, because as I have already mentioned, the cross-sections are very very low in the nanobarn range, less than nano barn for seaborgium nuclei, and also for what type of nuclear reaction one has to carry out, and finally, efficient detection as well as identification. The detection is done by the characteristic alpha decay, and the time-correlated alpha of the mother to the alpha of the daughter in the decay chain. I have shown that in this diagram, where you have ^{263}Sg, which is decaying to ^{259}Rf. So, ^{263}Sg has a half-life of only 0.9 s, and this is decaying to ^{259}Rf with a half-life of 3 s, which subsequently decays to ^{255}No, the 3.1minutes as the half-life. So, the alpha particles you see are from ^{263}Sg has nearly 50%alpha and 50% spontaneous fission. For ^{259}Rf, you have 97% alpha and 3% spontaneous fission, and for the ^{255}No, we have 62% alpha, and 38% in electron capture. So ultimately, when you do the counting, the seaborgium, as well as rutherfordium must have already decayed and so necessarily you have to count the ^{255}No. And if you can count ^{255}No, or if you can detect it, then you can always assume that ^{263}Sg has formed. Now the experimental challenges, because the production, and detection rate is very, very less, this is a very big challenge carrying out these experiments.

So, this is called a single atom chemistry or atom-at-a-time chemistry. You carry out the chemical reactions, then you are dealing with only one atom at a time. As I have already mentioned, they are very, very short half-lives, ranging from a few s to micro seconds, and also, there is uncertainty about what time the nuclei is exactly formed. However, that is not known, as it is a statistical process.



SUPER HEAVY ELEMENTS

--The heavy actinides undergo spontaneous fission and their half-lives become very short. But this depend on the number of neutrons. Neutron deficient nuclides have shorter half lives

Nuclide	Half life
Lr-254	13s
Lr-255	21.5s
Lr-256	27s
Lr-259	6.2s
Lr-260	2.7m
Lr-261	44m
Lr-262	3.6h
Lr-264	4.9h
Lr-266	10h

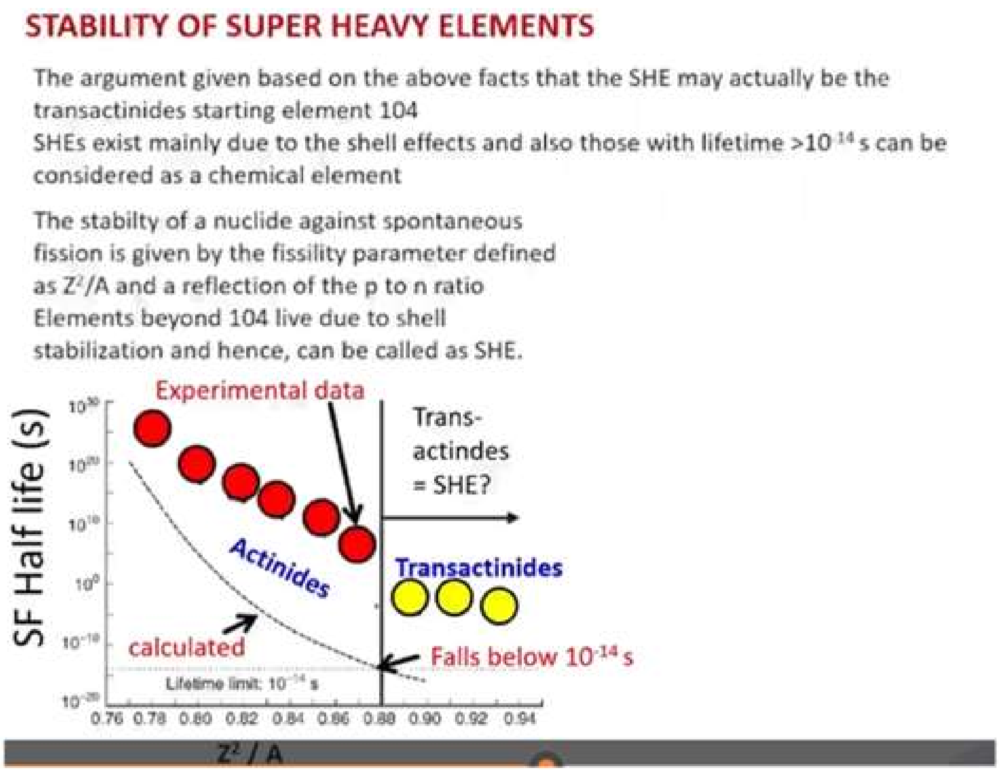
--On this basis, the transactinides should have lower half lives.

--The island of stability was predicted in the 80s at Z = 114 and N = 184 (predicted spherical shape)

--Subsequent theoretical calculations have suggested that N=162 is more likely and Z = 126 or may be 120 may give the more stable nuclides

With all this, it is very difficult to carry out these experiments. Many times thousands of experiments have to be carried out continuously over several days, and the data obtained are to be finalized after getting theresults. Now the requirements in the experimental setup, we need a fast transport and separation system. We also need an online detection system of high efficiency as well as high resolution. These challenges can be met with highly sophisticated automated instrumentation. Now when we are talking about the transactinides, many times there is this feeling that these are called previously as super-heavy elements. So these super-heavy elements or the transactinideas they are known. They are the heavy actinides that are undergoing spontaneous fusion, and their half-lives become very, very short. We know already that these heavy actinides like-Lr, have very short half-lives. I have given this table here, where this ^{254}Lr which has a 13 s half-life, and like that, it goes on ^{255}Lr, 21.5 s half-life. ^{256}Lr with a 27 s half-life, ^{259}Lr with 6.2 s, half-life. ^{260}Lr with 2.7 minutes half-life, ^{261}Lr with 44 minutes half-life, ^{262}Lr 3.6 hours half-life, ^{264}Lr 4.9 hours half-life and ^{266}Lr with 10 hours half-life. So, except for ^{259}Lr, you can see that mostly as the neutron number increases, the half-life becoming higher. So, on this basis;

the transactinides should have much, much lower half-lives because they are heavier radionuclides.



STABILITY OF SUPER HEAVY ELEMENTS

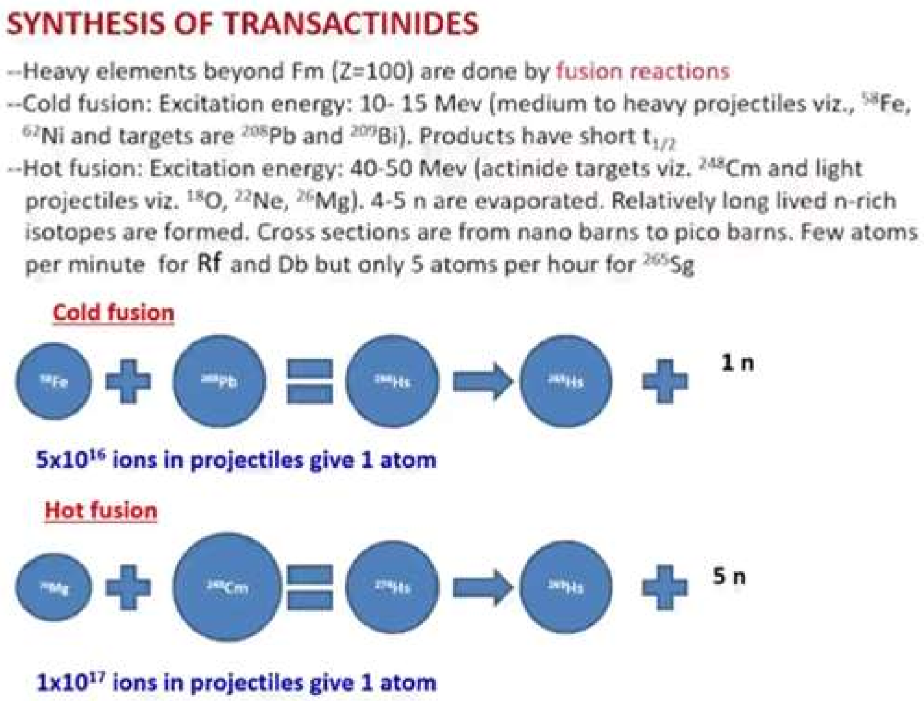
The argument given based on the above facts that the SHE may actually be the transactinides starting element 104
SHEs exist mainly due to the shell effects and also those with lifetime >10^{-14} s can be considered as a chemical element

The stabilty of a nuclide against spontaneous fission is given by the fissility parameter defined as Z^2/A and a reflection of the p to n ratio
Elements beyond 104 live due to shell stabilization and hence, can be called as SHE.

Also, from the nuclear physics point of view, there was a prediction that there would be an island of stability predicted based on the cell model at a Z of around 114, that is the total number of protons is 114, and the neutron number of 184. So this was predicted much earlier, and subsequent theoretical calculations have suggested that this island of stability may be at a neutron number of around 162, and with a Z value of maybe around 126 or maybe 120. This may give the most stable nuclei. If this is the case, then based on the neutron number, we can say that element number 104, may give a very stable radionuclide. So that means the superheavy elements with an island of stability may start somewhere around even element number 104 so that rutherfordium can be considered as one of the super heavy elements.

So it starts from Rutherfordium, and most of the transactinides can be called the superheavy elements. Now from the nuclear physics point of view, the superheavy elements, exist mostly because of the shell effects, that is because of the magic numbers, you get the extra stability. And those with a lifetime of greater than 10^{-14} s can be considered as a chemical element. That means if some radionuclides have lower values as the lifetime, we need not consider them as elements. So the stability of nuclei is mainly based on spontaneous fission, which takes place with the heavier actinides or the transactinides, and this is given by a parameter called the fissility parameter, which is defined as Z^2/A , where Z is the charge of the radionuclide.

And the reflection of this proton-to-neutron ratio also depends on the Z^2/A or the fissility parameter. Now based on the liquid drop model, you can calculate the lifetime of this or the decay lifetime, that is the spontaneous fission of thisradionuclide. The line in the figure, gives this calculated line from theliquid drop model., and those which are falling below 10^{-14} s, we call them non-existent. So that way, somewhere between the nobelium, and the rutherfordium, we find this region with the X value of 0.88. So, X is nothing but the fissility parameter at Z^2/A. So with this value, we can say that those elements will be non-existent. However, this is not the case, and we know that actinides up to Lr are there, and also the transactinide elements were discovered subsequently. Suggesting that this cannot bepredicted based on the fissility parameter, and the liquid drop model. So, the experimentally determined values suggest that the shell effects are very, very important, and the transactinides are the same as the super or it can be considered as same as the super heavy elements based on this.



SYNTHESIS OF TRANSACTINIDES

--Heavy elements beyond Fm (Z=100) are done by fusion reactions

--Cold fusion: Excitation energy: 10- 15 Mev (medium to heavy projectiles viz., ^{58}Fe, ^{62}Ni and targets are ^{208}Pb and ^{209}Bi). Products have short $t_{1/2}$

--Hot fusion: Excitation energy: 40-50 Mev (actinide targets viz. ^{248}Cm and light projectiles viz. ^{18}O, ^{22}Ne, ^{26}Mg). 4-5 n are evaporated. Relatively long lived n-rich isotopes are formed. Cross sections are from nano barns to pico barns. Few atoms per minute for Rf and Db but only 5 atoms per hour for ^{265}Sg

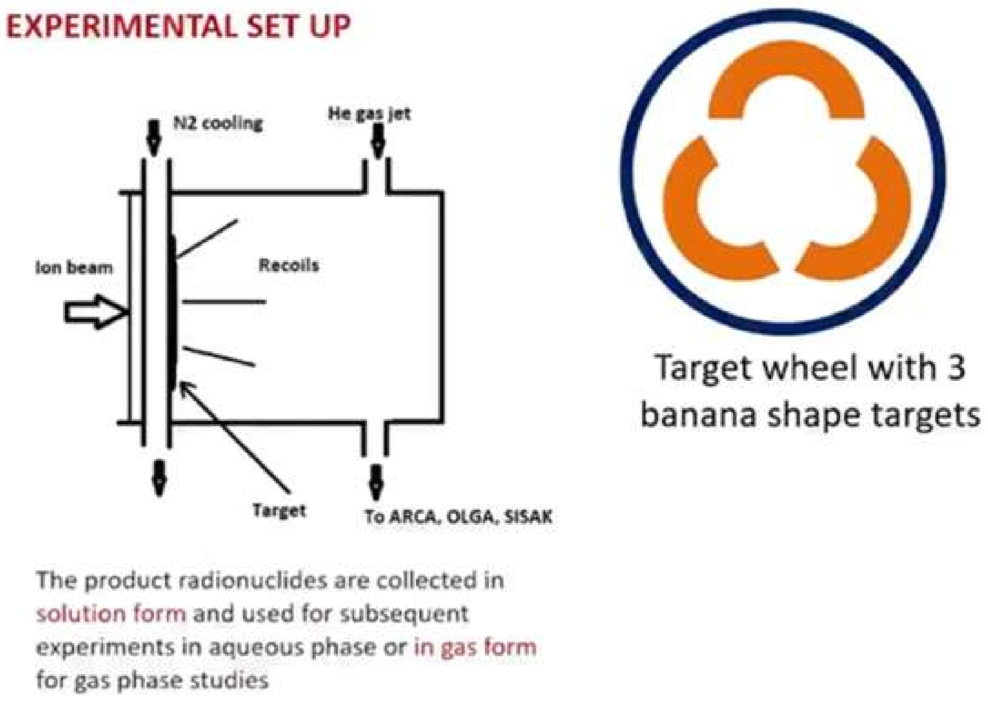
Cold fusion

$5x10^{16}$ ions in projectiles give 1 atom

Hot fusion

$1x10^{17}$ ions in projectiles give 1 atom

Now coming to the synthesis of the transactinides, heavy elements beyond fermium, that is Z equal to 100, are done by the fusion reactions and before fermium, these are done by neutron capture reactions in the nuclear reactors or by the in-pile reactions. Now, there are two types of fusion reactions. One is the cold fusion where the excitation energyis relatively less, that is the 10 to 15 MeV. So in that case, we use medium to heavy projectiles, that is iron 58, and nickel 62, these types of projectiles are used and also the targets are like ^{208}Pb, and ^{209}Bi. In this case, we have relatively neutron-deficient products formed, and the products have relatively short half-life. Another way of producing is by the fusion reaction is hot fusion where the excitation energy is as high as 40 to 50 MeV, and the target actinides are ^{248}Cm, ^{244}Pu, etc., with light projectiles such as ^{18}O, ^{22}Ne, ^{26}Mg, etc. In this case, 4 to 5 neutrons are evaporated as compared to only one neutron by the cold fusion reactions, and the relatively long-lived neutron-rich isotopes are formed. The cross-sections are from nanobarns to picobarns for these hot fusion reactions. But you have few atoms per minute for rutherfordium and dubnium, but only five atoms per hour for ^{265}Sg. The schematic of this cold fusion and hot fusion is given here, and this is the compound nucleus formed by a given reaction that is ^{58}Fe and ^{208}Pb you have the fusion, it gets a compound nucleus ^{266}Hs, and it gives out one neutron, and forms ^{265}Hs. In this case, we have 5×10^{16} projectiles on the target to produce only one atom. In the case of the hot fusion, we have the ^{248}Cm as the target, and the projectile is ^{26}Mg as given here and you have the fusion, and you have the compound nucleus as ^{274}Hs, and it is giving out around 4 to 5 neutrons to give either ^{269}Hs or ^{270}Hs. In this case, we have 1×10^{17} projectiles on the target, and we are getting one atom.



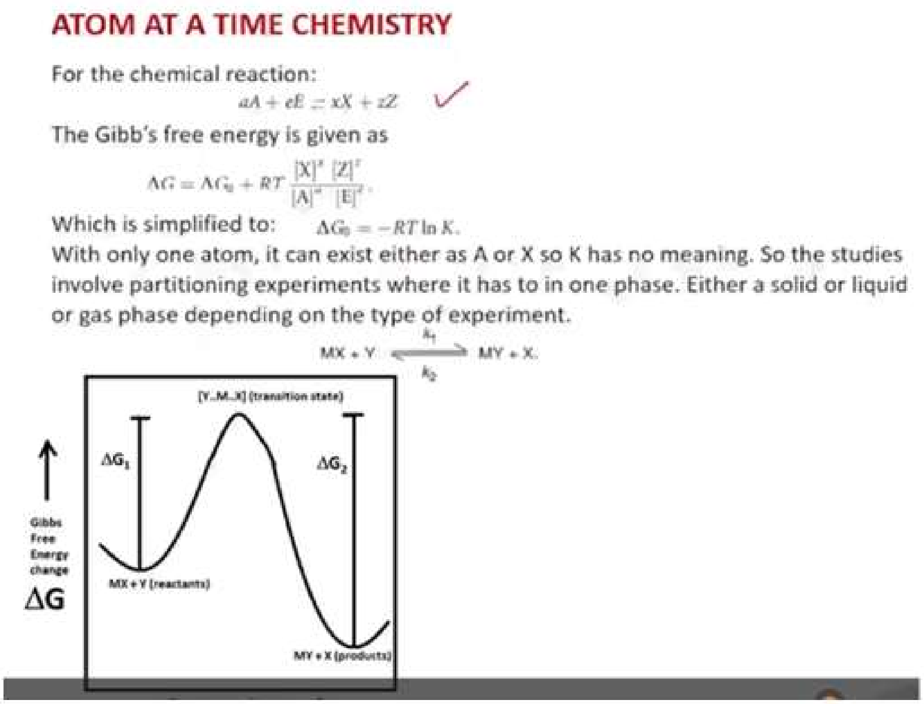
EXPERIMENTAL SET UP

Target wheel with 3 banana shape targets

The product radionuclides are collected in solution form and used for subsequent experiments in aqueous phase or in gas form for gas phase studies

The experimental setup is given here in the above slide, where you have the beryllium wrapped, the target is there as shown here, and the ^{18}O beam is coming this way, and this is that is the whole system is enclosed, and the pulling is done by nitrogen gas passing through this at 0.2 mg/cm^2, and this reaction is taking place, and the recoils whatever is coming out of this nuclear reaction, they are actually transported by the helium gas jet in the presence of aerosols, and this gas gel outlet which is going to the collection site where the experiments are carried out withthe special experimental setups like OLGA or ARCA. Now for the target, because the very large beam current is there, this target is going to be burnt very easily. That is why the cooling of the target has to be done, and also, we need to have this target rotated. So, one such schematic is given here where you have three banana-shaped targets, and this wheel actuallyis where it is mounted, this gets rotated, and then it gets cooled also so that at one time only one target is seeing the beam.

After that, this target is moved, and then the s target sees the beam, and finally, the third target sees the beam. That is how it is rotated, and alternatively, we get these targets exposed to the beam. Now the product from the radio-nuclides are collected in the solution form for the solution phase experiments, and in the gas form for the gas phase study.



ATOM AT A TIME CHEMISTRY

For the chemical reaction:

$$aA + eE \rightleftharpoons xX + zZ$$ ✓

The Gibb's free energy is given as

$$\Delta G = \Delta G_0 + RT \frac{[X]^x \, [Z]^z}{[A]^a \, [E]^e}.$$

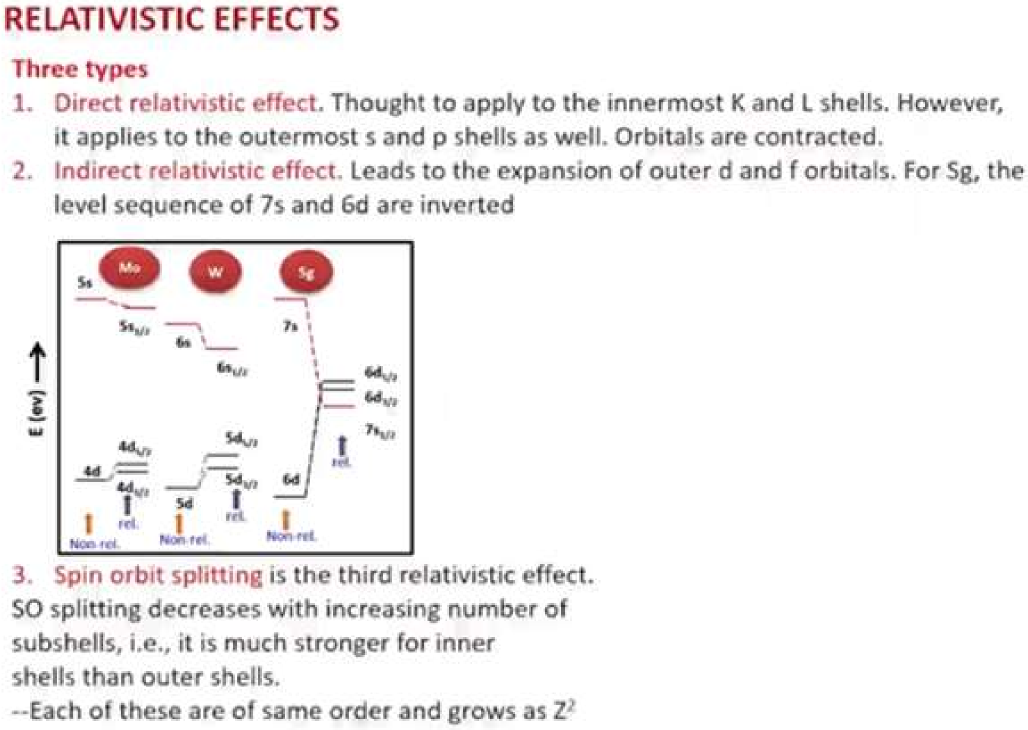
Which is simplified to: $\Delta G_0 = -RT \ln K.$

With only one atom, it can exist either as A or X so K has no meaning. So the studies involve partitioning experiments where it has to in one phase. Either a solid or liquid or gas phase depending on the type of experiment.

$$MX + Y \underset{k_2}{\overset{k_1}{\rightleftharpoons}} MY + X.$$

Now one important part here is the atom-at-a-time chemistry or the single atom chemistry. Now this becomes very vague if you have only one atom because when you are carrying out the chemical reaction, we know this chemical equilibrium which is given here that is A and E reacting to give X and Z. So, the reactants are A and E. So, a atoms of A, and e atoms of E, are reacting to give x atoms of X, and z atoms of Z as the product, and the Gibbs free energy for this is given by this equation which is simplified to give $\Delta G_0 = -RT \ln K$. The problem is when you have a bulk quantity then it is fine but when you have only a single atom, it can either exist as A or as X. So it can either be in the left side or it can be in the right side.So the equilibrium constant in that sense has no meaning. However, do these studies, how it hasto be carried out? So, it has been proposed that such studies can be carried out by partitioning experiments where the element that is formed, will be only in one phase.

That means if you have a solid-liquid partition or even partition between a gas phase, also depending on the type of the experiment, the metal that is formed will be either inone of these phases which are in equilibrium. So which is shown here,this figure shows the reaction coordinates versus the del G values., you see this, ΔG value if it is for this reaction MX + Y which is the reactant, which is the transition state is Y, MX, and the final product is MY + X. Now whether it will be depending on the MX or MY depends on this activation energy. Whether the forward reaction is taking place or the backward reaction is taking place is mentioned here in this equilibrium reaction. Now if the ΔG is less than 15 kcal, then the reaction time will be less than one s. So accordingly, if you carry out the reaction in a very very short time that is less than one s, then we have to find out the conditions in which the ΔG value should be less than 15 kcal.



RELATIVISTIC EFFECTS

Three types

1. Direct relativistic effect. Thought to apply to the innermost K and L shells. However, it applies to the outermost s and p shells as well. Orbitals are contracted.
2. Indirect relativistic effect. Leads to the expansion of outer d and f orbitals. For Sg, the level sequence of 7s and 6d are inverted

3. Spin orbit splitting is the third relativistic effect.

SO splitting decreases with increasing number of subshells, i.e., it is much stronger for inner shells than outer shells.

--Each of these are of same order and grows as Z^2

Another important aspect is the relativistic effect which is very important for the transactinides or the heavier elements. The relativistic effect is important, and it has three different types of relativistic effects are there. One is called the direct relativistic effect. Now this direct relativistic effect is thought to apply only to the inner most K, and the L shells. However, in the case of transactinides it applies to the outermost s, and p shells as well and that is how these outer most orbitals are also contracted. The indirect relativistic effect leads to the expansion of the outer d and f orbitals and so, for the seaborgium, the level sequence of 7s, and 6d are inverted.

I have shown herea picture actually where these energy levels are given, and you can see for Seaborgium there is a real reversal of these 7s falling below that of the 6d levels. So, this is how this relativisticeffect becomes important which decides the chemistry of this transactinide. Now there is a third relativistic effect that is called the spin-orbit splitting or the SO splitting, and this is called the third relativistic effect. This SO splitting decreases with an increasingnumber of subshells that is it is much stronger for the inner shells than for the outer shells.

So each of these is of the same order, which means all these three relativistic effects are of the same order and grow as Z square. That means increasing the charge it increases, these relativistic effects. and this becomes very very important for the transactinides. While seeing the chemistry of these transactinides, sometimes you find that it does not match well with the homologs because of these relativistic effects. Thank you.